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ABSTRACT

This book is one in the series of Interdisciplinary Approaches to Chemistry (IAC) designed to help students discover that chemistry is a lively science and actively used to pursue solutions to the important problems of today. It is expected for students to see how chemistry takes place continuously all around and to readily understand the daily problems facing them and their environment. Contents include: (1) "Introduction of Physical Chemistry"; (2) "The Gaseous State"; (3) "Liquids and Solids: Condensed States"; (4) "Solutions: Solute and Solvent"; (5) "The Colloidal State"; (6) "Changes in Energy"; (7) "Rates of Chemical Reactions"; (7) "Chemical Equilibrium"; and (8) "Electrochemistry". (KHR)

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COMMUNITIES OF MOLECULES

A PHYSICAL CHEMISTRY MODULE

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A PHYSICAL CHEMISTRY MODULE

Howard DeVoe

1817

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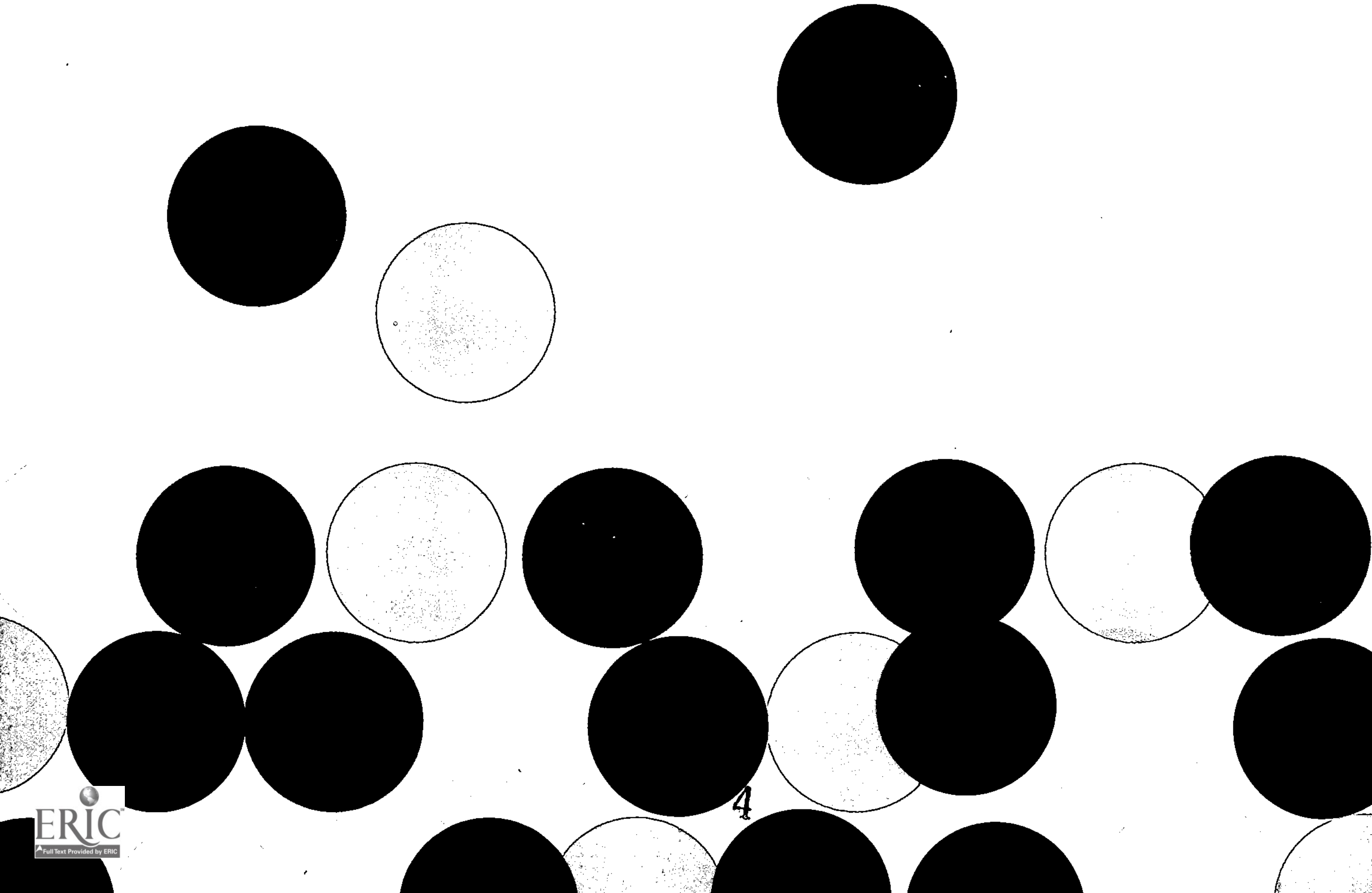

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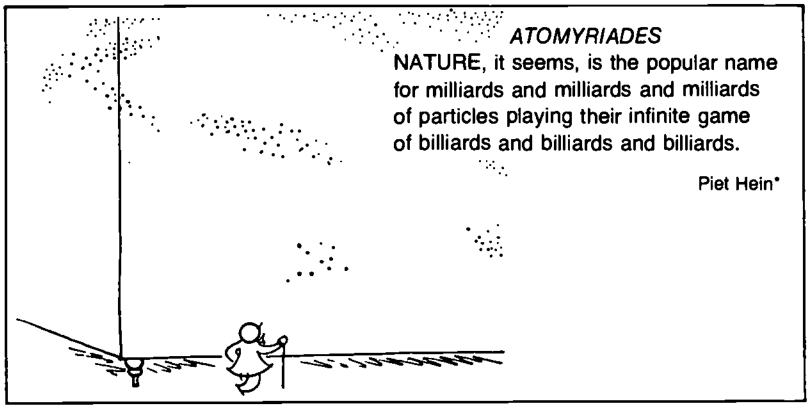
COMMUNITIES OF MOLECULES:
A PHYSICAL CHEMISTRY MODULE

HOWARD DEVOE

Howard DeVoe calls himself a physical chemist, although his research interests range all the way from the theory of liquid structure to reactions of dyes with DNA. This diversity of subjects simply illustrates the fact that the concepts and theories of physical chemistry can be applied to all fields of chemistry. Howard DeVoe received his Ph.D. from Harvard University and did postdoctoral work at the University of California. Before joining the faculty of the University of Maryland, he was a research chemist at the National Institutes of Health. He has had many articles published in a wide variety of scientific journals.



ATOMYRIADES

NATURE, it seems, is the popular name
for milliards and milliards and milliards
of particles playing their infinite game
of billiards and billiards and billiards.

Piet Hein*

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PREFACE

Welcome to IAC Chemistry. Enjoy this year as you explore this important area of science. Chemistry is to be enjoyed, cultivated, comprehended. It is part of our culture, of our everyday lives.

Polymers, paints, pharmaceuticals, people, and pollution all have something in common—a chemical base. IAC Chemistry is relevant, interdisciplinary, student centered, and filled with important concepts and processes.

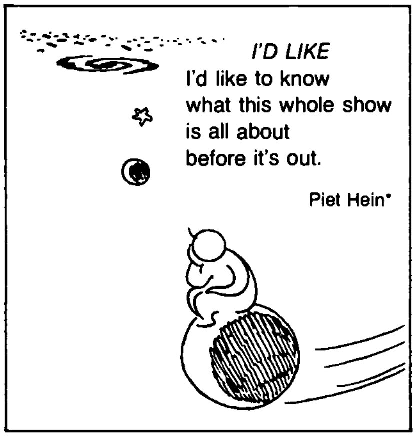
IAC will help you discover that chemistry is a lively science and being actively used to pursue solutions to the important problems of today. You will see how chemistry is taking place continuously all around. You will more readily understand the daily problems facing you and your environment.

Students throughout this country and in a number of other countries as well have let us know that they like and learn from the IAC modules. Classroom teachers have suggested changes to make them even better.

Since the IAC authors believe that student involvement in chemistry is very important, there are many activities that allow you to develop and apply chemistry concepts directly. We have tried to make the modules flexible, easy to read, and enjoyable, discussing everyday problems and adding a bit of humor that may help you remember some of the more important ideas. The Time Machines are intended to give you a sense of when the more important discoveries in chemistry happened in relation to other events.

Wonder—inquire—investigate. Think through all that you find here. But most of all—enjoy chemistry as you learn about the atoms, molecules, elements, and compounds that make up your universe. IAC is written for your learning pleasure.

Marjorie Gardner
Director
Interdisciplinary Approaches to Chemistry



I'D LIKE

I'd like to know
what this whole show
is all about
before it's out.

Piet Hein*

© 1966 by Piet Hein

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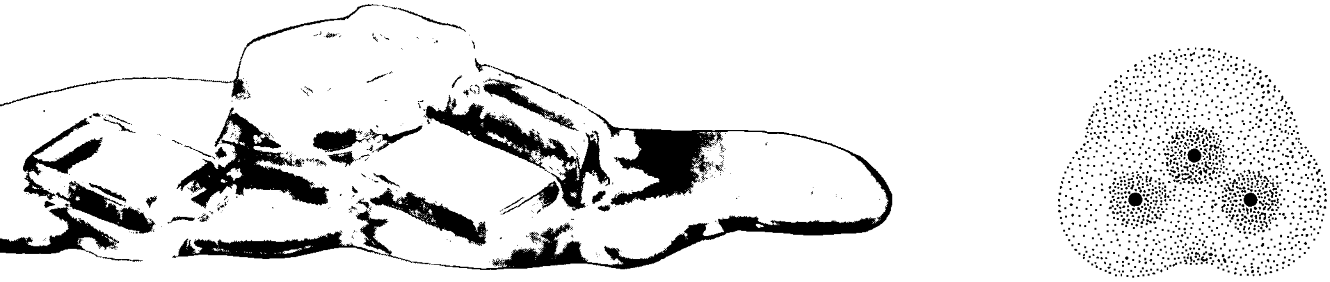
*Piet Hein is a Scandinavian poet who often served as a "mental Ping-Pong partner" for the famous chemist Niels Bohr.

CONTENTS

Introducing Physical Chemistry

How are molecules like people? One answer is that they both form communities! Look at it this way. A community is a group of individuals located in one place. The individuals, by their various activities and interactions with one another, determine the character of the community. Thus a quantity of a chemical material, made up of many molecules, may be thought of as a community of molecules.



A community of molecules (melting ice cubes) and a member of the community (a water molecule).

Molecules, like people, form many very different kinds of communities. A glass of milk, a melting ice cube, the air in a tire—these are all communities of molecules. This module uses the expression "community of molecules" to refer to any large group of the fundamental chemical particles: atoms, molecules, and ions. The scientific term for such a group is *chemical system*.

The branch of chemistry which deals with measurements of the properties of communities of molecules and the reasons for these properties is called *physical chemistry*. The knowledge which has developed in this subject has come from careful measurements of many different properties with scientific instruments, combined with mathematical calculations using theories from chemistry and physics.

Your study of physical chemistry can help you to understand many fascinating phenomena occurring in everyday life. For instance, as you read this module look for the answers to these questions about automobiles:

- The tires of an automobile contain air under pressure. As the tires become heated through friction on a long drive, the pressure increases. Why is this?
- Why do gasoline refiners change the amounts of various compounds in gasoline depending on the season of the year?
- In cold weather the radiator water must contain antifreeze. How does antifreeze prevent the water from freezing?
- Automobiles contain many materials which are called colloids. These include the waxes and polishes used to protect the body enamel, the enamel itself, the lubricating grease packed in the bearings, the smoke from the exhaust, and the material in the tire treads. How are these various materials similar?
- A chemical reaction, the combustion (burning) of gasoline, takes place in the cylinders of the engine. How does this reaction produce the energy which moves the automobile?

- Another chemical reaction occurs in the lead storage battery needed to run the electric starter motor. How does this reaction produce electricity?
- The metal bumpers are usually chromium plated for good appearance and protection from rusting. How is the chromium metal deposited on the bumper?

P-1 Macroscopic and Molecular: Two Worlds

By now in your study of chemistry, you are probably aware of two different worlds of size. There is the *macroscopic* world and the *molecular* world.

The term *macroscopic* means large enough to be observed with the naked eye. The communities of molecules you will study are macroscopic. You can see them with your eyes alone (or in the case of a colorless gas, such as air, you can see the container). By using ordinary senses and perhaps some simple instruments or chemical tests, you can measure various macroscopic properties such as color, mass, and temperature.

The individual molecules which make up macroscopic communities are, with rare exceptions, too small to be visible to the naked eye. In fact, most molecules are too small to be seen even with the aid of a microscope. Our evidence for the existence of these molecules comes from many different kinds of scientific measurements.

The first experiment will give you an idea of the size of a molecule. But, before starting this experiment, you should review the safety guidelines in Appendix I and keep these guidelines in mind for *all* of the experiments that you will carry out.

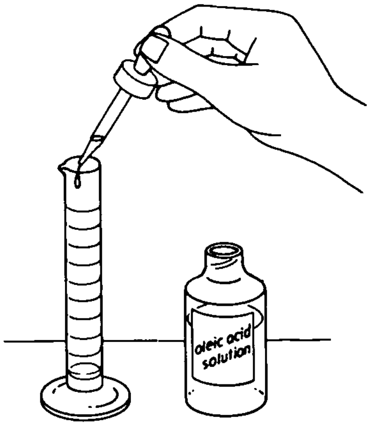
P-2 The Size of a Molecule

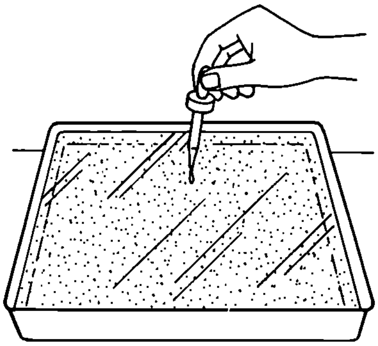
EXPERIMENT

Trying to measure the size of something as small as a molecule is not easy, but there are some clever ways of estimating the size. In this experiment you will estimate the length of one molecule of oleic acid. Oleic acid is a type of organic compound called a *fatty acid*. Its formula is $C_{17}H_{33}COOH$.

When a drop of oleic acid is placed in water it spreads out over the surface in a thin film. If there is enough room, the film spreads until it is only one molecule thick. By measuring the thickness of one of these films you will have an estimate of the length of an oleic acid molecule.

Obtain a dropper bottle of oleic acid solution. You will also need a 10 cm^3 graduated cylinder. (Remember that one cubic centimeter [cm^3] equals one milliliter in metric volume measure.) Count how





many drops are needed to make 1 cm^3. Calculate the volume of just *one* drop. The oleic acid solution is very dilute. Only 1/200 of the volume of each drop is oleic acid; the rest is alcohol. Calculate the volume of the oleic acid in *one* drop of solution.

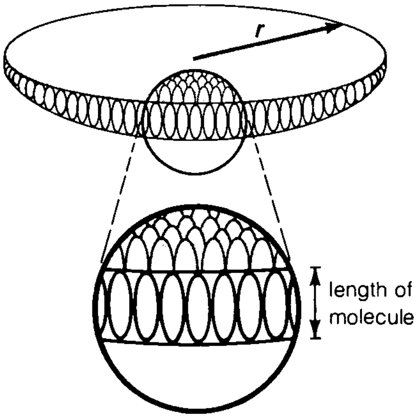
Fill a large shallow tray about 1 centimeter (cm) deep with water. Sprinkle a thin layer of chalk dust or lycopodium powder on the surface of the water. Holding the dropper vertical to and near the water surface, place one drop of *pure alcohol* on the surface. What happens? Now place one drop of oleic acid solution on the water surface. What happens to the alcohol in this drop?

Estimate the area of the oleic acid film by pretending that the film is circular and then measuring the average radius (one-half the diameter) in cm. Calculate the area from the formula

$$\text{area} = \pi r^2$$

(The value of π is 3.14.)

FILM OF OLEIC ACID
(one molecule thick)



Use the area and volume of the oleic acid film to calculate the approximate thickness. The formula for volume is

$$\text{volume} = \text{thickness} \times \text{area}$$

This formula can be rearranged into a formula for thickness

$$\text{thickness} = \text{volume}/\text{area}$$

Calculate the thickness of the film—that is, the length of the oleic acid molecule. Use scientific notation (explained in Appendix II). Since volume in your answer was expressed in cm^3 and the area was in cm^2 (square centimeters), the length will be in cm. In these calculations, the value of the length is only approximate because the area was an estimate; thus you can round off the value of the length to one significant figure (see Appendix II if you need help).

As you can see, an oleic acid molecule is exceedingly small. To measure the sizes of molecules and other distances in the molecular world, chemists often use the nanometer (nm), meaning 10^{-9} meters (m). One centimeter contains 10^7 nm. Therefore, multiply the length in cm by 10^7 to obtain the length in nm. Can you see why the nanometer is a convenient unit for distances in the molecular world?

Use a table similar to the following for your data:

drops in 1 cm^3 = ___ drops
vol. of 1 drop = ___ cm^3
vol. of oleic acid in 1 drop = ___ cm^3
average radius *(r)* = ___ cm
area = ___ cm^2
thickness (length) = ___ cm
thickness (length) = ___ nm

P-3 Journey into a Drop of Milk

We can get a feeling for the vast differences in size between objects in the macroscopic world and objects in the molecular world by going on an imaginary journey. Our "journey" will start with the

macroscopic world. Then, by a series of magnifications, one after another, we will arrive at objects in the molecular world.

What we observe will resemble the changes that a parachute jumper sees as he floats to earth from an airplane. At first the jumper can see a vast landscape: fields, woods, wide highways. As he comes down, he sees greater detail in a smaller area, such as plants in the fields, trees in the woods, and cars on the highways. Only when he is close to the ground can he observe individual leaves, pebbles, and other small objects.

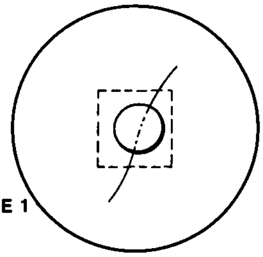
Our imaginary journey will be into a drop of that familiar substance, milk. Figure 1 shows a macroscopic drop of milk, life size, as it would look to the naked eye. A human hair has fallen into the drop. The square which is indicated by the dashed lines is 1 cm in length on each side. We all know that milk contains many different kinds of molecules, but how is this community of molecules arranged? The naked eye sees only a white structureless liquid with the hair in it.

Now suppose that we magnify a portion of the center of Figure 1 ten times. We could do this with a magnifying glass, as shown in Figure 2. The square in Figure 2 is one-tenth as large as the square in Figure 1, or 10^{-1} cm on each side as indicated under Figure 2. We can see the hair more clearly, with the milk surrounding it.

We will keep on magnifying the center of each picture ten times to make a new picture. The distance indicated under each picture is the size of the square shown in that picture.

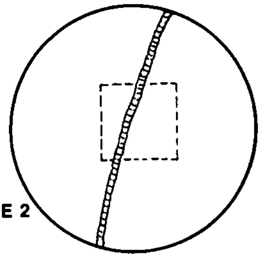
Figure 3 shows a closeup of the hair, with scales which can be seen in a microscope. In Figure 4 we see several bacteria, tiny one-celled organisms which occur naturally in raw milk. (Pasteurized milk is milk which has been heated to kill most of these bacteria.) The bacteria are each about 10^{-4} cm in diameter. Particles of this size can just barely be seen in a powerful microscope. Smaller particles than this cannot be seen in an ordinary microscope. To observe smaller particles we must use a more powerful instrument called an *electron microscope*. The electron microscope uses electrons instead of light to "see" the particles.

FIGURE 1



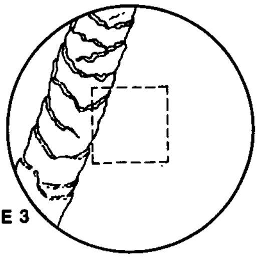
1 cm

FIGURE 2



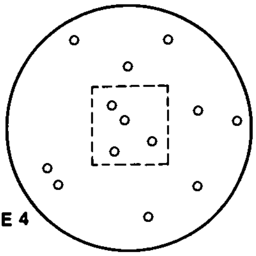
10^{-1} cm

FIGURE 3



10^{-2} cm

FIGURE 4



10^{-3} cm

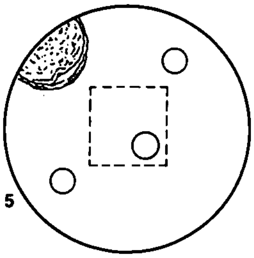


FIGURE 5

Up to this stage of our journey the milk has looked structureless, except for the hair and the bacteria. In Figure 5 we see a closeup of one of the bacteria. We also see for the first time that milk is actually a mixture. The dark circles are globules of a liquid oil (butterfat) surrounded by watery skim milk. The oil globules shown are so small (about 3×10^{-5} cm in diameter) that they do not float to the surface. Particles of this size or smaller are called *colloidal* particles. We will learn more about colloidal particles later.

In Figure 6 we see a closeup of one of the oil globules, as well as several smaller colloidal particles of protein. These particles can be seen to be made up of spherical subunits, which in turn contain protein molecules not yet visible.

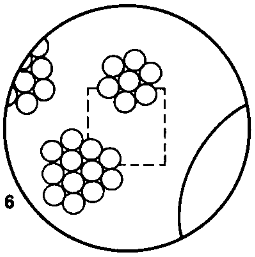


FIGURE 6

Figure 7 shows individual molecules for the first time on our journey. We have entered the molecular world. Recall that a molecule is made up of atoms joined by covalent bonds. These bonds would have to be broken in order to alter the molecule or split it up into smaller pieces, whereas two individual molecules can separate without breaking any covalent bonds.

The molecules in Figure 7 are oval-shaped molecules of the principal milk protein, casein. They are shown organized into part of one of the spherical subunits which appeared within the particles of Figure 6. The length of these molecules is about 10^{-6} cm. Molecules of this size are considered to be "large" molecules, or macromolecules, since they contain hundreds of atoms. Macromolecules can easily be seen with an electron microscope.

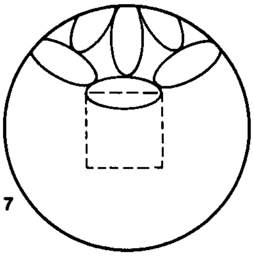


FIGURE 7

In Figure 8 we see the molecules that make up almost 90 percent of the mass of milk, namely, water molecules. They fill the "empty" spaces of the preceding pictures. Water molecules are "small" molecules containing only three atoms each and measuring about 3×10^{-8} cm across. What is their size in nanometers? Molecules of this size are a little too small to be "seen," even with the most powerful electron microscopes.

How many water molecules lined up in a row would fit along one side of the 1 cm square shown in Figure 1? Answer:

$$\frac{1\ \text{cm}}{3 \times 10^{-8}\ \text{cm/molecule}} = 3 \times 10^{7}\ \text{molecules—about 30 000 000 molecules!}$$

How many water molecules in a layer one molecule thick would fit into the 1 cm square? (Hint: Take the square of the number of molecules along one side.) Finally, how many water molecules would fit into a cube of 1 cm^3 volume? Compare the number of molecules in this community of 1 cm^3 volume with the number of people in the community of the entire human race, which presently numbers about four billion people (4×10^{9}).

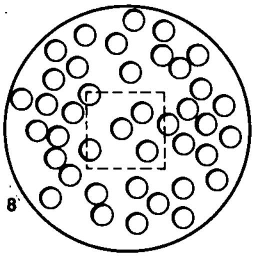


FIGURE 8

Figure 9 is the last scene in our journey. Here we can see in our imagination some details of a single water molecule. An oxygen atom and two hydrogen atoms bonded to it are outlined by clouds showing where the electrons are moving. Buried within the clouds are the nuclei. This picture is static, but if we could really see the molecule it would be constantly vibrating and moving.

In the following section, we will begin to consider the different ways in which molecules are organized into communities and how the macroscopic properties of these communities (the properties you can observe and measure) are the result of the structure and behavior of these molecules. We will find that there are four fundamental types of organization, or *states of matter:* gases, liquids, solids, and colloids.

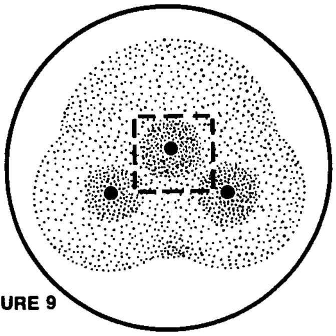


FIGURE 9

QUESTIONS

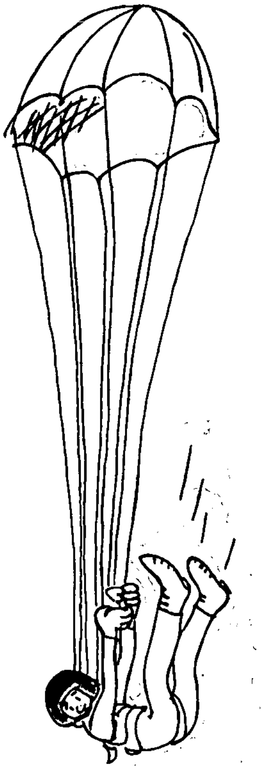
1. Express the following numbers in scientific notation, rounded off to two significant figures: 0.000 54; 8346; 41 648 218.
2. Do the following calculations. Express your answers in scientific notation, with the proper number of significant figures:

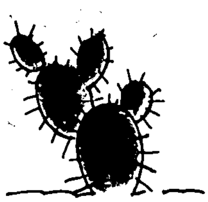
$$(3 \times 10^6) \times (4 \times 10^{-8}) =$$

$$\frac{18 \times 10^{-2}}{3 \times 10^4} =$$

$$\frac{31\,000}{0.31} =$$

3. What is the length in nm of the macromolecules shown in Figure 7?
4. If 10 liters (1×10^4 cm^3) of oil is spilled in the ocean and spreads out into a film which is 10 nm (1×10^{-6} cm) thick, what will be the area of the film in cm^2? If this oil slick has a square shape, how long will each side of the square be? Express the length in centimeters, meters, and kilometers.
5. One water molecule has a mass of 2.99×10^{-23} g. The water contained in a volume of 1 cm^3 has a mass of 1.00 g. From these values, calculate how many water molecules are contained in a volume of 1 cm^3. Compare your answer obtained by this method with the calculation you made in section *P-3*, where you estimated the number of water molecules that would fit into a cube of 1 cm^3 from the size of the molecules.
6. If the number of water molecules that are contained in a volume of 1 cm^3 were divided equally among all the people in the world (4×10^9 people), how many molecules would each person receive?





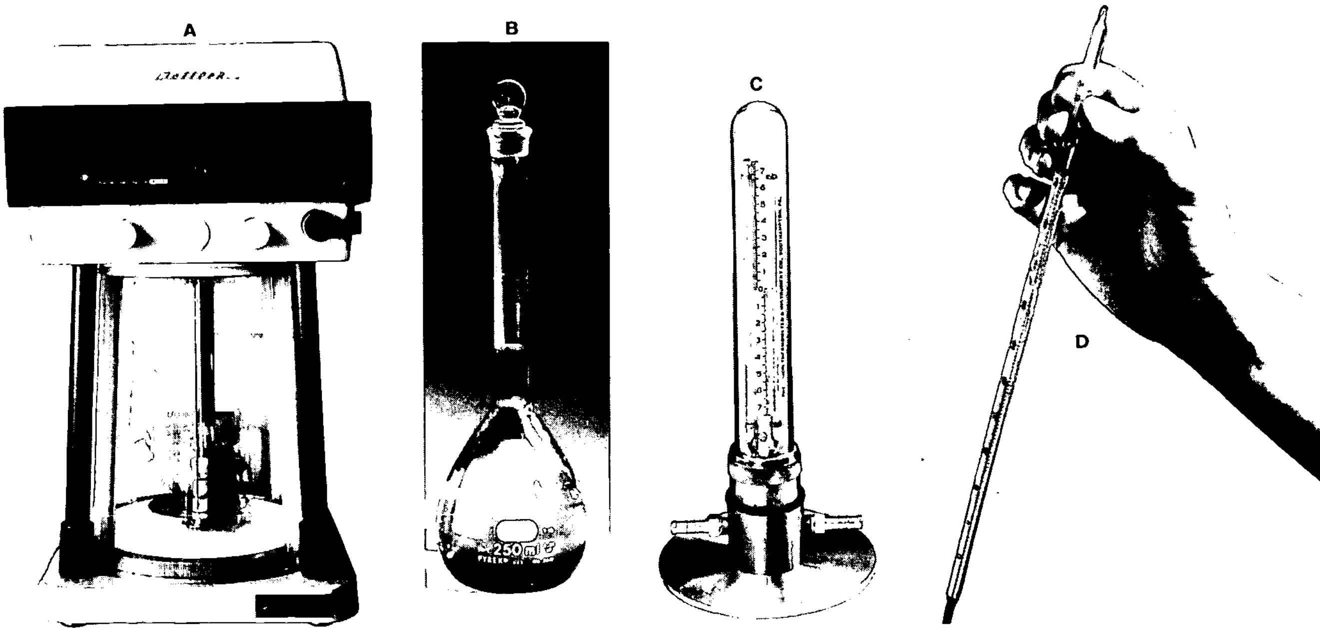
The Gaseous State

A gas is a community of molecules that completely fills any container and takes on the shape and volume of the container. A gas may contain only one kind of molecule, or it may be a mixture. We will investigate some macroscopic properties of gases and explain them by the kinetic molecular theory.

P-4 Measuring Gases

We can measure four important properties of a gas:

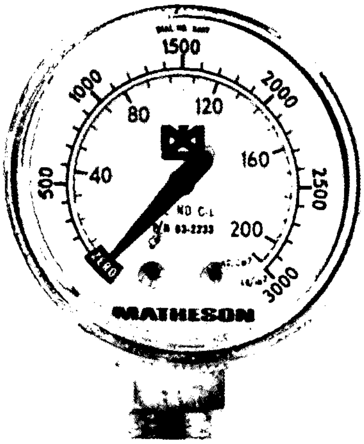
1. The *mass* of the gas. This depends on how many molecules are in the container and on what kinds of molecules these are (because different kinds have different masses). The mass cannot change if we allow no molecules to leave or enter the container. Chemists often measure mass in units of grams.
2. The *volume* of the gas. We can change this by changing the volume of the container. Volume may be measured in units of cubic centimeters.
3. The *temperature* of the gas. This can be measured in degrees Celsius, using a thermometer. The ordinary laboratory thermometer is a glass capillary tube and bulb containing liquid mercury. The markings on the thermometer are arranged so that when the thermometer is placed in melting ice it reads zero degrees Celsius (written as 0°C), and when it is placed in boiling water it reads 100°C. (The melting ice and boiling water must be at a pressure of one atmosphere, as we shall see.)
4. The *pressure* of the gas. A gas pushes out with a force against the walls of the container. The force acting on a unit area of the wall is the pressure. Thus pressure = force/area. Pressure may be measured in centimeters of mercury (cm Hg), or in atmospheres (atm), as will be explained presently. In the International System of Units (SI), the SI derived unit of pressure is the *pascal*. The pascal unit is not yet widely used by chemists. For convenience, we will use centimeters of mercury units and atmosphere units.



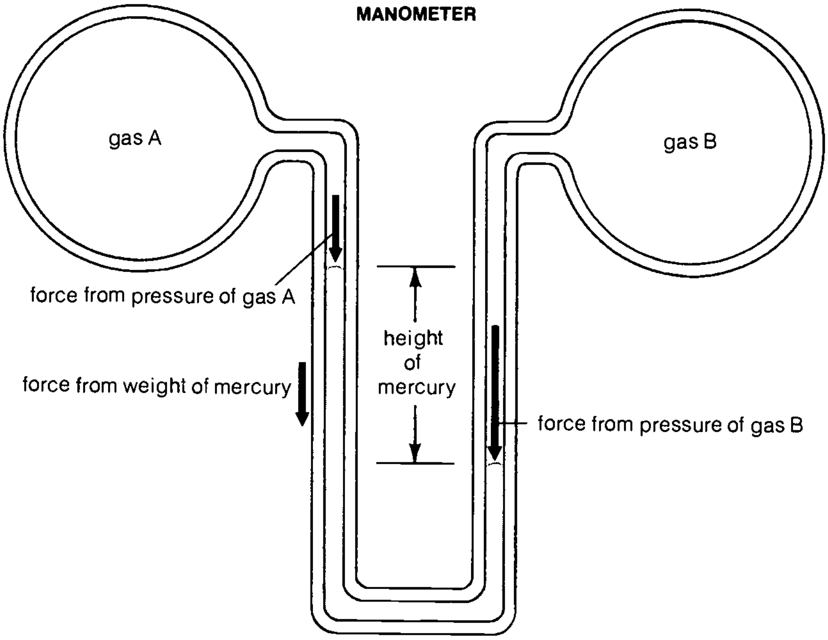
In the laboratory an analytical balance (A) is used to measure mass; a volumetric flask (B) to measure the volume of a liquid; the manometer (C) to measure gas pressure differences; and a standard laboratory thermometer (D) calibrated in °C to measure temperature.

The earth's atmosphere is a gas which is *not* enclosed in a container. The attraction of the earth's gravity keeps the molecules from escaping into outer space. The atmosphere pushes with a certain force against every unit of area of an object placed in it. This force per unit area is called the atmospheric pressure. Atmospheric pressure is equal in every direction, but it becomes gradually less at higher elevations and reaches zero in the vacuum of outer space.

Chemists use various instruments to measure gas pressure. You may be familiar with pressure gauges on cylinders of compressed gas or with tire gauges. A *manometer* is often used to measure gas pressures in the laboratory. The manometer measures the *difference* in pressure between two gases. The following diagram illustrates how a manometer works.



Both a pressure gauge *(top)* and a tire gauge *(bottom)* tell the user how much gas is left in the container.



The two gases push against opposite ends of the liquid mercury in the tube. If the pressures of the two gases are equal, both ends of the mercury come to the same level. If one gas has a greater pressure than the other, however, the levels change until the weight of mercury contained between the two levels exactly balances the difference in pressure. In the manometer in the preceding illustration, gas B has a greater pressure than gas A. The mercury level is higher at the left than at the right.

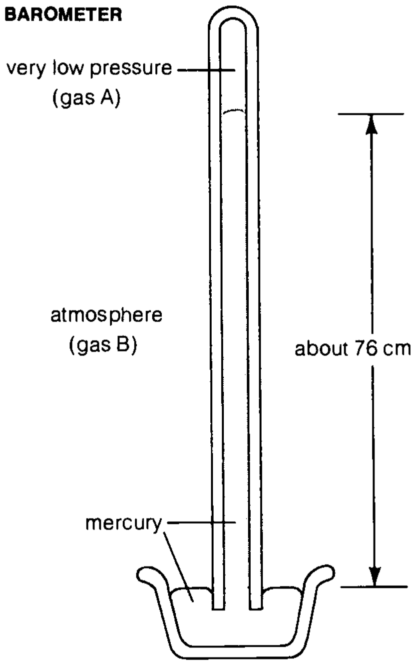
To measure the pressure difference, all we have to do is measure the *height* of the mercury between the two ends. For instance, if the height is 2.0 cm, we say that the pressure of gas B is greater than that of gas A by 2.0 cm of mercury (2.0 cm Hg). A gas pressure of 2.0 cm Hg means that the gas pushes against the walls with the same force per unit area as the weight of a 2.0-cm length of mercury in a tube with a cross section of unit area.

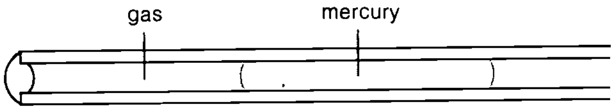
The marginal diagram shows a manometer used to measure atmospheric pressure. This instrument is called a *barometer*. It is basically the same device as before, except that gas A contains only mercury atoms and has a very low pressure. Gas B is the atmosphere. Thus the height of the mercury column in the barometer tells us the pressure of the atmosphere.

Notice that the height is measured vertically from the upper surface of the mercury to the lower surface; the depth of the mercury in the container at the bottom has nothing to do with the gas pressure. The mercury height at sea level usually is about 76 cm, so a pressure of exactly 76 cm Hg is called one *atmosphere* (atm) of pressure. Naturally the atmospheric pressure can be larger or smaller than one atmosphere. For instance, it is lower at high elevations and in wet weather.

The volume of a gas changes with a change of pressure. Does an increase in pressure bring about an increase or a decrease in volume? You can answer this question by doing an experiment. To do the experiment, you will work with a glass capillary tube sealed at one end. The tube contains a length of mercury which traps gas (air) in the tube as shown in the diagram. This simple little device is a gas container and a manometer combined.

BAROMETER

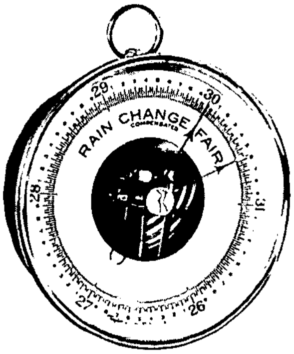




If the tube is tipped so that one end of the mercury is higher than the other, the weight of the mercury will cause the pressure of the gas to be different from the atmospheric pressure. You can use the vertical height of the mercury to measure the pressure difference between the gas and the atmospheric pressure.

As long as the gas does not get out past the mercury, one of the properties listed at the beginning of this section (mass, volume, temperature, pressure) cannot change. Which property is it?

Since the inside diameter of the capillary tube is the same everywhere along the tube, each centimeter of length in the tube is equal to a certain volume. Thus, in effect, by measuring the length of the gas column you are measuring the *volume* of the gas. You will see how this volume changes with pressure.



A standard mercury barometer, as described in the text *(left)*; and an aneroid (mechanical) barometer *(right)*.

miniexperiment

P-5 Pressure and Volume

This symbol represents three of the common hazards in a chemistry laboratory—flame, fumes, and explosion. It will appear with certain experiments in this module to alert you to potential hazards.

Handle the capillary tube carefully so that the mercury does not separate or spill. **Caution:** *Liquid mercury and mercury vapor are poisonous.*

Using a metric ruler, measure the length of the mercury column in your tube. Record this length to the nearest 0.1 cm.

When the tube is horizontal, the mercury moves until the pressure of the gas, *P*, is equal to the atmospheric pressure. This pressure will be posted in the laboratory. Lay your tube horizontally on a table and measure the length of the gas column. Record this length to the nearest 0.1 cm.

When the tube is held vertically with the open end *up*, the pressure of the gas, *P*, is greater than the atmospheric pressure. How can you calculate this gas pressure if you know the length of the mercury column and the atmospheric pressure?

Hold the tube vertically with the open end up and measure the length of the gas column to 0.1 cm. You may want to clamp the tube in a buret holder to steady it. Record this length and your calculated gas pressure.

When the tube is held vertically but with the open end *down*, the pressure of the gas is *less* than atmospheric pressure. Measure and record the gas column length and the gas pressure for the tube in this position.

Use a table similar to the following for your data:

atmospheric pressure = ____ cm Hg
Hg column length = ____ cm

tube horizontal:
P = ____ cm Hg
length = ____ cm
P × length = ____ cm Hg · cm

tube open end up:
P = ____ cm Hg
length = ____ cm
P × length = ____ cm Hg · cm

tube open end down:
P = ____ cm Hg
length = ____ cm
P × length = ____ cm Hg · cm

Now you have three different values for the pressure of the gas and the volume (or column lengths) of the gas at these pressures. When the pressure increased, did the volume increase, decrease, or stay the same?

The last step is to calculate, for each of the three positions of the tube, the *product* of the pressure times the column length. By looking at your results, can you state a mathematical rule for the product of pressure times volume of a gas? This rule is called *Boyle's law*.

What do you predict would happen to the volume of a gas if the pressure were doubled?

TIME MACHINE

1659	Rahn first uses the division sign.
1660	Quakers hold first meeting in the Massachusetts Bay Colony.
1661	King Louis XIV assumes absolute power in France.
1662	**Robert Boyle, British chemist, discovers Boyle's law.**
1664	British forces seize the city of New Amsterdam and rename it New York.
1665	Isaac Newton invents differential calculus.

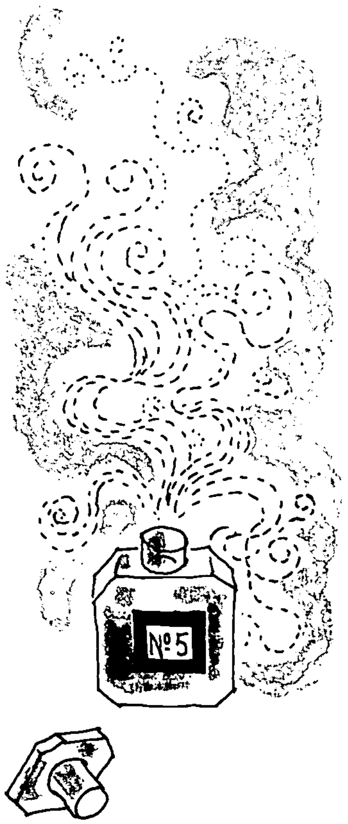
P-6 It's a Hit!

Your measurements have shown that when you change one property (the pressure), another property (the volume) also changes. In other words, some properties are *dependent* on one another instead of being independent. It really makes no difference whether you consider that the volume changed because you changed the pressure, or the pressure changed because you changed the volume. Both properties change together, and you can point to either one as the "cause" and the other as the "effect."

The *kinetic molecular theory* helps us to explain the properties of a gas and how these properties are dependent on one another. The kinetic molecular theory is introduced in *Reactions and Reason: An Introductory Chemistry Module*. According to the theory, each molecule in a gas moves in a straight line in some direction. Eventually the molecule collides with either another molecule or one of the inside walls of the container which holds the gas.

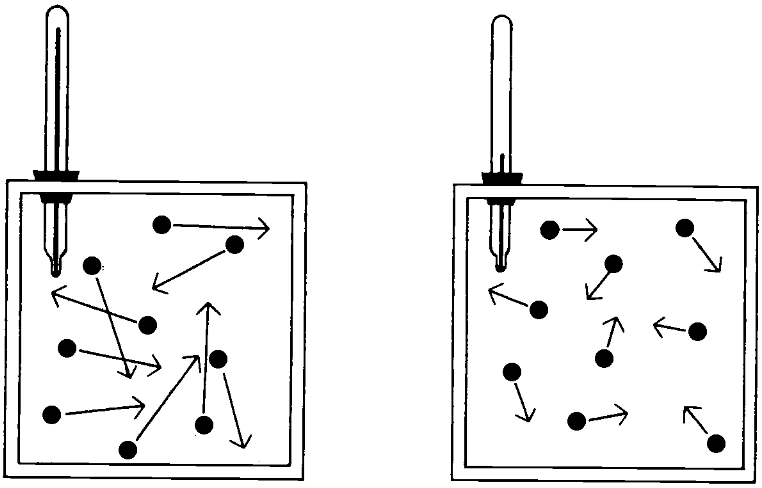
Before it collides, the molecule has no interaction with other molecules. It is independent and moves along at a constant speed, just as if it were the only molecule for miles around. The collision causes the molecule to change its direction. Off it goes in a new direction (usually at a different speed, also). If the molecule collides with another molecule, *both* molecules change their direction. Thus over the course of time all of the molecules of the gas move in a zigzag fashion in random directions.

Think of what happens when you open a bottle of perfume or after-shave lotion. If you move away from it, the odor can reach your nose across a room, even in still air. Does the kinetic molecular theory offer an explanation?



Let us now see how the kinetic molecular theory explains the four macroscopic properties of gases we discussed earlier. The mass and volume are simple. The *mass* of the gas is just the sum of the masses of all the gas molecules. As long as we let no new molecules enter the container, nor let any escape, the mass cannot change. The *volume* is just whatever volume is enclosed by the container walls.

The *temperature* of the gas is a measure of the average kinetic energy (energy of motion) of the molecules. When we heat a gas, we cause the average speed of the molecules to increase. Since the kinetic energy is equal to $(1/2)mv^2$ (where m is the mass and v is the velocity or speed), the kinetic energy also increases and the temperature goes up. If the average speed decreases, the temperature goes down.



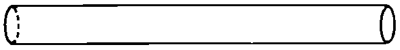
Most of the molecules have speeds close to the average speed, but at any one time some of the molecules have speeds close to zero and others have speeds much greater than the average speed. Remember, each molecule keeps changing its speed as it hits other molecules and the walls. At a fixed temperature, some molecules lose speed every fraction of a second and others gain speed; but the average speed stays the same.

You may be surprised to learn how fast the average speed is. Let us consider nitrogen (N_2), the most abundant gas in the atmosphere. At 25°C, which is approximately room temperature, nitrogen molecules have an average speed of 1700 km per hour, or one and one-half times the speed of sound! Remember, however, that the nitrogen molecules in the atmosphere continually collide with other molecules and change directions. Because of their zigzag path, none of them is able to go 1700 km in one direction during the course of one hour.

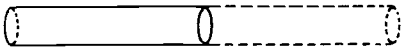
Since gas molecules collide with the walls of a container, they push against the walls with a force that depends on the mass and speed of the molecules. This force causes the macroscopic property we call *pressure*. In a container holding pure nitrogen gas at one atmosphere pressure and a temperature of 25°C, each square centimeter of area is hit 3×10^{23} times every second by N_2 molecules. This is an enormous number of collisions!

Now let us see how we can explain the results of miniexperiment *P-5 Pressure and Volume* by using the kinetic molecular theory of gases. The pressure is the total force per unit area of the gas molecules hitting the container walls. If the number of molecules hitting a unit area every second increases, the pressure also increases. (Imagine the stinging sensation from sand hitting your skin in a sandstorm on a desert; the more sand that hits you every second, the greater the sensation.) In the experiment the number of gas molecules and the temperature did not change, but the volume and pressure did change.

Suppose that we start with a certain volume of gas in the capillary tube, and then force the volume to become half what it was, as shown below:



original length



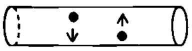
one-half original length

Let us see how often gas molecules hit the walls of the container in the new smaller volume compared to the original larger volume. For simplicity, we will forget about the collisions between the molecules. These collisions do not affect how often molecules hit the walls.

First consider the molecules which are moving *along* the length of the capillary tube:

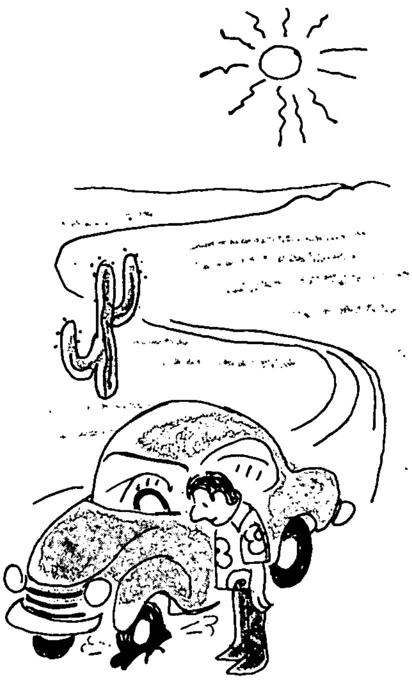
These molecules have only half as far to move before hitting the round ends of the container as compared to the original volume. Thus these molecules hit the ends twice as often. (Of course, when they hit they bounce off and move in the opposite direction.) The pressure on the ends of the container becomes twice the original pressure.

What about molecules that are moving *across* the container?



These molecules have as far to move as in the original volume, but there is only half as much area of the cylindrical side wall to hit. Thus each unit area of the side wall is hit twice as often by these molecules. Again, the pressure is doubled.

Some of the molecules move diagonally in the tube. These molecules, also, hit twice as often per unit area when the volume is halved. Thus when the volume of the gas is halved, the pressure on



each wall is doubled. How does the product of pressure times volume change in this case? Is this behavior in agreement with your laboratory results?

Here is something to think about. Suppose that you add *more* molecules of gas to a container without allowing its volume or temperature to change. What happens to the frequency with which molecules hit a unit area of the wall, and how will the pressure change? If you are uncertain of what the change will be, think of what happens when you add more air to an automobile tire or an inflatable ball.

Now we can answer one of the questions in the introduction, about why tire pressure increases as the tire gets hot. When the temperature rises, the average speed of the molecules of the air inside the tire increases. The faster-moving molecules hit the tire walls more often and also hit them harder, increasing the force per unit area for both reasons. Thus the pressure increases. (To return to the sandstorm analogy: the stinging sensation on your face increases if the wind speed picks up and blows the sand particles at you faster.)

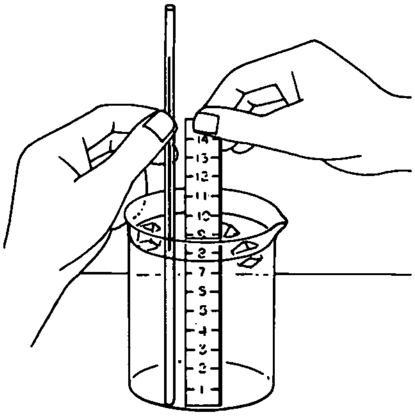
The next experiment is designed to show another relation between the properties of a gas. This time you will keep the pressure constant and change the temperature. You will use the same kind of capillary tube as in the previous experiment. By keeping the open end of the tube up, you will insure that the pressure of the trapped gas (air) remains constant regardless of the temperature.

EXPERIMENT

P-7 Temperature and Volume

Use a dry thermometer to measure the temperature of the room, and record it. Hold your capillary tube vertically with the open end *up* and measure the length of the gas column at this temperature to the nearest 0.1 cm.

Place the tube, open end up, into a 400-cm³ or larger beaker containing water and ice. Stir and keep the tube in the water for several minutes until it has a chance to reach a stable temperature near 0°C. Then measure the length of the gas column by inserting the ruler into the beaker next to the tube. Record this temperature and length.



Repeat the measurement in a beaker containing hot water. Check the temperature of this water with a thermometer. It should be between 50°C and 60°C (hot water from the sink may be hot enough; otherwise use a Bunsen burner). Be sure to wait several minutes before measuring the length. Record the temperature and the length of the gas column.

Make a graph of your results. If necessary, consult with your teacher on how to label the axes. Draw points on the graph

Use a table similar to the following for your data:

room temperature:
t = ___ °C
length = ___ cm
T = ___ K
length/t = ___ cm/°C
length/T = ___ cm/K

ice water:
t = ___ °C
length = ___ cm
T = ___ K
length/t = ___ cm/°C
length/T = ___ cm/K

hot water:
t = ___ °C
length = ___ cm
T = ___ K
length/t = ___ cm/°C
length/T = ___ cm/K

showing the three temperatures you used and the lengths of the gas column at these temperatures. Draw a small circle around each point to make it stand out.

Do your three points seem to lie on a straight line? If they do, draw the best possible straight line through the points with a ruler.

How warm would the tube have to be in order to make the length of the gas column become double the length at room temperature? Make an estimate by referring to your graph. At what temperature would the gas column be one half its normal length?

At what temperature would the length become zero? Do you think a zero reading is possible?

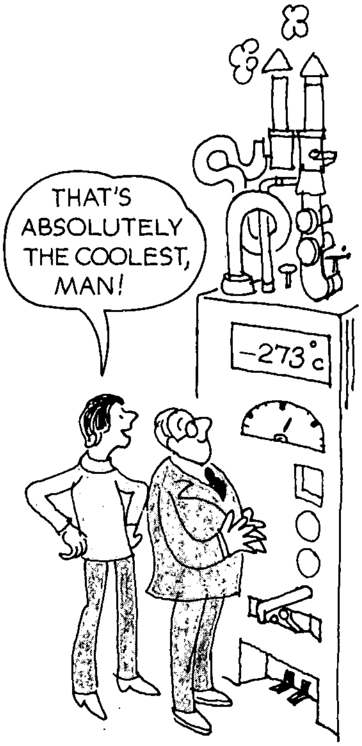
You should have found that there is an approximately straight line relation between the temperature of a gas and the volume of a gas at constant pressure. This straight line relation means that every time the temperature is raised by one degree Celsius, the volume of the gas increases by a certain fixed amount. This relation between temperature and volume is known as *Charles' law.*

The kinetic molecular theory helps us to understand Charles' law. Remember, if we keep the *volume* constant as we increase the temperature (as in the heated tire example), the pressure will increase. Suppose we want to lower the pressure back to its original value after we have increased the temperature of the gas. To lower the pressure with the gas at the new higher temperature, we need to increase the volume of the container. With increased volume, the gas molecules will not hit a unit area of the container as often as before. Thus when the temperature of the gas increases at constant pressure, the volume also increases.

Your results raise a very curious point. According to the straight line on your graph, if you continued to cool the gas, a temperature would eventually be reached at which the volume would be zero! This temperature is called *absolute zero.* From careful measurements on numerous gases, absolute zero is predicted to occur at −273°C. (Compare this value with the value you found from your graph.)

TIME MACHINE

1946	Chester Carlson invents xerographic process for fast copying.
1947	Scientists at Bell Laboratories invent transistor.
1948	Free State of Israel is proclaimed.
1949	**William Glauque, American physical chemist, receives the Nobel Prize for the study of substances at temperatures close to absolute zero.**
1950	The Korean War begins.
1951	An address by President Truman inaugurates first coast-to-coast television.
1952	J. D. Salinger publishes *The Catcher in the Rye.*
1953	N.Y. Yankees win fifth consecutive World Series.



No gas ever actually reaches a volume of zero because eventually as it is cooled the gas turns into a liquid or solid and behaves differently. Nevertheless, absolute zero has a fundamental significance. It is the lowest possible temperature a scientist can conceive of. By hard work and elaborate apparatus, scientists have found it possible to cool some substances down to within 0.000 1 degree Celsius of absolute zero.

The base unit of temperature in the International System of Units is the *kelvin* instead of the degree Celsius. Temperatures measured in kelvins are based upon absolute zero, since a temperature of zero kelvins is the same as absolute zero. To change any temperature measured in degrees Celsius to kelvins, simply add 273. We may express this relation by an algebraic equation:

$$T = t + 273$$

where T stands for the temperature in kelvins and t stands for the temperature in degrees Celsius. According to this equation, absolute zero or −273°C is the same as 0 kelvins (abbreviated 0 K).

Calculate the value of T for each of the three temperatures you measured in the experiment. Then, for each of the temperatures, calculate values of length/t and length/T. Which values are the same? Can you state a mathematical rule for the values of length/T? This rule is another way of stating Charles' law. It also shows why the kelvin temperature scale is important.

P-8 There Ought to Be a Law

An interesting consequence of the kinetic molecular theory is the prediction that equal volumes of any two gases at the same temperature and pressure contain equal *numbers* of molecules. Or, to put it another way, we can say that equal volumes of gases at the same temperature and pressure contain the same number of *moles* (abbreviated mol) of gas molecules. (Remember, a mole is just a convenient measure of a large number of particles. One mole of molecules is 6.02×10^{23} molecules.)

This prediction is found to be correct for many gases. In fact, it was verified experimentally by Avogadro in the early 1800s before anyone had stated the kinetic molecular theory. The proven hypothesis now is known as *Avogadro's law.* The gases which obey Avogadro's law are called *ideal gases.* An ideal gas is any gas in which the molecules have no interactions except when colliding, as assumed by the kinetic molecular theory. Under ordinary conditions of temperature and pressure, air and many other gases behave as ideal gases.

Chemists find that 24 464 cm^3 of any ideal gas at 25°C (room temperature) and one atmosphere pressure contain one mole of

This postage stamp records Amedeo Avogadro's discovery of properties of gases, known as *Avogadro's law.*

Both the blimp and the balloons are filled with helium gas. Helium was not always used in lighter-than-air balloons. Do you know which gas was? Is helium more or less efficient than this gas? Why is this other gas not used today?

molecules. Calculate the *mass* of this volume of helium (He) and nitrogen (N_2). (See the *Table of International Relative Atomic Masses* on page 112.) Are they the same mass? Can this explain why helium is used in lighter-than-air balloons?

There ought to be a law that summarizes the various properties of ideal gases, and there is! It is called the *ideal gas law,* and it can be expressed by the equation

$$PV = nRT$$

In this equation, P stands for the pressure, V stands for the volume, n stands for the number of moles of gas molecules, and T stands for the temperature on the kelvin scale. The remaining symbol R stands for a constant called the *gas constant.* If you express P in atmospheres (atm), V in cubic centimeters, n in moles, and T in kelvins, then the value of R turns out to be $82.1\ \text{cm}^3 \cdot \text{atm/K} \cdot \text{mol}$.

Does this equation agree with what we have learned about the properties of gases? First, consider Boyle's law. The right-hand side of the ideal gas law equation is constant for any fixed temperature and mass of gas. Thus the equation states that PV is a constant for a fixed mass of gas at constant temperature, which is Boyle's law.

Try your hand at getting the ideal gas law to agree with Charles' law and Avogadro's law. Use the equation in the rearranged forms

$$\frac{V}{T} = \frac{nR}{P} \quad \text{and} \quad V = \frac{nRT}{P}$$

Most familiar gases are ideal gases at room temperature. However, as any gas is cooled down close to the temperature at which it turns into a liquid, interactions between the molecules begin to become important. The molecules no longer travel at constant speeds between their collisions, and the ideal gas law is no longer obeyed. We now must discuss the nature of these interactions. The interactions are responsible for the liquid and solid states of matter, as will be seen in the next section.

QUESTIONS

1. A bicycle pump contains 5.0×10^2 cm^3 of air at 1.0 atm pressure. The pump outlet is closed so that no air can escape, and the handle is pushed down until the volume is changed to 2.0×10^2 cm^3. Assuming that the temperature does not change, what is the new pressure? (See worked solution in margin.)
2. An ideal gas is used to construct a gas thermometer. When the temperature of the gas is 0°C, the volume of the gas is 2.00 cm^3. What is the volume of the gas when the temperature is raised to 100°C (with the pressure remaining constant)? (See worked solution in margin.)
3. What is the volume of 1.00 mol of gas molecules at a pressure of 2.00 atm if the temperature is 327°C? (See worked solution in margin.)
4. The air in a tire at a pressure of 2.4 atm contains 4.0 mol of gas molecules. If 1.0 mol of the gas molecules is released through the valve, what is the new pressure in the tire (at the same temperature and volume as before)? (Hint: Find an expression for P_2/P_1.)
5. The largest blimp ever built had a volume of 4×10^{10} cm^3. What *mass* of helium would be needed to fill this volume at 27°C and 1 atm pressure? (Hint: How many moles of helium are needed? What is the mass of each mole?)
6. If the pressure of a certain mass of gas is doubled at a constant temperature, what is the ratio of the new volume to the old volume?
7. If the temperature of a certain mass of gas is changed from 27°C to 327°C, what is the ratio of the temperatures on the kelvin scale? What is the ratio of the new volume to the old volume (at a constant pressure)?
8. Explain why the pressure goes down when the volume of a certain number of moles of a gas is increased.
9. A sample of gas has a volume of 200. cm^3, a temperature of −73°C, and a pressure of 60 cm Hg. If the volume is changed to 300. cm^3 and the temperature is changed to 27°C, what will the pressure be? (Hint: Use the expression P_2/P_1 from question 4.)

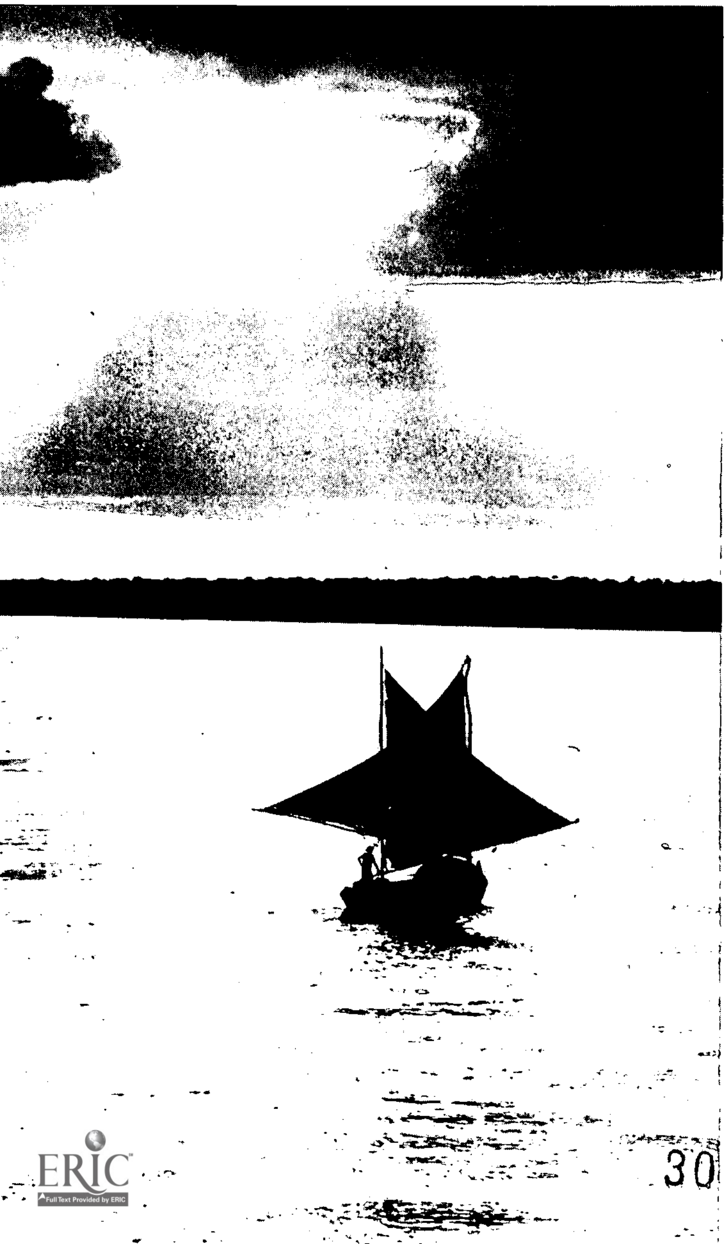
Solution to question 1:
$P_1V_1 = P_2V_2$
$1.0 \text{ atm} \times 5.0 \times 10^2 \text{ cm}^3 =$
$P_2 \times 2.0 \times 10^2 \text{ cm}^3$
$P_2 = 1.0 \text{ atm} \times 5.0 \times 10^2 \text{ cm}^3/2.0 \times 10^2 \text{ cm}^3$
$P_2 = 2.5 \text{ atm}$

Solution to question 2:
$T_1 = 0 + 273 = 273 \text{ K}$
$T_2 = 100 + 273 = 373 \text{ K}$
$V_1/T_1 = V_2/T_2$
$2.00 \text{ cm}^3/273 \text{ K} = V_2/373 \text{ K}$
$V_2 = 2.00 \text{ cm}^3 \times 373 \text{ K}/273 \text{ K}$
$V_2 = 2.73 \text{ cm}^3$

Solution to question 3:
$PV = nRT$
$2.00 \text{ atm} \times V = 1.00 \text{ mol}$
$\times (82.1 \text{ cm}^3 \cdot \text{atm/K} \cdot \text{mol}) \times 600 \text{ K}$
$V = 1.00 \text{ mol} \times (82.1 \text{ cm}^3 \cdot \text{atm/K} \cdot \text{mol})$
$\times 600 \text{ K}/2.00 \text{ atm} = 2.46 \times 10^4 \text{ cm}^3$

Liquids and Solids: Condensed States

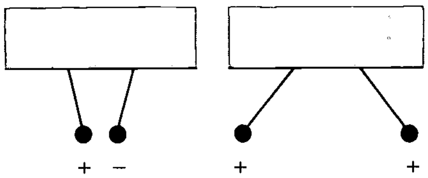
In a gas, each molecule is so far away from other molecules most of the time that there is very little interaction. The molecules in a gas are like solitary human beings. In liquids and solids, the arrangement is distinctly different. Liquids and solids are called *condensed states of matter*. The molecules are held close together by attractive forces—somewhat like crowded human communities. But what causes these attractive forces?



P-9 The Attraction of Molecules

Most types of attractive forces between molecules can be explained by *Coulomb's law:*

$$\text{force between two charges} = \frac{q_1 q_2}{cd^2}$$

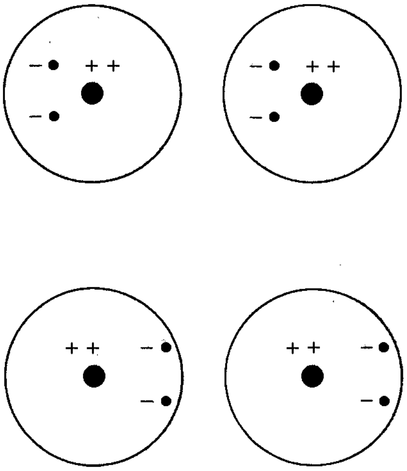


where q_1 and q_2 are the sizes of two electric charges, c is a constant, and d is the distance between the charges. The force between two charges is *attractive* if one of the charges is positive and the other is negative. It is *repulsive* if the two charges have the same sign. Just remember that opposite charges attract and like charges repel. According to Coulomb's law, the force is greater when the size of the charges (q_1 and q_2) is greater and also when the charges are closer together (that is, when d is smaller).

Recall that atoms and molecules contain negatively charged electrons and positively charged nuclei. The overall force between two molecules is the result of the forces between all the charges in the two molecules.

Now, how can we explain the fact that helium gas turns into a liquid at −269°C? (Liquid helium has the lowest boiling point known, only 4 degrees Celsius above absolute zero.) Helium consists of single, neutral atoms containing two electrons of charge −1 and a nucleus of charge +2. The electrons move rapidly around the nucleus. The electrons of one helium atom are *attracted* to the nucleus of a nearby helium atom (since opposite charges attract). But this attraction is counterbalanced by the *repulsions* between the electrons and the repulsion between the two nuclei.

HELIUM ATOMS



The illustration of two helium atoms explains how an overall attraction can result. At this instant the electrons of both atoms are located to the left of the nuclei. According to Coulomb's law, the strongest force is between the closest charges. The sketch shows that the strongest force between the two atoms is between the nucleus of the left atom and the electrons of the right atom. Therefore the attractive force predominates.

Notice that in the second set of helium atoms the electrons are to the right of the nuclei. This occurs just as often as in the first situation. Again there is an attraction, this time between the electrons on the left and the nucleus on the right. Of course, the electrons in one atom are in different places at different times, but the electrons in the other atom tend to move in a way which allows an overall attraction.

The overall attraction is called the *London force,* after the theoretician, F. London, who first explained it (1930). The London force is always attractive, and it occurs between all kinds of atoms or molecules. However, as we shall see, there are other, stronger kinds of attraction present when the molecules are polar (that is, when they have a positive and a negative end). In the case of helium, the London force is weak, but it is the only attractive force present. When the temperature of helium gas is lowered to −269°C or below (at one atmosphere pressure), the London force pulls the atoms together and liquid helium forms.*

As we have seen, the London force is caused by the attraction between electrons and nuclei. Thus we expect that the greater the number of electrons, the greater the force. This explains why the greater the number of electrons, the higher the boiling point for similar molecules. For instance, notice the trend in boiling points as the number of electrons changes in this table of diatomic molecules.

Hydrogen and oxygen are commonly used as rocket fuels. To save space, they are stored in the rocket as liquids. As you can see from the boiling points in the table, gaseous hydrogen and oxygen must be cooled to very low temperatures in order to condense them to liquids.

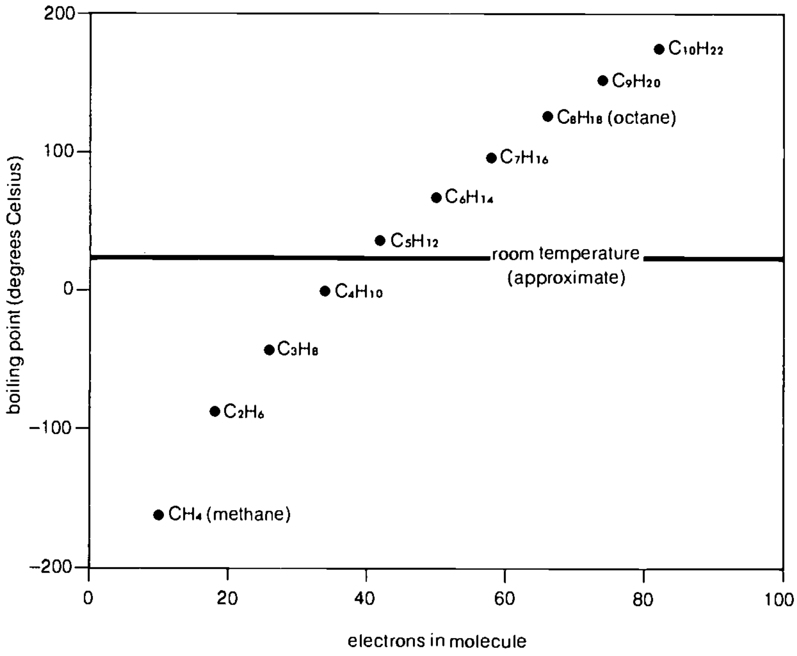
TIME MACHINE

1927	Broadway musical *Show Boat* opens in New York.
1928	Women compete in the Olympics for the first time.
1928	Maurice Ravel composes *Bolero*.
1929	U.S. stock market crashes.
1930	**German physicist Fritz London identifies London force.**
1931	Frank Whittle develops first jet-propulsion engine.
1932	James Chadwick discovers the neutron.
1933	Fay Wray stars in the original *King Kong*.

Table of Diatomic Molecules

Molecule	Number of electrons	Boiling point (°C)
H_2	2	−253
N_2	14	−196
O_2	16	−183
Cl_2	34	−35

The graph below shows the boiling points of some straight-chain hydrocarbons.



Does this graph show the same trend of the boiling point with the number of electrons? Which of these compounds are gases at room temperature?

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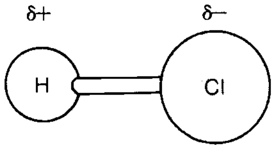
*Sometimes the force which causes gaseous helium to liquefy is referred to as the *van der Waals force* instead of the London force. The van der Waals force is the total attractive force between two molecules. In the case of helium and other nonpolar atoms and molecules, the van der Waals force is the same as the London force. For polar molecules the van der Waals force includes other kinds of forces in addition to the London force.

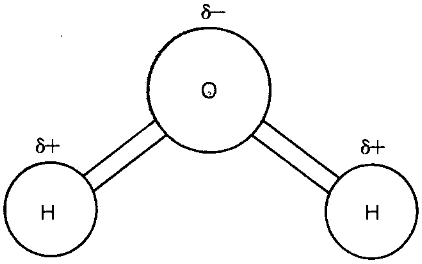
Gasoline motor fuel is a mixture of hydrocarbon molecules. Most of the molecules contain from six to ten carbon atoms. With a change in seasons, the gasoline refiners change the composition of the mixture. In winter the refiners manufacture gasoline which evaporates more readily in the carburetor to make cold weather starting easier. In warm weather the refiners produce a fuel which boils less readily in order to avoid vapor lock (bubbles of gasoline vapor in the fuel line which cut down the supply of gasoline to the engine). Do you think the refiners favor those molecules with fewer or more carbon atoms in the winter? Which do they favor in the summer?

P-10 Special Attraction: Polar Molecules

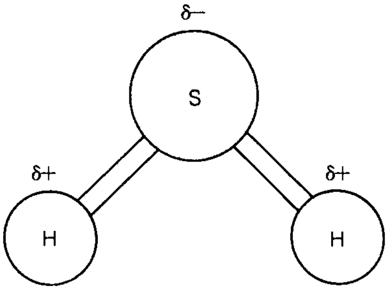


HYDROGEN CHLORIDE (HCl)

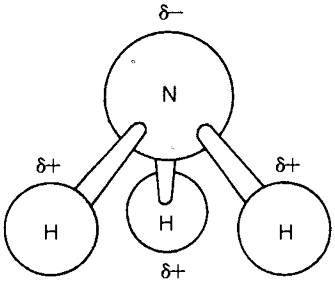
You will recall from *Reactions and Reason: An Introductory Chemistry Module* that a neutral molecule with a positive end and a negative end is called a *polar molecule.* For instance, the hydrogen chloride molecule (HCl) is polar because the hydrogen and the chlorine atoms do not share the electrons in the covalent bond equally. The electrons in the bond spend more of their time near the chlorine atom because the chlorine nucleus has a larger positive charge than the hydrogen nucleus. This attraction of the shared electrons towards the chlorine puts a partial negative charge on the chlorine atom and a partial positive charge on the hydrogen atom. The partial charges in a polar molecule are smaller than the charge of an electron. This is why they are called *partial* charges. They must add up to a net charge of zero in order for the molecule to be neutral.



WATER (H_2O)

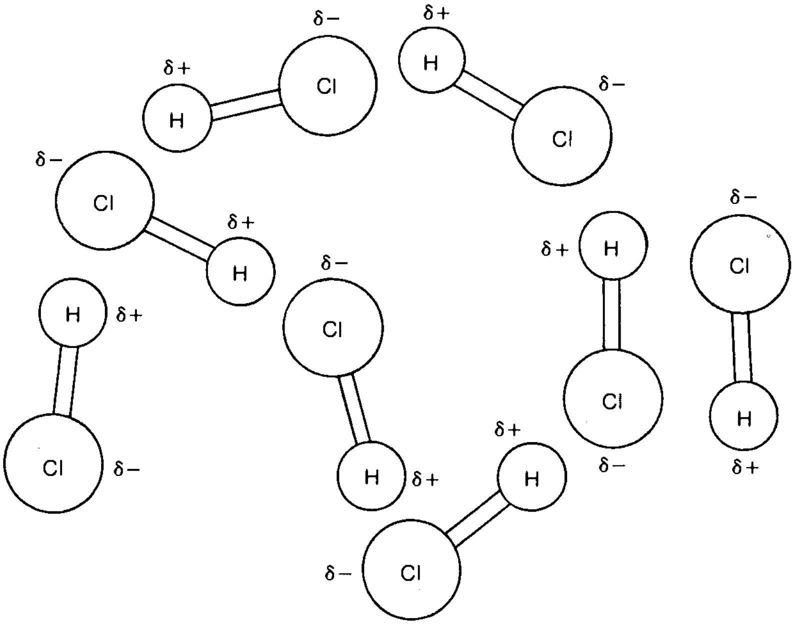


HYDROGEN SULFIDE (H_2S)



AMMONIA (NH_3)

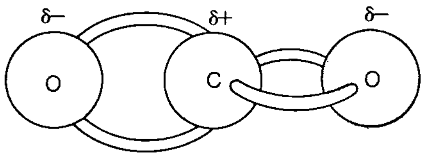
As we would expect from Coulomb's law, the positive end of one polar molecule is attracted to the negative end of any nearby polar molecule. We can call this attractive force a *polar attraction*. The polar attraction exists in addition to the London force, and often it is much stronger than the London force. As a result, polar molecules in a liquid or gas tend to arrange themselves with the positive end of one molecule close to the negative end of another molecule. In the illustration of liquid hydrogen chloride, you can see an example of the polar attraction of molecules.



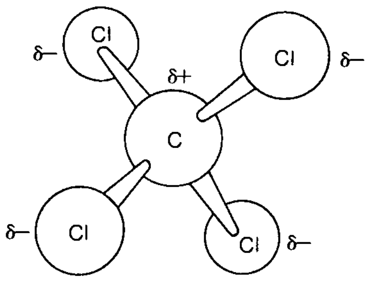
LIQUID HYDROGEN CHLORIDE

Arrangements such as this don't last very long because the molecules in a liquid constantly move. But each new arrangement tends to again have the positive ends of the molecules close to the negative ends of other molecules. The situation is a little like children holding hands in a ring, where a left hand is usually holding a right hand rather than another left hand.

Some molecules which contain partial charges are *not* polar, because of their shape. They are nonpolar because the partial charges are arranged in a symmetrical fashion which does not make one side of the molecule more positive or negative than the other. Two examples of such nonpolar molecules are carbon dioxide (CO_2) and carbon tetrachloride (CCl_4).

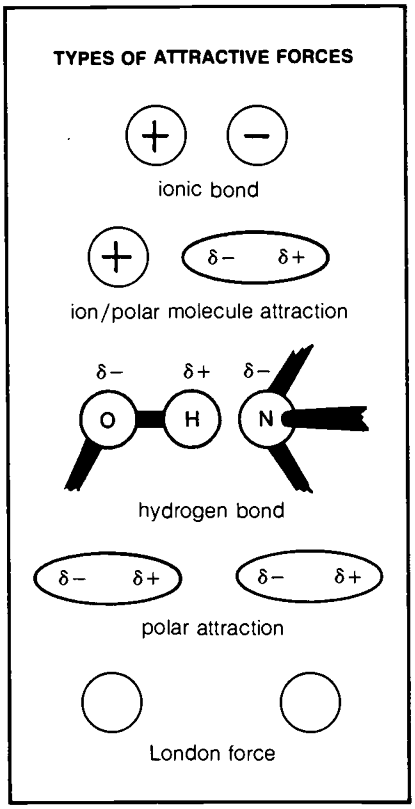


CARBON DIOXIDE (CO_2)



CARBON TETRACHLORIDE (CCl_4)

The importance of polar attractions can be seen by the fact that polar compounds generally have higher boiling points than nonpolar compounds with the same number of electrons. For instance, hydrogen sulfide (H_2S), with eighteen electrons, boils at −61° C, but ethane (C_2H_6), with the same number of electrons, boils at −89° C. Polar compounds also usually dissolve in water to a much greater extent than do nonpolar compounds because of the polar attraction between water molecules and other polar molecules.


TYPES OF ATTRACTIVE FORCES

A particularly strong polar attraction occurs when a hydrogen atom which is bonded to a nitrogen, oxygen, or fluorine atom in the molecule comes close to a nitrogen, oxygen, or fluorine atom in another molecule. This strong attraction is sometimes called a *hydrogen bond*. Hydrogen bonds are important in holding molecules of ammonia (NH_3), water (H_2O), and hydrogen fluoride (HF) together in the liquid states of these compounds. They can also be important forces in determining the solid structures of compounds containing N—H, O—H, or F—H bonds. (An example of O—H bonding is ice.) Hydrogen bonds are crucial for the three-dimensional shapes of macromolecules in living systems, such as proteins and DNA (see *Molecules in Living Systems: A Biochemistry Module*).

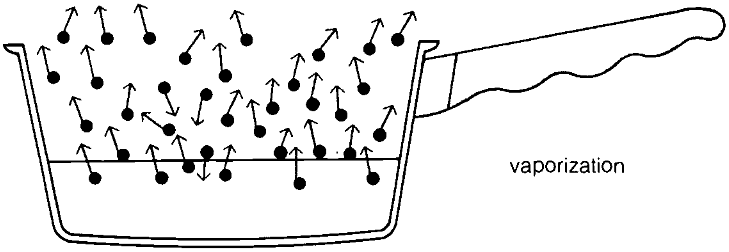
The strongest attraction of all takes place between oppositely charged ions. *Ions* are molecules (or single atoms) that are charged because they contain unequal numbers of electrons and protons. Since the charge of an ion is at least as large in size as the charge of an electron, Coulomb's law predicts stronger forces between ions than between neutral polar molecules that contain only partial charges. The attractive forces between oppositely charged ions in liquids and solids are called *ionic bonds* (see *Diversity and Periodicity: An Inorganic Chemistry Module*).

It may have occurred to you that, since the partial charges of a polar molecule can be strongly attracted to other polar molecules, an ion should be attracted even more strongly. This is the case: ions have strong attractions to polar molecules. For instance, in a water solution of sodium chloride (NaCl), the Na^+ ions are attracted to the negative O atoms of the water and the Cl^- ions are attracted to the positive H atoms of the water. This helps to explain why common salt dissolves easily in water.

P-11 The Vaporization of a Liquid

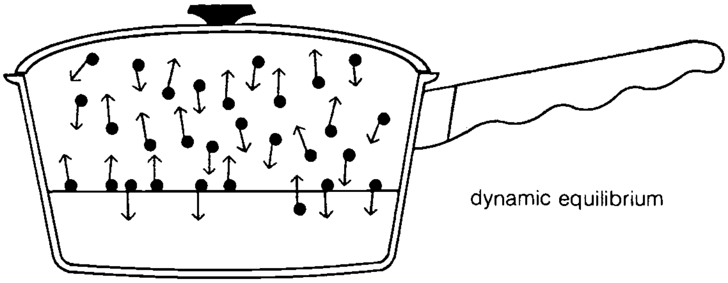
A liquid is a community of molecules in which attractive forces keep the molecules close to one another but still permit them to move. Because the molecules are congregated together, they need not fill the entire volume of the container (as a gas does) but instead stay at the bottom. The molecules in a liquid move past one another, bounce off one another, and constantly change their directions, just as in a gas. But in contrast to a gas, these molecules resemble people at a crowded party who are milling around, jostling past one another, and able to move only slowly in any direction.

We know that water left in an open pan normally vaporizes (evaporates) until the pan is dry. This is a macroscopic observation. In the molecular world, H_2O molecules are escaping from the surface of the liquid and entering the atmosphere as gas molecules that are no longer held by the attractive pull of the liquid. (This is like people at the edge of a crowded party who escape to the outdoors and fresh air!)



Chemists use the term *phase* to refer to a quantity of homogeneous (uniform) material in a particular state of matter. In the vaporization of water we would say that molecules are leaving the liquid phase and entering the gas phase (sometimes called the *vapor* phase).

If we now place a tight lid on the pan of water, the vaporization soon seems to stop. Molecules of H_2O continue to escape from the liquid phase as frequently as before. But because the lid prevents the gas molecules from leaving the pan, they collide with the lid and the walls of the pan and also with the surface of the liquid water. Some of the gas H_2O molecules that hit the liquid stick in it because of the attractive forces. As the number of H_2O molecules in the gas phase builds up, the molecules hit the liquid more frequently. Eventually, H_2O molecules enter the liquid from the gas as frequently as they escape to the gas from the liquid. Thus there is no *net* vaporization, even though individual molecules are still vaporizing.



This balance in the rates of two opposing molecular processes (going from gas to liquid and from liquid to gas) is called a *dynamic equilibrium*. We shall encounter several other examples of dynamic equilibria in this module. In the macroscopic world, no change can be observed. We say that the liquid phase and the gas phase are *in equilibrium* with one another.

The process of *condensation* is the opposite of vaporization. Molecules enter the liquid phase from the gas phase faster than they escape. For instance, condensation occurs when moist air hits a cool surface, forming dew. In automobiles, oily compounds called plasticizers (used to keep the vinyl upholstery flexible) can vaporize from the upholstery and condense on the windows. This causes an annoying sticky film to form on the glass.

When a liquid phase and a gas phase are in equilibrium with one another, the gas is said to be *saturated* with the vapor of the liquid. For instance, when there is no longer any net vaporization of the water in the covered pan, the air in the pan is saturated with the water vapor. The amount of water in each cubic centimeter of the air depends on the temperature. If the pan is heated, the number of H_2O molecules contained in each cubic centimeter of saturated air increases.

Chemists refer to vapor pressure in order to describe the amount of water contained in the saturated gas. Suppose that some of the gas, saturated with water vapor, is put into a closed flask, and then somehow all of the gas molecules except the H_2O molecules are taken out of the flask. The pressure of the gas that is left—the pressure of the water vapor—is called the vapor pressure of the liquid water. The *vapor pressure* of a liquid is the pressure caused by the molecules of the liquid which are present in the saturated gas phase.

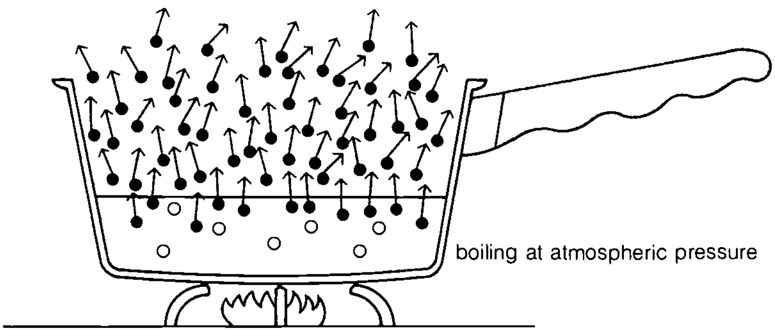
TIME MACHINE

1822	Charles Babbage invents first calculating machine.
1823	**Michael Faraday, British scientist, describes the condensation of H_2S, CO_2, and other gases by cooling with a salt-ice mixture.**
1824	University of Virginia campus is completed according to designs by Thomas Jefferson, architect and former U.S. president.
1825	The Erie Canal, a waterway from Albany to Buffalo, is completed.
1826	Felix Mendelssohn composes overture to *A Midsummer Night's Dream.*
1827	*Birds of America* drawings bring fame to John James Audubon.

P-12 The Boiling Process

The vapor pressure of a liquid increases as the temperature of the liquid is increased. At a temperature of 25°C, water has a vapor pressure of 2.4 cm Hg, but at 70°C it has a vapor pressure almost ten times greater (23 cm Hg).

If you heat a covered pan of water, the vapor pressure increases until eventually it becomes the same as the atmospheric pressure. If you uncover the pan and continue to add heat to the liquid water, bubbles of steam appear throughout the liquid and escape upwards into the atmosphere. This process is called *boiling*.



boiling at atmospheric pressure

If the atmospheric pressure is one atmosphere, water boils at 100°C. This is because the vapor pressure of water reaches 76 cm Hg, or one atmosphere, at 100°C. As long as the pressure remains at one atmosphere and liquid water is left in the pan, the boiling temperature remains at 100°C.

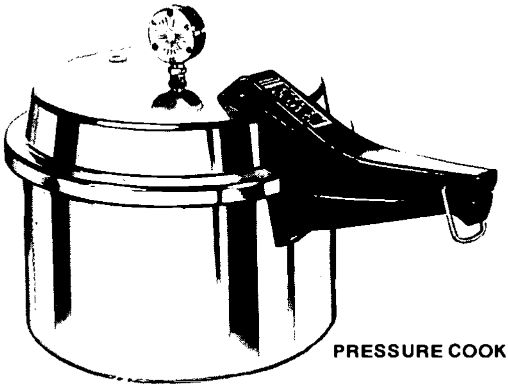
What has been said about water is true of any other liquid. The liquid boils when its temperature is high enough to make the vapor pressure equal to the pressure of the gas above the liquid. If the container holding the liquid is open to the atmosphere, this pressure is the atmospheric pressure. The *normal boiling point* of a pure substance is the boiling temperature when the pressure is exactly one atmosphere. Usually we speak simply of the boiling point.

As we have already seen, the boiling point is a convenient measure of the strength of the attractive forces in the liquid. Liquids with strong attractive forces have higher boiling points, and also lower vapor pressures, at room temperature, compared to liquids with weaker attractive forces. For instance, compare gasoline with water. At room temperature, gasoline evaporates faster than water; it is said to be more *volatile*. Thus gasoline has a higher vapor pressure than water. Do you expect gasoline or water to have the higher boiling point? Which liquid has stronger attractive forces between the molecules?

Suppose that a liquid is in a closed container having a pressure which is always greater than the vapor pressure. In such a container, the liquid can never boil. For instance, a pressure cooker is a container with a tightly fitting lid. When liquid water is heated in a pressure cooker, the pressure inside exceeds atmospheric pressure. At such a pressure, the contents can be cooked at temperatures greater than 100°C without a loss of water through boiling. Autoclaves and sterilizers used in hospitals to kill bacteria by heating work on the same principle.

Modern water-cooled cars have radiators with pressure caps which allow the pressure to rise to about two atmospheres. The purpose of the cap is to permit the radiator water to heat up to about 120°C without boiling away.

HATS OFF
TO THE "GOOD" OLD DAYS

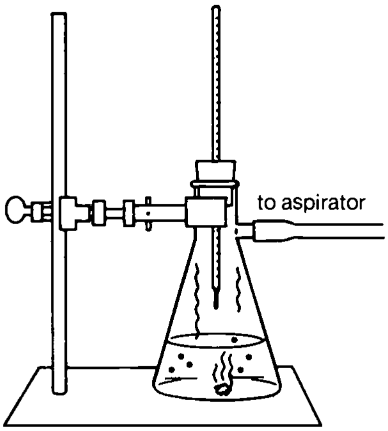


PRESSURE COOKER

AUTOCLAVE

miniexperiment

P-13 Boiling at Reduced Pressure



What do you predict will happen to the temperature at which a liquid boils if the pressure in the container is *lowered* below one atmosphere?

Test your prediction by placing some hot tap water and a boiling chip in a hard glass filter flask. Close the neck of the flask with a stopper into which a thermometer has been inserted. Connect the tubing to a water aspirator pump and turn on the water. When boiling begins, record the temperature. The thermometer does not have to be in the water to measure the boiling temperature. Why?

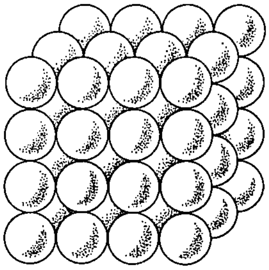
Continue to observe as the water boils, and record the temperature every 30 seconds for 5 minutes. Explain the results.

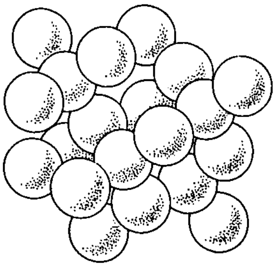
At high elevations, where atmospheric pressure is usually less than one atmosphere, boiling occurs at a lower temperature than the normal boiling point because the vapor pressure does not have to be as high as 76 cm Hg. For instance, in Denver, at an elevation of almost 2 km above sea level, the atmospheric pressure is usually about 63 cm Hg. Water usually boils at about 95°C in locales with elevations similar to Denver's. Does it take longer to cook a hard-boiled egg in Baltimore, which is at sea level, or in Denver?

P-14 Solid Structures

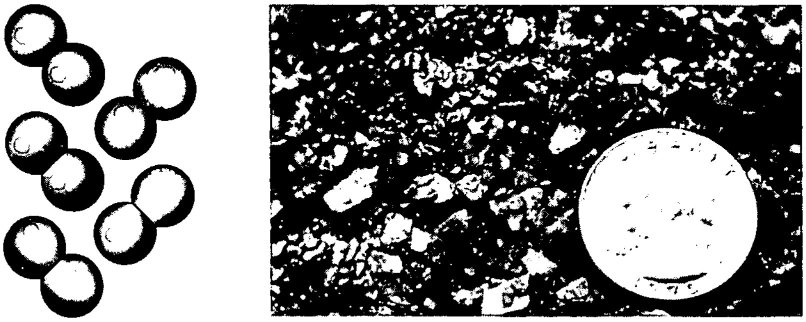
The molecules of a solid do not readily move past one another. They are held in place next to one another by the same kinds of attractive forces that cause a gas to condense to a liquid. The average kinetic energy of the molecules is so low in a solid, compared with the attractive forces, that the molecules are locked into stable positions. The molecules move back and forth in the spaces left by neighboring molecules, but they cannot move freely throughout the community as in a liquid. Thus unlike a liquid, a solid is rigid and has a definite shape.

The molecules in many solids are arranged in a neatly organized pattern. In others, the molecules are jumbled together in helter-skelter fashion. The first kind of solid, in which the attractive forces have pulled the molecules together into a repeating structure, is called a *crystal*. The second kind of solid is called an *amorphous solid*, meaning a solid without form. A crystal is like the audience seated at a concert in a theater, neatly packed into rows. An amorphous solid is more like the crowd at an outdoor concert, sprawled out on the ground in no particular order.

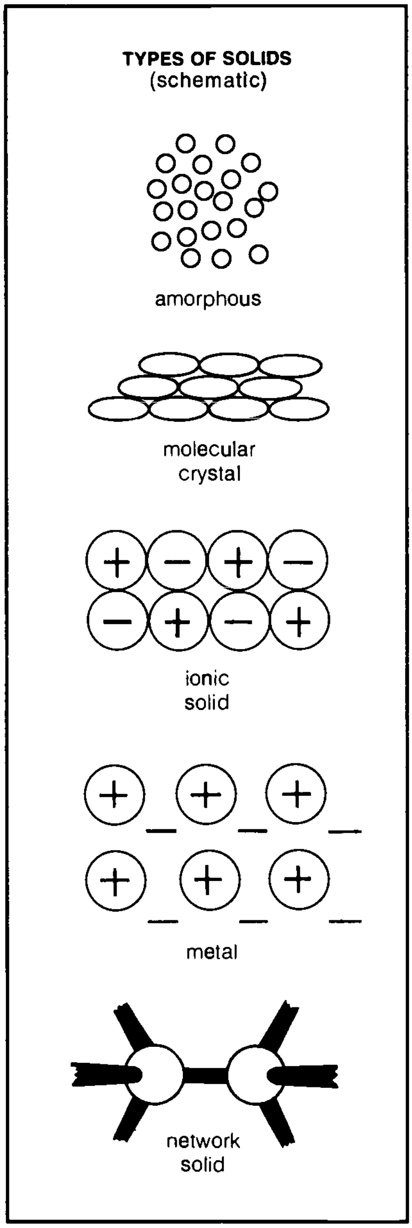




We can distinguish four general types of crystals according to the kinds of attractive forces between the particles contained in them. *Molecular crystals* contain electrically neutral molecules held together by relatively weak forces such as London forces. Examples are naphthalene (mothballs), paradichlorobenzene (the more modern kind of moth repellent), iodine crystals, and solid CO_2 (Dry Ice). Ordinary ice is a molecular crystal held together chiefly by hydrogen bonds between the H_2O molecules.



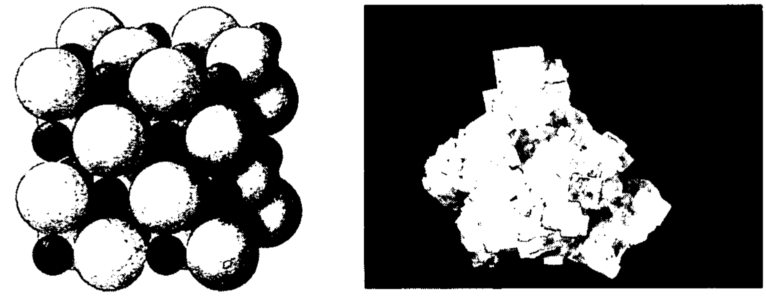
A model of iodine molecules in iodine crystals *(left)* and iodine crystals in their solid state *(right)*.



TYPES OF SOLIDS
(schematic)

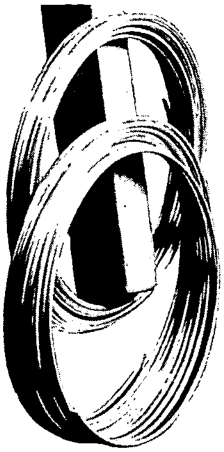
Molecular crystals are usually soft and easily melted because the forces between the molecules are relatively weak. Individual molecules can easily escape from the crystal into the gas phase, a process called *sublimation*. You can readily detect the sublimation of moth repellents by their odor. The sublimation of ice is illustrated by the tendency of snow to evaporate in cold weather without melting and by the manufacture of freeze-dried coffee from brewed coffee.

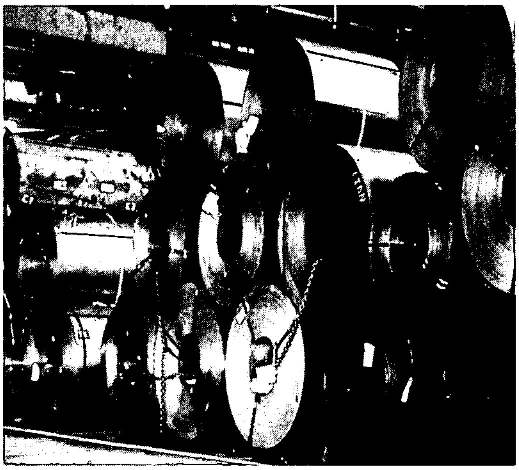
Ionic solids are a second type of crystal. They are ordered arrangements of ions held together by ionic bonds. Because these bonds are strong, ionic crystals tend to be hard and to have high melting points. Sodium chloride (NaCl), for example, melts at 801°C.

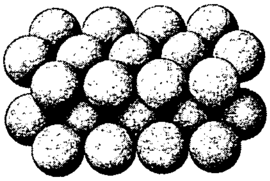


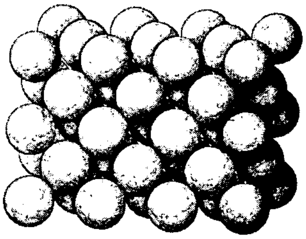
Crystal lattice structure of sodium chloride *(left)*. Rock salt (halite) in its crystallized state *(right)*. An electron micrograph of salt crystals magnified nineteen times *(below)*.

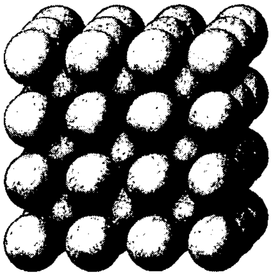
Metals form a third type of crystal with a unique kind of bonding. In a solid metal, such as copper or aluminum, the neutral atoms of the metallic element are held together by their valence electrons, which can move throughout the crystal (see *Diversity and Periodicity: An Inorganic Chemistry Module*). This free movement of electrons allows metals to conduct electricity. Metals are generally good heat conductors, have a metallic luster, and may be easily deformed without breaking apart.

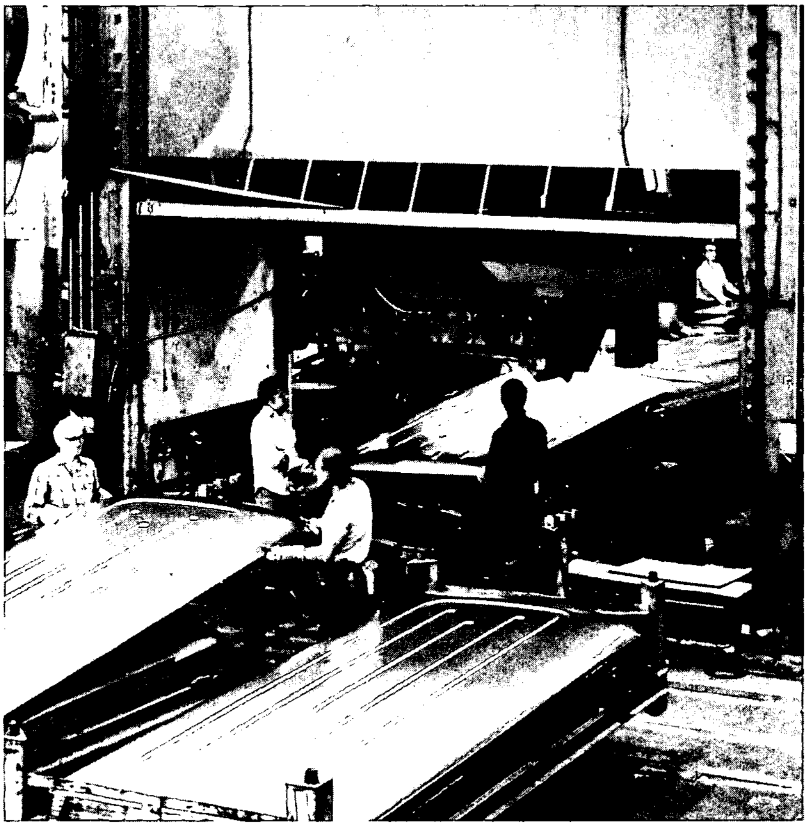








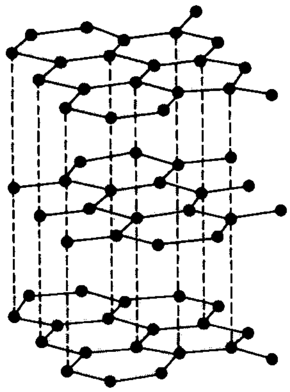


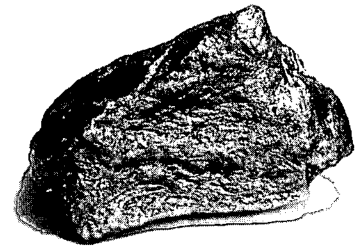


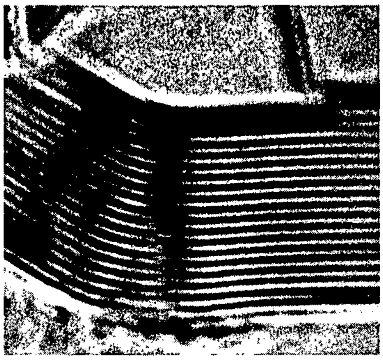
Crystal lattice models of various metals *(above)*. Metal in wire form, sheet, and sheet metal being formed into automobile parts on a multiton press *(left)* helps illustrate the malleability and ductility of metals.

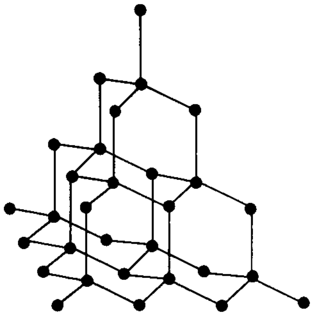
The fourth type of crystal is called a *network solid*. It consists of atoms joined by covalent bonds into an array which extends throughout the crystal. A network solid is really a single gigantic molecule which cannot exist as a liquid or a gas. Such a molecule is the only kind which can be seen with the naked eye. Asbestos fibers, mica sheets, quartz crystals (SiO_2), and two crystalline forms of carbon (graphite and diamond) are all network solids.

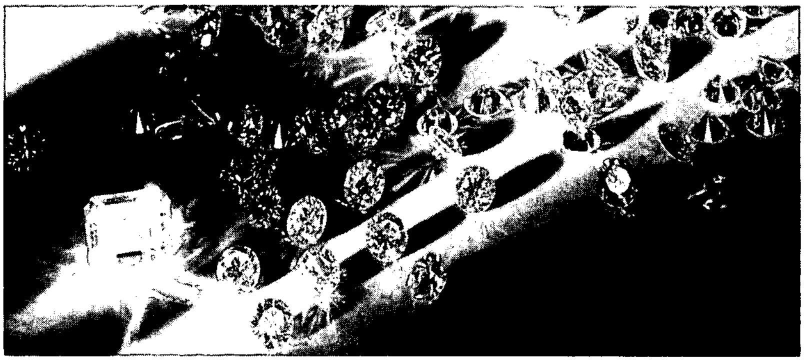
Compare the model of the network structure of graphite *(left)* with the sample of graphite *(middle)* and with the electron micrograph—magnified about six million times *(right)*. The carbon layers are about 0.34mm apart and are not bonded to each other. These layers can slide past each other easily, which makes graphite an excellent lubricant.

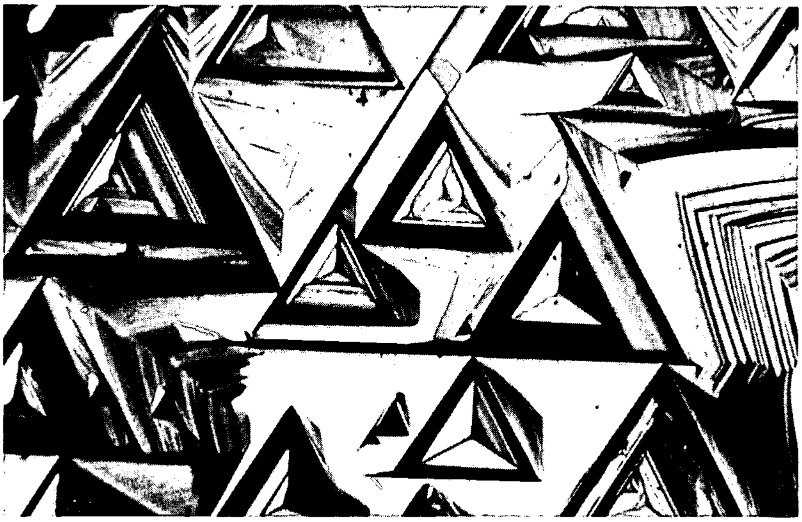




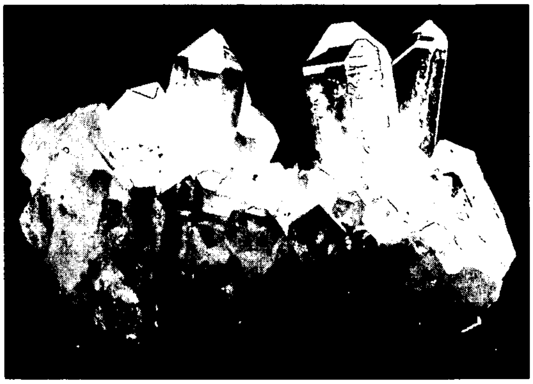








Note the bonding in the model of the network structure of a diamond *(left)*. Does this give you a clue to why a diamond *(right)* is the hardest of the known elements? Microphoto of the surface of a diamond magnified two hundred times *(bottom)*.

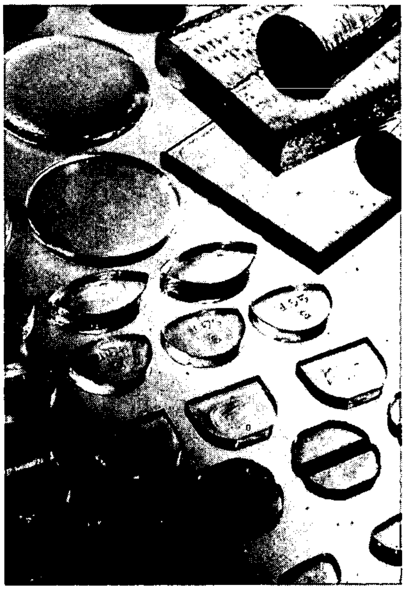


Both mica *(left)* and quartz *(right)* are examples of network solids. What do you suppose models of these networks would resemble?

Among the familiar amorphous noncrystalline solids are common glass, many plastics such as polyethylene, and various solid waxes such as paraffin wax. (Some waxes, however, when they are pure, may be crystalline.) When an amorphous solid is heated, it generally softens and, at a high enough temperature, may eventually become a liquid. However, there is no sharp melting point at which this change occurs, as there is for crystalline solids.

An uneven surface shows up along the edge of glass. In contrast, a crystal tends to give clean breaks along a line called a *cleavage plane*.

Because glass is an amorphous solid, it has no specific melting point and softens when heated before turning into a liquid. The glassblower takes advantage of these properties when fashioning glass into its many useful forms. Optical lens blanks are drawn from melting tanks. The different shapes are stamped out of these molten strips and cylinders.

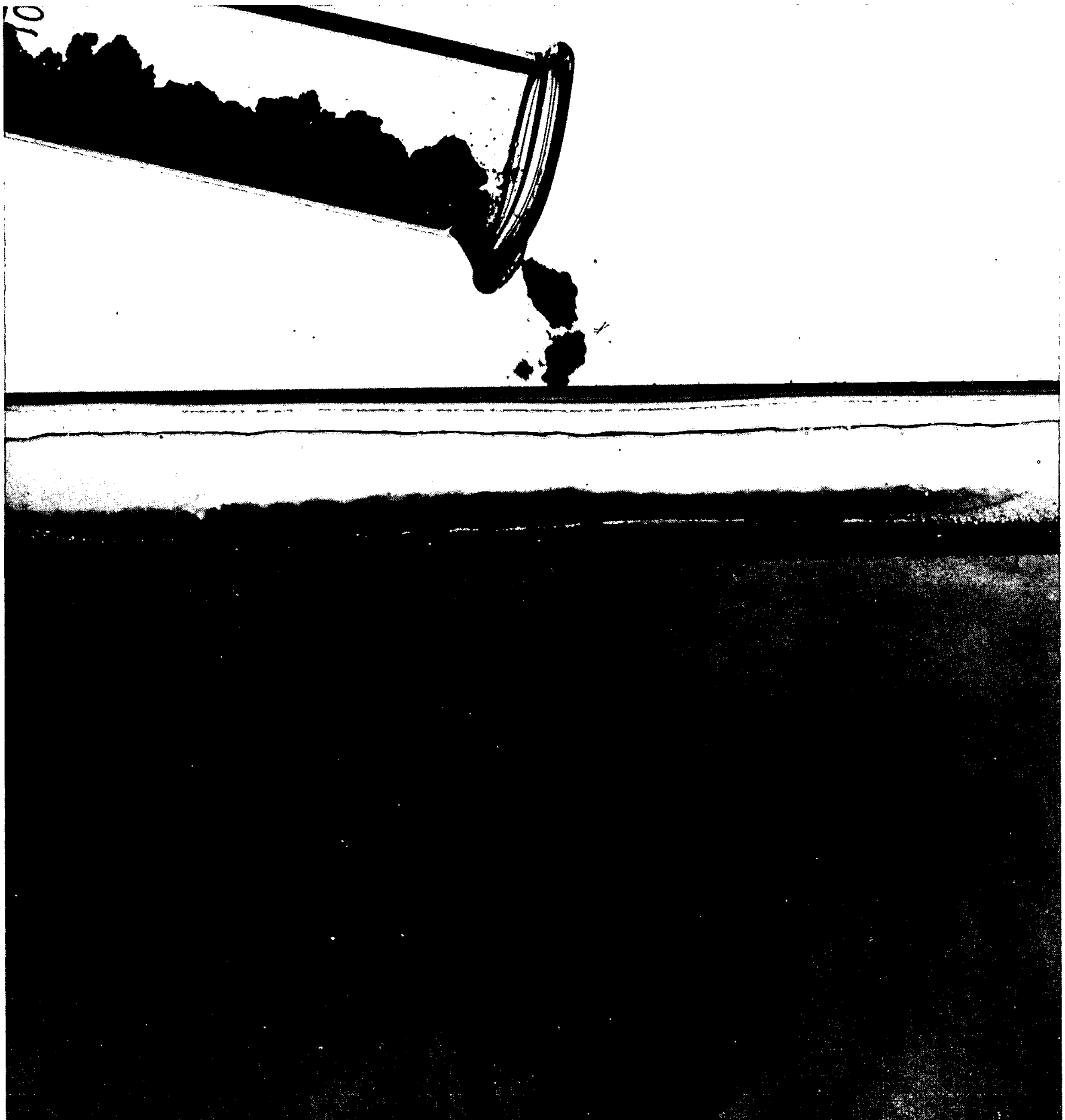


QUESTIONS

1. Explain the following differences:
   (a) Molecules of methane (CH_4) and water (H_2O) have equal numbers of electrons (how many?), but methane is a gas while water is a liquid.
   (b) Carbon tetrafluoride (CF_4) is a gas; carbon tetrachloride, (CCl_4) is a liquid; carbon tetrabromide (CBr_4) is a solid.
   (c) Molecules of hydrogen chloride (HCl) and fluorine (F_2) have equal numbers of electrons (how many?); the boiling point of hydrogen chloride is $-85°C$ while that of fluorine is $-188°C$.
   (d) Sodium chloride (NaCl) is highly soluble in water but practically insoluble in carbon tetrachloride.
   (e) Carbon in the form of a diamond is an extremely hard solid, while nitrogen (N_2) is a gas.
   (f) Iodine crystals are soft, while sodium iodide crystals are hard.
2. Hard candies are made by heating crystalline sugar until it melts at 185°C into a syrup. The syrup is then cooled to form a hard, brittle solid. If this solid is reheated, it gradually softens. Explain what has happened to the sucrose molecules to cause this change.
3. Classify each of the following into one of the five general types of solids: Plexiglas, aluminum foil, sucrose (sugar) crystals, sodium hydroxide, and charcoal.

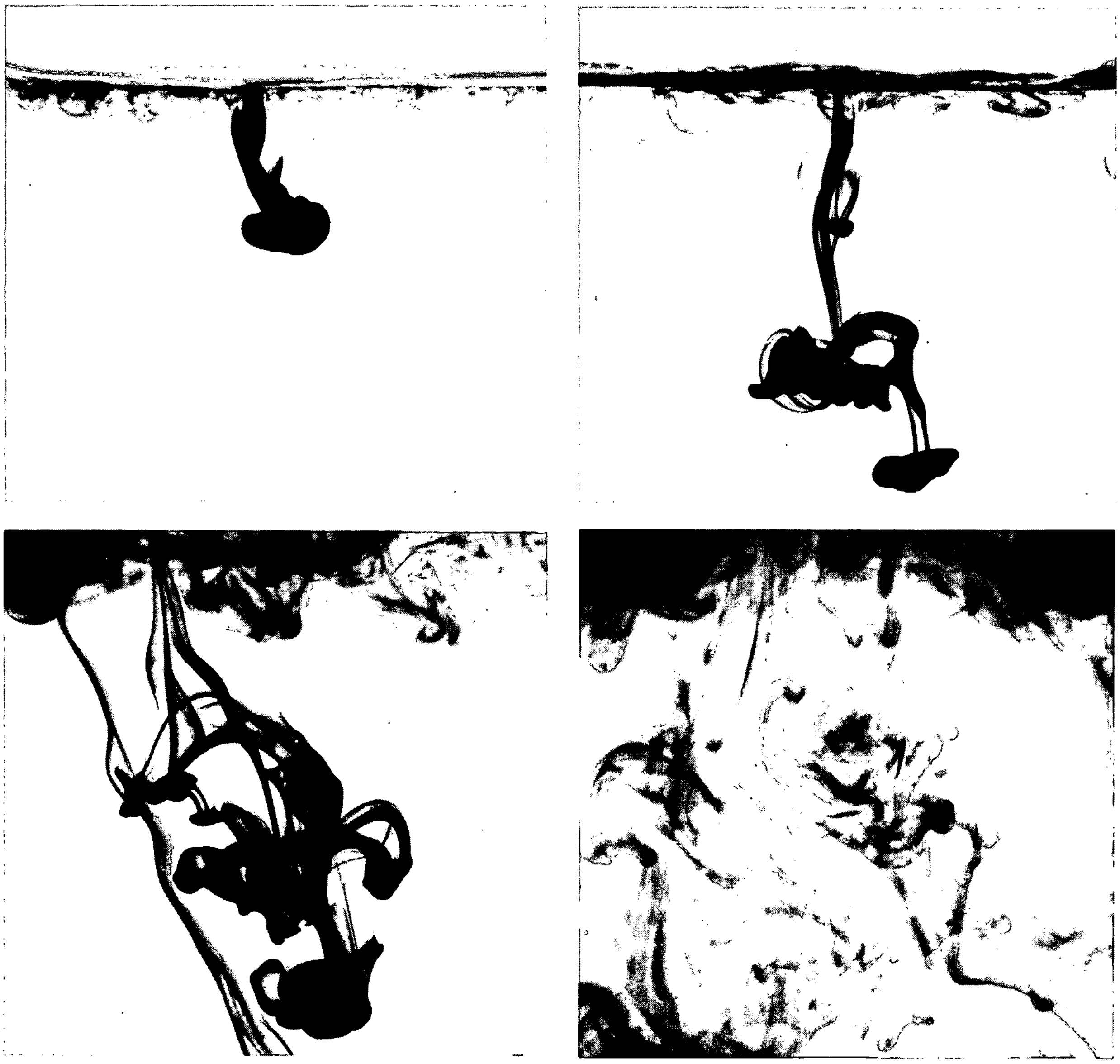
Solutions: Solute and Solvent

A homogeneous (uniform) mixture of more than one substance is called a *solution*. While a solution may be a gas or a solid, the most common solutions are liquids. You can prepare a liquid solution by dissolving a solid or a gas in a pure liquid. The compound which is dissolved is called the *solute*. The liquid is known as the *solvent*.



You can easily make a solution by dissolving salt in water. Salt (NaCl), a solid, is the solute. Water (H_2O), a liquid, is the solvent. Another familiar solution is soda water, made by dissolving carbon dioxide (CO_2), a gas, in water. The carbon dioxide is the solute, and the water is the solvent.

Another way of making a solution is to mix two different pure liquids whose molecules are able to form a single liquid phase. Liquids which can mix in this way, such as alcohol and water, are said to be *miscible*. When two liquids cannot mix in this way to form a single phase, they are *immiscible*. For example, gasoline and water are immiscible. If gasoline and water are stirred together, they separate. A layer of the gasoline floats on top of the water.



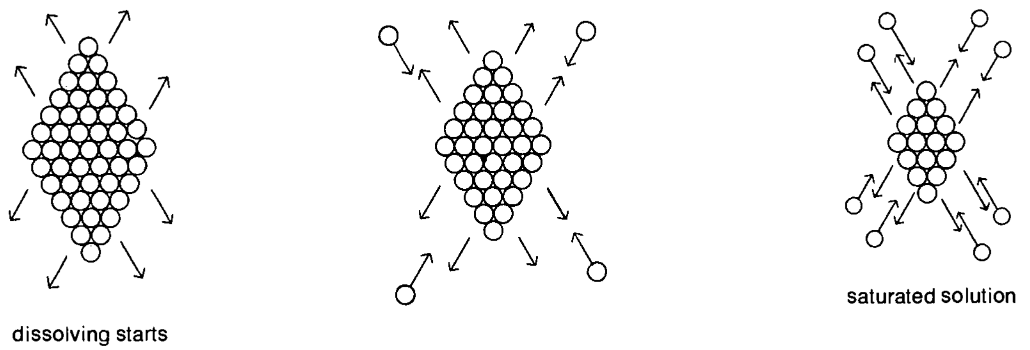
A colored liquid solution is placed in another liquid: water. Note how the solute molecules spread out into the solvent, water.

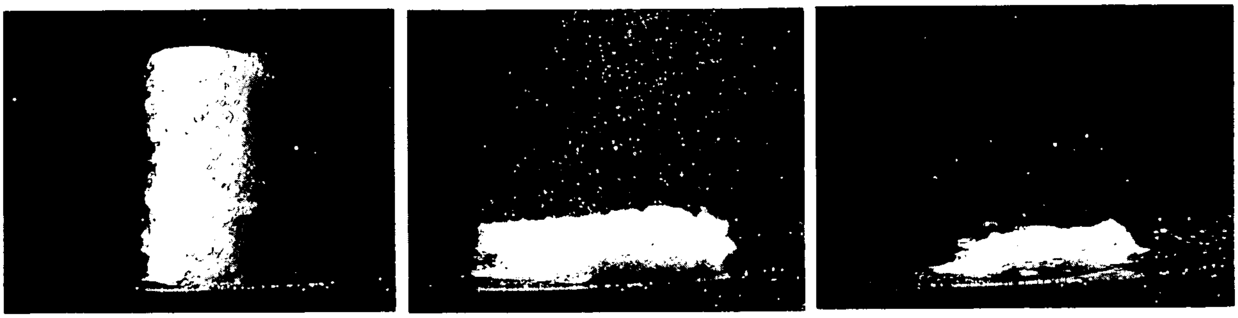
Once a solution is stirred, it stays homogeneous; that is, it has the same properties in every part of the phase. Solute molecules or ions do not sink to the bottom of a liquid solution, as would grains of sand. Nor do the molecules float to the top. The solute molecules remain uniformly distributed in the solvent because neighboring molecules are constantly hitting them and knocking them about. In comparison with the collision forces, the pull of gravity on the tiny molecules is negligible. The solute molecules are as likely to be at the top of the solution as at the bottom.

P-15 The Dissolving Process

If you pour crystals of sucrose (ordinary sugar) into a glass of water and stir the mixture, the crystals begin to dissolve to form a solution. In the molecular world, sucrose molecules located at the surfaces of the crystals become detached and move into the spaces between the water molecules in the liquid phase. Every second, a certain constant number of these surface molecules detach themselves from each unit area of crystal surface. The crystals gradually become smaller in size, and the concentration of the solution increases. (The concentration of a solution is the amount of solute in each unit volume—for example, moles per liter.)

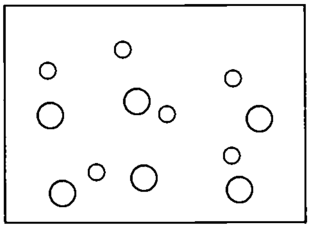
THE SOLUTION PROCESS



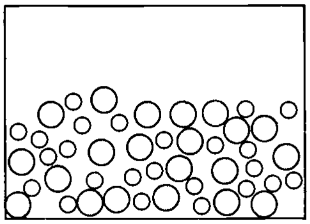


A sugar cube made up of sugar crystals (sucrose) dissolves in water. Each sugar crystal breaks down into individual molecules. The sugar molecules move into spaces between the water molecules.

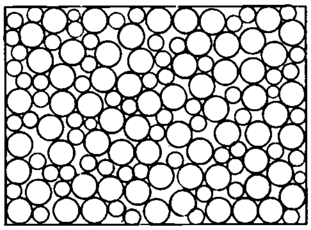
A GAS SOLUTION



A LIQUID SOLUTION



A SOLID SOLUTION



An opposing process, precipitation, also occurs. Sucrose molecules in the solution collide with the crystals and become reattached through attractive forces. The number of sucrose molecules which precipitate every second on a unit area of crystal surface is proportional to the concentration. That is, when the concentration doubles, the rate of precipitation on a unit area also doubles.

In the macroscopic world you observe the net result of dissolving and precipitation. The net dissolving of the crystals slows down as the concentration of the solution increases, since the rate of precipitation increases. Finally, the crystals either dissolve completely or they apparently stop dissolving and form a saturated solution.

A saturated solution of a solid is a solution which is in equilibrium with the solid. This dynamic equilibrium occurs when the concentration of the solution is just large enough to make the rate of precipitation equal to the rate of dissolving. The concentration of the saturated solution of a particular solid depends only on the temperature, *not* on the amount of solid present. If you add more sucrose crystals to a saturated solution of sucrose, you will observe no additional net dissolving. You have simply increased the area of the surface, where *both* dissolving and precipitation take place.

Solid sucrose is an example of a molecular crystal. An ionic solid can also dissolve and precipitate, but the solution contains solute ions instead of neutral molecules.

Sometimes it is possible to prepare a solution of a solid which is *more* concentrated than the saturated solution. If no solid phase is present in the solution, it is difficult for the precipitation process to begin. What do you suppose will happen to this supersaturated solution when you add some of the solid phase? A miniexperiment provides the answer to this question.

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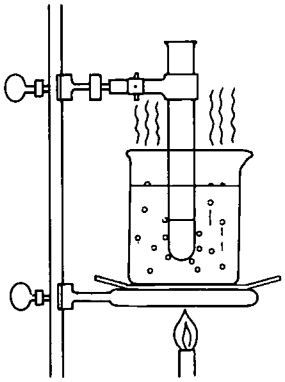
miniexperiment

P-16 Supersaturation



Place about 20 grams (g) of solid sodium thiosulfate pentahydrate [photo hypo ($Na_2S_2O_3 \cdot 5H_2O$)] in a large test tube. Heat some water in a beaker until it boils. Place the test tube in the boiling water until the solid decomposes to form a solution of sodium ions (Na^+) and thiosulfate ions ($S_2O_3^{2-}$) dissolved in the water which was present in the solid. Place the test tube in a beaker of cold water until it has cooled down. Do *not* stir or otherwise disturb the solution. You now have a supersaturated solution of $Na_2S_2O_3$ in water.

Remove the test tube from the beaker. Drop in one small crystal of solid sodium thiosulfate pentahydrate. What happens? Feel the outside of the test tube. What change do you notice?

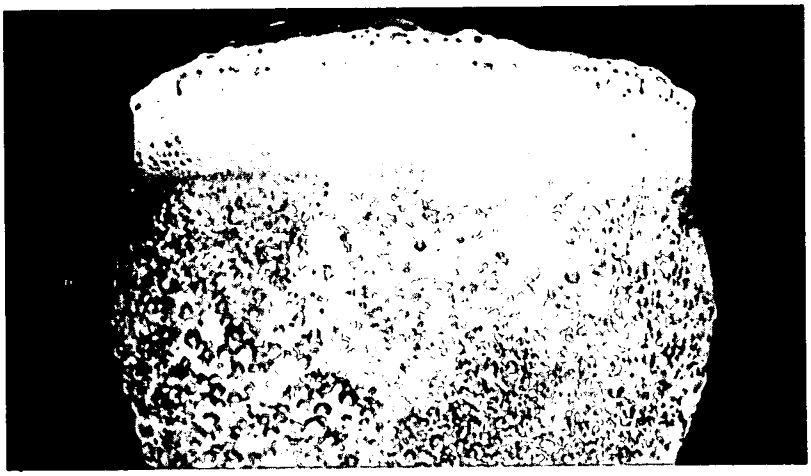
P-17 Dissolved Gases: Fizzle and Pop

Gas molecules can dissolve in a liquid to form a solution. These solutions are different in one important way from solutions made by dissolving a solid; that is, the concentration of the saturated solution depends on the concentration of solute molecules remaining in the gas phase. The greater the number of molecules in each cubic centimeter of the gas phase, the greater is the concentration in the saturated solution.

This principle may be illustrated by the preparation of soda water and other carbonated beverages. Carbon dioxide gas (CO_2) is pumped into water under pressure. The high pressure increases the concentration of the CO_2 gas, making it possible to dissolve more CO_2 in the water. Once the CO_2 dissolves, it reacts with the water to form carbonic acid (H_2CO_3), but some of it remains in the form of dissolved CO_2 molecules. When you remove the cap from a soda bottle, the pressure drops to atmospheric pressure and some of the dissolved CO_2 gradually returns to the gas phase (the soda goes flat).

Air also dissolves in water to a limited extent. Drinking water is sometimes aerated to make it taste better and to remove some impurities. Fish obtain their oxygen from the air dissolved in water.

When divers descend to great depths, the increased pressure makes an extra amount of nitrogen gas (N_2) from their lungs dissolve in their blood. Then they have to be careful to return to the surface slowly, otherwise nitrogen will leave the blood in the form of gas bubbles which painfully distend the tissues (a condition known as the "bends"). The problem can be avoided by breathing a mixture of oxygen and an inert gas such as helium, which is less soluble in blood.



Carbon dioxide (CO_2) molecules dissolved under pressure in a soft drink are returning to the gas phase because the pressure has been lowered.

P-18 Antifreeze: Cure for the Common Cold

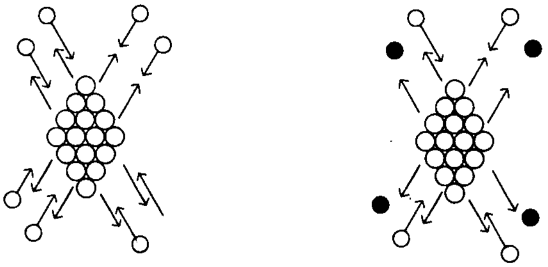
With the molecular picture of solubility we have been discussing, we can understand why a solution of water and alcohol or water and ethylene glycol (permanent antifreeze) freezes at a lower temperature than does pure water. This time the solid phase is ice, and the solution contains water and an organic molecule.

Suppose we start with a mixture of liquid water and solid ice in equilibrium at 0°C. Now, when we dissolve a solute such as ethylene glycol in the liquid phase, a cubic centimeter of the solution contains fewer H_2O molecules than an equal volume of the original pure water. The ethylene glycol molecules take up part of the volume of the solution. This means that the water concentration is lower in the solution, and H_2O molecules do not hit the ice crystals as often as before.

However, H_2O molecules continue to leave the ice crystals at the original rate. The ice crystals lose more molecules than they gain. As a result, if we keep the temperature at 0°C the ice melts completely.

If we want to prevent the ice from melting in the solution, we have to allow the temperature to fall below 0°C. At a lower temperature, the rate at which the H_2O molecules leave the ice crystals becomes equal to the rate at which they come back from the solution. The temperature of a good antifreeze solution for a car radiator would have to go down to −25°C or lower before ice would form.

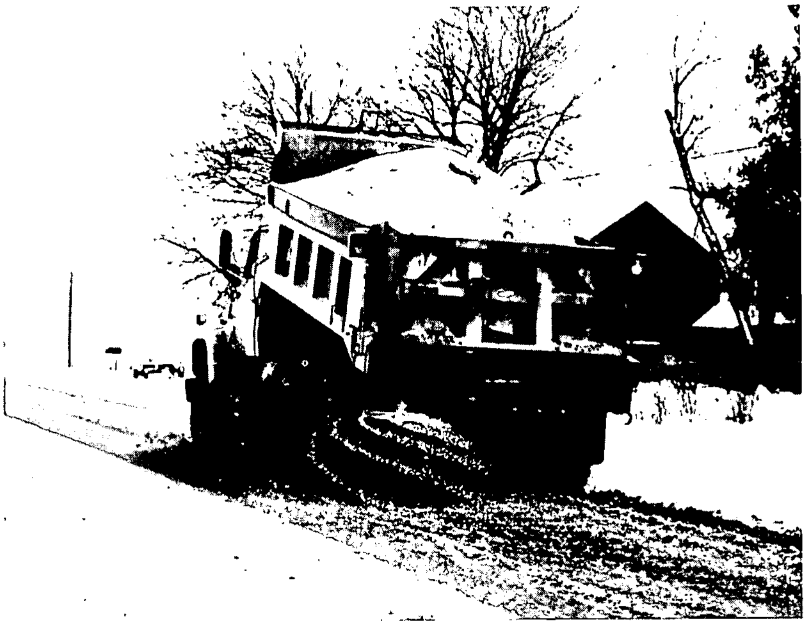
THE SOLUTION PROCESS



ice in equilibrium with liquid water (0°C)

ice melting in a solution (0°C)

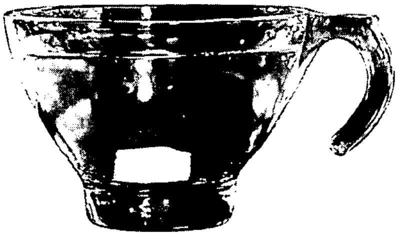
A solution of an ionic solid such as sodium chloride (NaCl) could also be used as an antifreeze, but it would corrode the radiator and engine block. Salts such as sodium chloride (NaCl) and calcium chloride ($CaCl_2$) are spread on icy roads in winter. When the salt dissolves in slush on the road, the ice in contact with the solution melts.



A salt-spreader "salts" a city highway after a heavy snowfall. If these salts can corrode the radiator in a car, what do they do to the body of the car? How does a car owner avoid this type of corrosion?

QUESTIONS

1. When two pure immiscible liquids are mixed and allowed to separate into two layers, is either of the layers still pure? Ask yourself whether you would be willing to put gasoline that was floating on top of some water into your gas tank. Also ask yourself whether you would be willing to drink the water!
2. Describe what would happen in each case if you were to drop a lump of sugar into a cup of tea which was unsaturated with sugar, saturated with sugar, or supersaturated with sugar.



The Colloidal State

As you look at various materials around you, you may notice communities of molecules which do not seem to be gases, liquids, or solids. To what state of matter does whipped cream belong? What about toothpaste, mayonnaise, smoke, and gelatin dessert? These and many other familiar materials are examples of *colloidal systems*, or *colloids*. They belong to the *colloidal state of matter*.

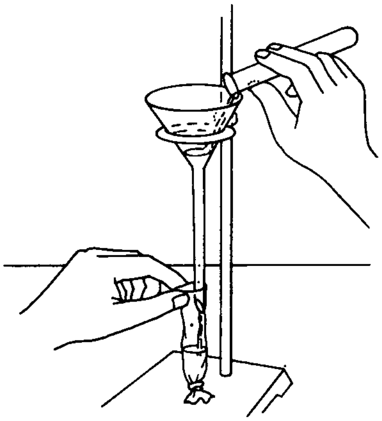
A colloidal system contains particles, fibers, or films which are larger than ordinary molecules but which are often too small or too thin to be readily observed in a microscope. These structures are thus intermediate in size between the macroscopic world and the molecular world.

Some colloidal systems may be classified as liquids and solids. Chemists do not consider these liquid and solid colloidal systems to be perfectly homogeneous because they contain structures that are larger than ordinary molecules. Milk, for instance, is a liquid colloidal system. Because milk contains colloidal particles and is not homogeneous, it is not a true solution. You can observe some differences in the behavior of true solutions, colloidal particles, and macroscopic precipitates by doing an experiment.

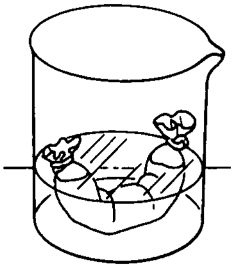
P-19 Some Properties of Colloidal Particles

EXPERIMENT

Obtain three 50-cm^3 beakers and set them in a row. Put about 20 cm^3 of a colored solution into the first beaker. Put about 20 cm^3 of skim milk into both the second beaker and the third beaker. (As we discussed on our "journey" into a drop of milk, skim milk contains small colloidal particles made up of molecules of casein, a protein.) To the third beaker containing skim milk, add about 5 cm^3 of 3 M acetic acid. (M means moles per liter.) Stir with a glass rod. A precipitate of casein, called the *curd,* forms.



Place a filter paper in a funnel, and filter the contents of the first beaker into a test tube. Use a clean funnel and new filter paper to filter a small amount of the contents of the second beaker into a second test tube. Repeat this procedure for the third beaker. Are any particles large enough to be retained by the filter paper? If so, which ones?



Obtain two short lengths (approximately 20 cm) of dialysis tubing and soak them in clean water. Tie off one end of each tube with a knot. Pour a little of the liquid from the first test tube into one bag and a little of the liquid from the second test tube into the second bag. Tie off the other end of each bag to keep the liquids inside. Rinse off both bags with water and place them in separate beakers of clean water. The dialysis tubing material (cellulose) contains pores which are much smaller than those in the filter paper. Do you see evidence that some substances can pass through these pores? Wait to see whether the colloidal particles pass through. Do the colloidal particles seem to be larger than the solute particles in the solution?

Have you ever wondered why milk has a white, cloudy appearance? Colloidal particles give milk its white color. The colloidal particles in milk scatter light in all directions, making the milk white and cloudy instead of clear and transparent. Many other colloidal systems look cloudy for the same reason. A true solution is clear because the molecules are not large enough to scatter the light; instead, light passes through a solution in straight lines.

The dialysis tubing you used in the experiment is useful for separating colloidal particles and large molecules (those containing several hundred atoms) from small molecules and ions. The pores in the tubing act like a sieve. Biochemists use such tubing to remove impurities from proteins. A similar type of membrane is used in artificial kidney machines used to remove wastes from blood (see *Molecules in Living Systems: A Biochemistry Module*).

The casein particles in milk are not electrically neutral. There are negative charges on the particle surfaces. These charges help to keep the particles from coming together because like charges repel. When you added the acetic acid, H^+ ions were attracted to the negative charges on the surfaces and neutralized them. The particles were then no longer stable, and they clumped together to form the curdy precipitate. A similar process is used to produce various dairy products. The process consists of adding certain acid-producing bacteria to milk to turn it into yogurt, buttermilk, cottage cheese, or sour cream.

TIME MACHINE

1859	Charles Dickens writes *A Tale of Two Cities*.
1860	Abraham Lincoln is elected 16th president of the United States.
1861	The American Civil War begins.
1862	**Thomas Graham, British chemist, discovers that substances such as gelatine do not pass through parchment membranes and calls them colloids.**
1863	Battle of Gettysburg ends General Lee's campaign in the North.
1865	Leo Tolstoy begins writing *War and Peace*, which is published four years later.
1865	The American Civil War ends.

P-20 The Importance of Surfaces

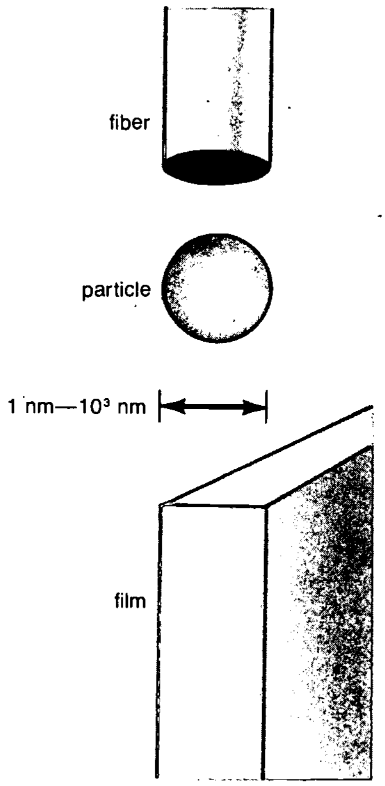
Colloidal systems contain particles, fibers, or films having at least one dimension in the size range of approximately 1 nm to 1000 nm (10^{-7} cm to 10^{-4} cm). In some colloidal systems containing fibers or films, only one or two dimensions of the structures may be in the 1 to 1000 nanometer range. For instance, the oleic acid film you prepared in experiment *P-2 The Size of a Molecule* was a colloidal system because its thickness was about 3 nm. Although it is not possible to observe such a short dimension in a microscope, you easily detected the two horizontal dimensions of the film by eye.

The fact that charges on the surface help to keep casein particles from precipitating may give you a hint that surface characteristics are important in determining colloidal properties. In fact, one definition of a colloidal system is that it contains structures whose properties are largely determined by the surfaces.

The total surface area of a substance depends very much on the size of the particles. To understand this mathematical fact, suppose that you have a certain amount of a solid in the form of a cube measuring 1 cm on each side. The total volume is 1 cm^3. The cube has six faces, each with an area of 1 cm^2. Therefore, the *total* surface area of the cube is 6 cm^2.

Now suppose that you slice up the solid cube into smaller cubes only 10^{-5} cm or 100 nm on each side. This is the average size of the

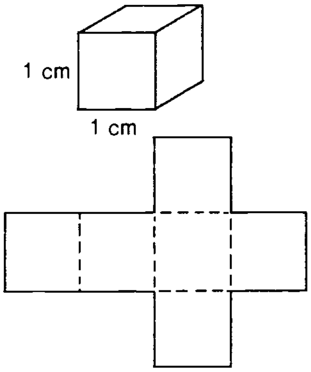
COLLOIDAL STRUCTURES



casein particles in milk. The large cube is split into 10^{15} small cubes. The total surface area of the small cubes is 6×10^5 cm^2, which is 100 000 times the surface area of the original large cube!

If you slice up the large cube into cubes 1 nm on each side (the smallest size of a colloidal particle), the total surface area is 6×10^7 cm^2. This area is slightly larger than a football field, including the end zones!

A large surface area is important in many colloidal systems because the special nature of the molecules at the surfaces allows the colloid to exist. For example, colloidal casein particles would settle to the bottom of the milk, or they would precipitate, if they did not have surface charges to keep them apart. In other colloids, molecules called *surfactants* are present at the surfaces of the particles or films to make them stable in the surrounding environment.



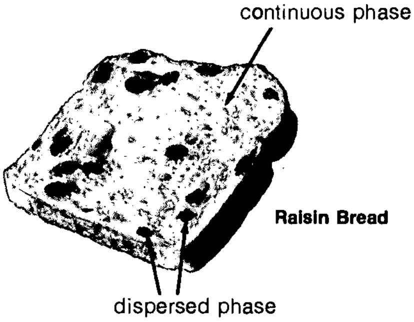
A cube with a surface area of 6 cm^3 is made up of six squares measuring 1 cm on each side.

P-21 Small Wonder: Colloidal Dispersions

Most familiar colloids contain particles of one kind of material dispersed in another material. The particles may be bubbles of gas, droplets of liquid, or solid particles. The particles are called the *dispersed phase*. They are surrounded and separated by the *continuous phase*, which may also be a gas, a liquid, or a solid.

A colloidal dispersion is like a loaf of raisin bread. The bread dough and raisins are in *every* part of the loaf, but there are many raisins (the dispersed phase) and only one continuous mass of bread dough (the continuous phase).

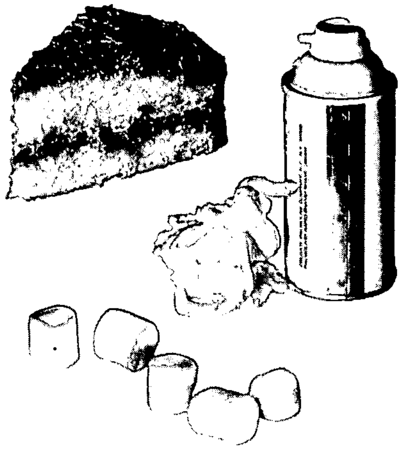
COLLOIDAL DISPERSION
(a model)



We can set up a table showing the possible combinations of dispersed and continuous phases and the general name of each combination as follows:

DISPERSED PHASE	CONTINUOUS PHASE		
	Gas	Liquid	Solid
Gas	—	liquid foam	solid foam
Liquid	fog	emulsion	liquid-in-solid dispersion
Solid	smoke	sol	solid-in-solid dispersion

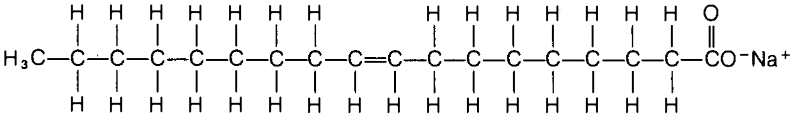
Note that there is no combination of a gas dispersed phase and a gas continuous phase. Two gases placed in contact with one another mix to give a single homogeneous gas phase, instead of a colloidal dispersion.



Referring to the table, we see that *foams* are dispersions of gas bubbles in a liquid or a solid. You can find many everyday examples of foams around your home and on the shelves in supermarkets. Whipped cream, whipped toppings, soap bubbles, and foam shave cream are all liquid foams. Among familiar solid foams are bread, cake, marshmallows, foam pillows, and foam mattresses.

Foams differ in one respect from the other colloidal dispersions. In foams, it is the continuous phase that is of colloidal dimensions instead of the dispersed phase. The films of liquid or solid separating the bubbles are often only a few molecules thick. This thickness cannot be observed in a microscope.

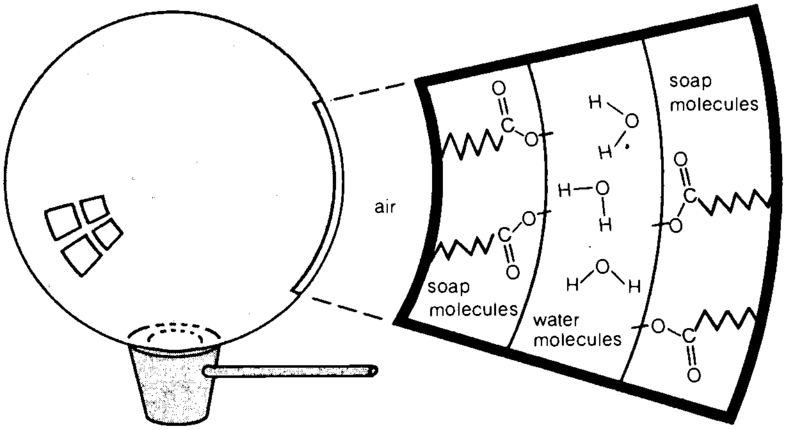
In order for a stable liquid foam to form, molecules of a surfactant compound must be present at the surface. The surfactant makes it easier for the liquid to be next to the gas. To make a foam from water, for instance, you must add a surfactant such as soap. The film of a soap bubble contains water molecules sandwiched between two layers of soap molecules. The way in which soap molecules stabilize the bubble can be seen from the structure of a typical soap molecule, sodium oleate.



$$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}O^-Na^+$$

The sodium oleate molecule has a long nonpolar hydrocarbon chain with a charged group of atoms at one end. The charged end is strongly attracted to the polar water molecules, and the nonpolar chain does not mind being in contact with a gas. Thus the soap molecules act as a kind of glue to help stabilize a large surface area of water next to the gas bubbles.

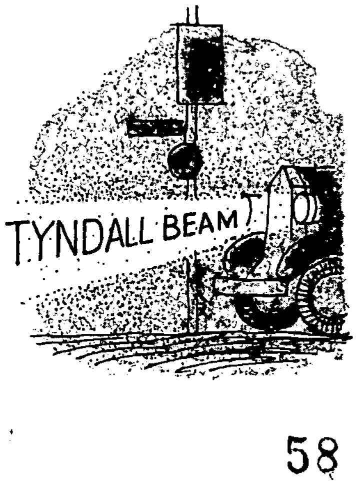
Soap bubbles are not really very stable compared to other foams. The layer of water tends to drain out from between the soap molecules. The film becomes thinner and eventually breaks.

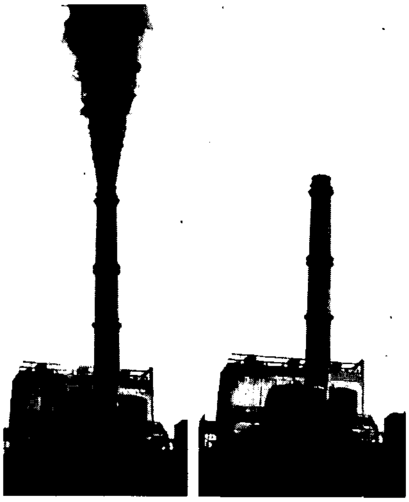


Fogs and *smokes* are liquid droplets or solid particles of colloidal size suspended in a gas, such as air. Both fogs and smokes are sometimes called *aerosols.* Some common fogs which you frequently have observed are outdoor clouds and mist. Such fogs consist of water droplets suspended in air. Among the familiar smokes are automobile exhaust, cigarette smoke, and various air pollutants released from smokestacks. (Of course, many air pollutants are gases rather than colloidal particles. Unlike colloids, you can't see them, but you often can smell them!)

Fogs and smokes are cloudy or opaque. The droplets or solid particles scatter light in all directions, just as in milk. A narrow light beam allowed to shine through the fog or smoke can be seen as a lighted ray, called a *Tyndall beam*. A cloud of dust gives the same effect, although dust particles are usually much larger than colloidal particles.

Why don't the particles settle out of a fog or smoke? The particles are so small that the constant bombardment of the even smaller gas molecules keeps them moving randomly past one another in all directions. The particles may also be charged and are even less likely to settle because they repel one another.





An off-and-on operation demonstrates the efficiency of an electrostatic precipitator designed to limit air pollution around industrial complexes. The precipitator eliminates fly ash from smokestack emissions and traps colloidal particles and dust.

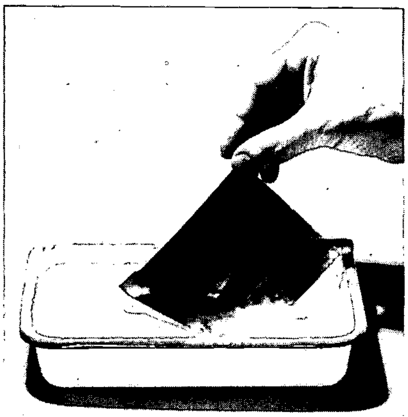
The *Cottrell electrostatic precipitator* is an antipollution device for removing the particles from industrial fogs, smokes, and dusts. The precipitator works by first charging the particles electrically and then passing them between charged plates. Each particle is attracted to the plate having the opposite charge. The particles are deposited on the plates and may be periodically removed.

A *sol* contains solid colloidal particles dispersed in a liquid. Toothpaste contains abrasive colloidal particles in a liquid. Milk of magnesia consists of colloidal particles of magnesium hydroxide [$Mg(OH)_2$] in water. Muddy water and chocolate drinks are also sols.

Enamels and oil-based paints are sols containing solid pigment particles dispersed in an oily liquid. The pigment gives the paint its color. After the paint is applied, some of the compounds in the oil evaporate and others react with oxygen to form a protective coating. Water-based latex paints contain large macromolecules and pigment particles. They are dispersed in a water phase which evaporates to produce the protective coating.

Black printing ink is usually a dispersion of colloidal carbon particles (carbon black) in mineral oil. The carbon particles are between 20 nm and 60 nm in diameter. The ink dries by penetration of the oil into the paper. Lubricating grease is also a sol in which colloidal crystals or fibers of soap are dispersed in oil.

With its colloidal casein particles, skim milk is not strictly speaking a sol—as you might think. The casein particles are not considered to be chunks of a solid. Instead, they are clusters of subunits containing casein molecules arranged in a specific way, as you may recall from our journey into a drop of milk. (The technical word for one of these clusters is *micelle.*)

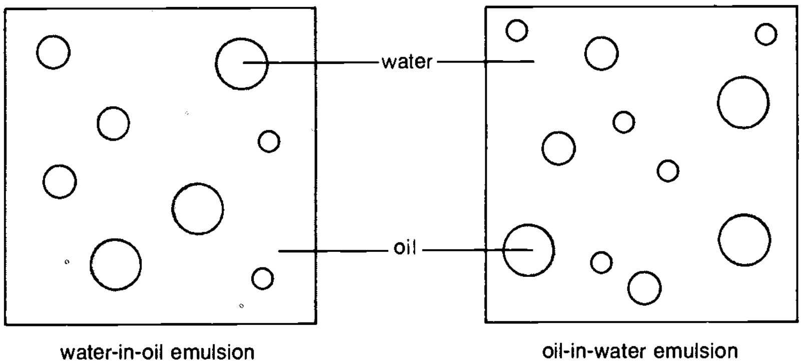


The emulsion on a photographic negative is being fixed after the development process. The colloidal crystals of silver salts, which have been exposed to light, are chemically reduced to silver grains by the developer. The unexposed crystals are then dissolved in the fixer solution in order to remove them from the film.

The entire art and technology of photography depends on solid-in-solid dispersions called *photographic emulsions*. The light-sensitive coating on photographic films is a photographic emulsion. Photographic emulsions consist of crystals of silver bromide (AgBr), silver iodide (AgI), and silver chloride (AgCl) dispersed in gelatin. The crystals are between 50 nm and 5000 nm in diameter. Some colored glasses and gems are solid-in-solid dispersions containing colloidal crystals of metals or metallic oxides.

As we have noted, printing ink contains carbon black. Carbon black, a solid colloidal particle, also has many other uses. In this country, the chief use of carbon black is in the manufacture of automobile tires. The tread of an automobile tire consists of colloidal carbon black particles dispersed in amorphous solid synthetic rubber. The carbon black gives the tread its color. The carbon particles are necessary to keep the rubber molecules from tearing apart under the abrasive wear of the road.

An *emulsion* is a colloidal dispersion in which droplets of one liquid are suspended in another liquid. The two liquids must be immiscible, otherwise they would mix to form a solution. Usually one of the liquid phases contains mostly water, and the other phase is an oil. Depending on whether the water phase or the oil phase is the dispersed phase, we can have a water-in-oil emulsion or an oil-in-water emulsion as shown in the following illustration:



The droplets of the dispersed phase have a tendency to merge with one another into larger drops which may eventually form a separate liquid layer. When this happens, the emulsion is said to break. To prevent an emulsion from breaking, and to make it easier to prepare in the first place, a small amount of a surfactant called an *emulsifier* is usually present. The emulsifier molecules coat the surface of the droplets and stabilize them.

The color in glass comes from colloidal crystals of metals or metallic oxides. Common coloring ions are those of cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), gold (Au), and iron (Fe). For example, in colored glass cobalt is responsible for much of the blue, iron oxide produces green, and copper oxide or gold oxide creates a ruby color.

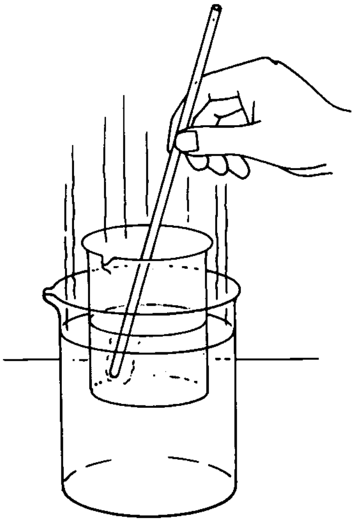
P-22 Making Oil and Water Mix

EXPERIMENT

In this experiment you will prepare an oil-in-water emulsion and a water-in-oil emulsion by using water, mineral oil, and commercial emulsifiers. You will learn how to test these emulsions to tell whether they are of the oil-in-water type or the water-in-oil type. Then you will apply the same tests to some household emulsions which you have been asked to bring to class.

Part 1: Preparation of Emulsions
Start the experiment with your laboratory partner. Heat a 400- or 600-cm³ beaker of water to about 50°C to serve as a hot water bath in a later step.

Measure 50 cm³ of mineral oil (also called paraffin oil) in a dry graduated cylinder and pour it into a dry 150-cm³ beaker. Add 4 cm³ of liquid Tween 40 to the mineral oil in the beaker. Tween 40 is a water-soluble emulsifier. Weigh about 4 g of Span 40 and add it to the mineral oil. Span 40 is an oil-soluble emulsifier.



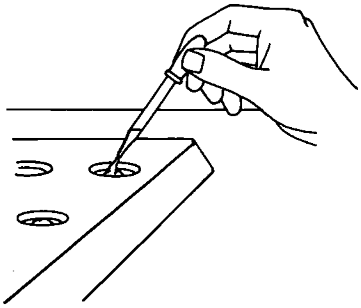
Place the beaker containing the mixture in your hot water bath to melt the Span 40. Stir the mixture with a glass stirring rod until it looks homogeneous.

Pour half of the mixture into another 150-cm^3 beaker. Then take one of the portions and perform the rest of the steps by yourself. Let your laboratory partner work with the other portion. You do not have to wait for the mixture to cool.

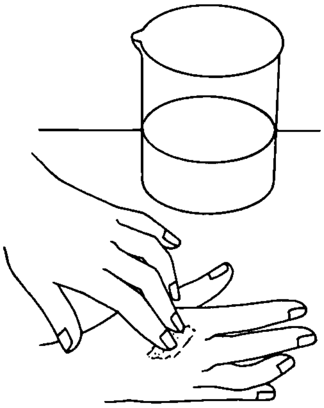
Slowly add small dribbles of water to your mixture from either an eye dropper or a plastic squeeze bottle. Stir thoroughly after each addition of water, using a glass stirring rod. Continue to add water and stir until the mixture becomes milky white.

Perform the following tests on small portions of your emulsion to determine what type it is. After each test, record your observations and your conclusions.

1. Rub a little of the emulsion between your fingers. A water-in-oil emulsion feels oily because oil is the continuous, outside phase.
2. Touch a little of the emulsion to a dry piece of filter paper. If a grease spot forms immediately and soaks through to the other side of the paper, this indicates a water-in-oil emulsion.
3. Place two small samples of the emulsion into wells of a porcelain spot plate or onto a clean waterproof surface. Onto one of the samples place a tiny drop of blue water-soluble dye (diluted food coloring). Onto the other sample place a tiny drop of red oil-soluble dye. Stir each sample gently with the clean end of a stirring rod. Stir just a little. Observe carefully. The water-soluble dye tends to mix evenly only with an oil-in-water emulsion, and the oil-soluble dye tends to mix evenly only with a water-in-oil emulsion. In general the dye can mix with the continuous phase only if it is soluble in that phase.



After performing these tests, continue to stir in small amounts of water to your remaining emulsion. Continue until it becomes thicker and stiffer. As you add more portions of water, the emulsion type will change in a process called *inversion*. After the emulsion has become fairly thin again, perform the tests over again to see what type it now is. Record your conclusions.



You now have prepared a typical hand lotion. Other ingredients such as lanolin or perfume could be added. When the water evaporates, oil is left on the skin. Compare the feel of the hand lotion on your skin with the feel of water and mineral oil separately. Can the hand lotion be rinsed from your skin? Do you see any other advantages in having the oil in the emulsion form?

Just for fun, try stirring large amounts of water into your remaining emulsion. Is there any limit to the amount of water you can add?

Part 2: Testing Household Emulsions

Now that you have gained some experience in telling the difference between oil-in-water and water-in-oil emulsions, make the same tests on several household emulsions and record your conclusions. Suggestions for testing: mayonnaise, cold creams, hand lotions, hair creams, sun-tan lotions, "waterless" hand cleaners. (Most of these emulsions contain commercial emulsifiers such as the ones you used in the experiment. On the other hand, the emulsifier in mayonnaise is egg yolk.)

As you noticed in the experiment, emulsions are frequently more viscous (thicker) than either of the liquids they contain. The viscosity tends to be high when the dispersed phase contains more material than the continuous phase. Mayonnaise is viscous because as much as 90 percent of its volume is vegetable oil, dispersed in vinegar with egg yolk as the emulsifier.

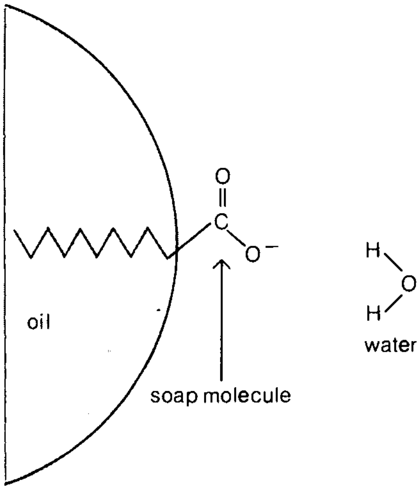
You also can observe another property of emulsions. Emulsions scatter light and give a Tyndall beam effect in the same way as fogs and mists. Moreover, some emulsions block the light completely, that is, are opaque, even when the two liquid phases separately are clear and transparent.

One of the most familiar emulsions is the dairy milk which we visited on our "journey" into a drop of milk. Each 100 g of milk as it comes from the cow contains about 4 g of oil (butterfat) in the form of droplets, of colloidal size and larger, suspended in skim milk. Milk proteins coat the droplets, serving as emulsifiers. If left alone, the droplets rise to the top and cluster together as cream. When churned, the cream undergoes inversion from an oil-in-water emulsion to a water-in-oil emulsion called butter. (Margarine is also a water-in-oil emulsion, manufactured from water and vegetable oil with emulsifiers added.)

A process called homogenization is used to prevent butterfat from rising to the top of milk. The milk is pumped through small holes at high pressure. This process breaks the butterfat up into colloidal droplets which remain uniformly dispersed in the skim milk. The result is homogenized milk.

Soaps and detergents are excellent emulsifiers. This property enables them to clean oily films and oily dirt particles from objects. The soap or detergent molecules allow a stable oil-in-water emulsion to form in the wash water. This emulsion is easily rinsed from the formerly dirty object, and down the drain goes the dirt.

Solid particles being suspended in a liquid to form a sol.



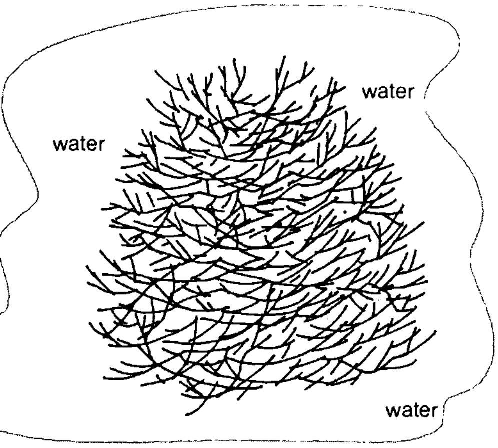
P-23 Making a Gel

miniexperiment

Measure 50 cm^3 of 95 percent ethanol and place in a dry 150-cm^3 beaker. Pour 5 cm^3 of a saturated solution of calcium acetate into the beaker. Notice what happens. The material that forms is a *gel*.

Carefully remove the gel with your hand. Squeeze the gel over the beaker to remove excess ethanol. Then place it on the asbestos center of a wire gauze resting on a ringstand ring or another heat-resistant surface. Dry the ethanol from your hands and ignite the gel with a match. **Caution:** *Be very careful to keep hair and clothing away from the flame.*

STRUCTURE OF A GEL



Gels are semirigid materials containing a random network of colloidal fibers or crystals with liquid in the remaining spaces. The molecules of the liquid may be able to move in these spaces, or they may stick to the network structure because of strong attractive forces. The structure of a gel is like a brush heap of branches covered with water. The gel is soft and easily deformed, but it has a definite shape.

The gel you made contains colloidal crystals of calcium acetate. The ethanol caused the crystals to precipitate from the solution. The material is not a sol because the crystals are touching one another.

Some common gels are jams, jellies, some puddings, gelatin desserts, and thick mud. Gelatin contains water and long fibrous protein macromolecules (collagen). In the gel the macromolecules are attracted to one another by hydrogen bonds.

Lubricating grease may sometimes be considered to be a gel. In such a gel the soap crystals or fibers have thickened the oil considerably. Another gel is napalm, which was invented during World War II for use in incendiary munitions. Napalm has caused untold suffering because the burning material clings to the skin. It is made from gasoline that is thickened with special soaps, or macromolecules of polystyrene.

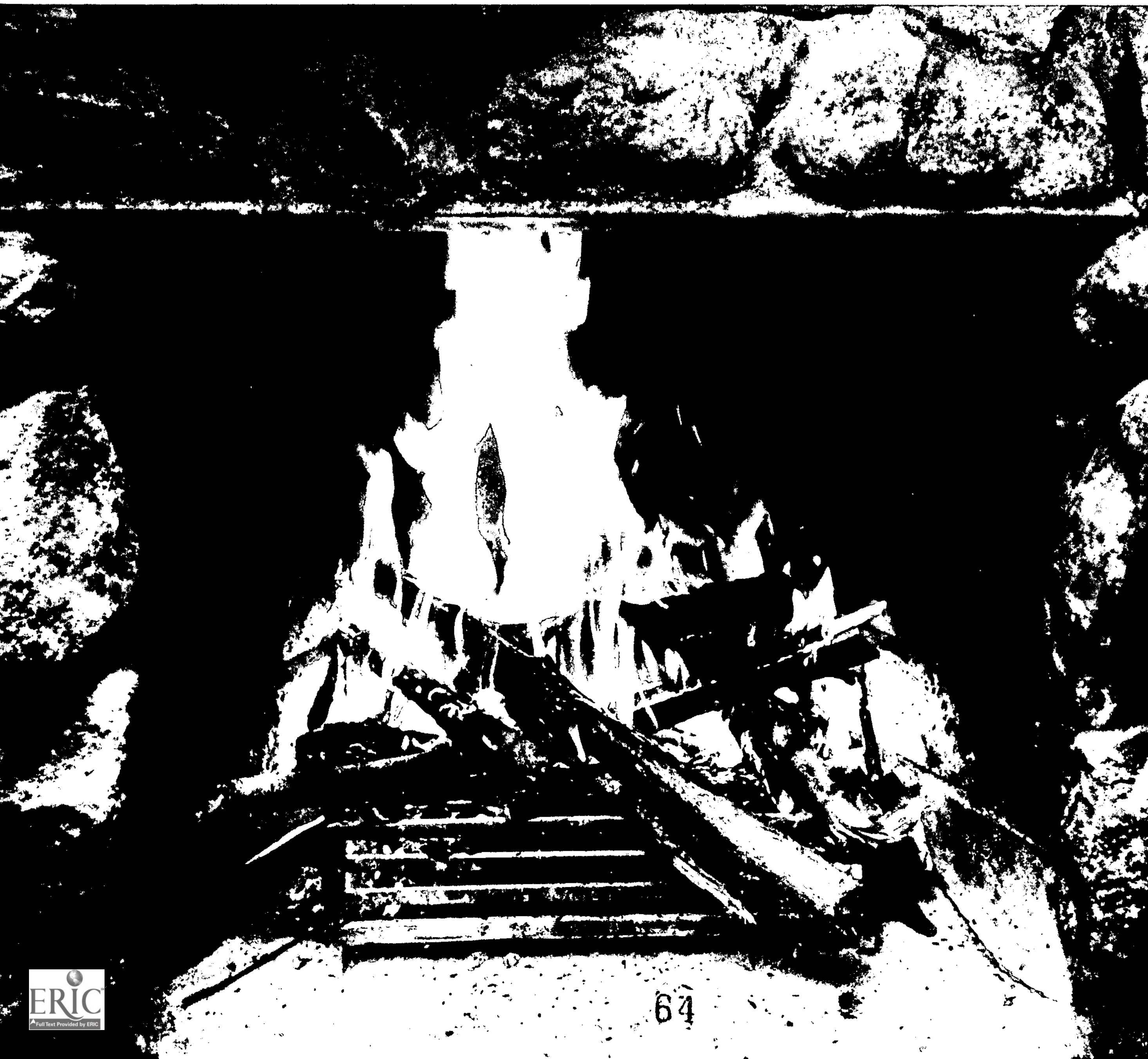
Up to now we have discussed four states of matter found in communities of molecules. These states are gases, liquids, solids, and colloids. The colloidal systems which we have examined in detail are colloidal dispersions (foams, fogs, smokes, sols, solid-in-solid dispersions, and emulsions) and gels. In the next section we will begin to consider how molecular communities can change over a period of time.

QUESTION

Gold, iodine, marshmallows, butter, and gelatin are all soft, easily deformed "solids." Describe how each of these communities of molecules is organized.

Changes in Energy

Have you ever wondered why a fire is hot? Or why a breeze makes moist skin feel cool? In both of these examples, a reorganization of molecules occurs. In the fire, molecules of the fuel react with oxygen molecules. The breeze causes water molecules to vaporize from the skin. Evidently, the temperature changes in the macroscopic world are caused by these reorganizations in the molecular world.



P-24 Counting Calories

The temperature of a community of molecules is a measure of the amount of *thermal energy* that the community possesses. The thermal energy may be explained by the constant movement of the molecules in random directions. Even in a solid, the molecules move back and forth for short distances in the spaces left by the neighboring molecules.

Each moving molecule has a kinetic energy, or energy of motion. The kinetic energy is given by the formula K.E. = $\frac{1}{2}mv^2$, where m stands for the mass of the molecule and v stands for its velocity (speed). Now the thermal energy, in the simplest picture, is just the total kinetic energy of all of the molecules in the community. Thus if something happens which makes the molecules move faster on the average (increase in v), the total kinetic energy increases and the thermal energy increases.

In the macroscopic world, this *increase* in the thermal energy is observed as a *rise* in the temperature. On the other hand, a *decrease* in the thermal energy results in a *lowering* of the temperature. A thermometer indicates the temperature of the community of molecules by using the kinetic energy transmitted to it by collisions of the molecules to change the volume of the indicating liquid.

It takes a definite increase in the thermal energy of one gram of water to raise the temperature of the water by one degree Celsius. This amount of energy is called the *calorie* (cal). In the International System of Units (SI), the derived unit of energy is the *joule*. One calorie is the same as 4.18 joules. While it has been traditional in the past for chemists to express energies in calorie units, joule units will probably be preferred in the future. For our purposes, it will be more convenient for you to use calorie units.

If the temperature of a community of molecules changes, you can use a measurement of the temperature change to calculate the change in the thermal energy of the community. The formula is

$$\text{thermal energy change} = Cm(t_2 - t_1)$$

where C is the *specific heat capacity*, m is the mass of the community, t_1 is the initial (starting) temperature, and t_2 is the temperature after the change.

The meaning of the specific heat capacity C is that this is the increase in the thermal energy which results in a unit temperature increase for unit mass. Each substance or mixture has a value of C. From what has been said previously, you can see that water has a specific heat capacity of one calorie per degree Celsius per gram, or C = 1.00 cal/°C · g for water.

Here is an example of how to use this formula. What is the change in the thermal energy of 2.00 g of water if the temperature falls

TIME MACHINE

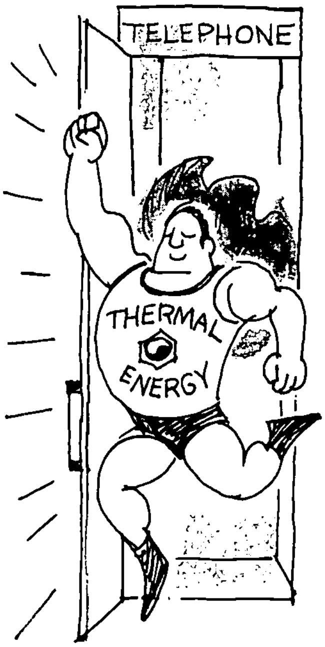
1839	Abner Doubleday invents the game of baseball.
1841	James Fenimore Cooper publishes *The Deerslayer*, first of the Leatherstocking Tales.
1842	Crawford Long, an American surgeon, performs the first operation using ether.
1843	**James Joule, British physicist, measures the mechanical equivalent of thermal energy.**
1844	Samuel Morse sends the first telegraph message—from Washington to Baltimore.
1845	Edgar Allan Poe wins acclaim for "The Raven."
1846	Elias Howe patents sewing machine.

from 24.00°C to 20.00°C? Answer: thermal energy change = (1.00 cal/°C · g) × 2.00 g × (20.00 − 24.00)°C = −8.00 cal. Since the answer is negative, the thermal energy of the water *decreases* by 8.00 cal.

Another form of energy in a community of molecules is *chemical energy,* which depends on the organization of the molecules. The chemical energy usually changes when the molecules change from one form to another or when a chemical reaction takes place.

There is an important connection between the thermal energy and the chemical energy of a community. This connection exists because of a general principle called the *conservation of energy,* which states that the *total* amount of energy in the universe stays constant. Energy cannot be created out of nothing, nor can energy disappear into nowhere.

Energy may, however, travel from one place to another and change from one form into another form. Thus the thermal energy of a community of molecules may increase because energy enters the community from outside or decrease because energy leaves. For instance, a pan of water on a hot stove becomes warm because *heat* flows into the pan from the burner. Heat is a flow of energy from a warmer place to a cooler place.

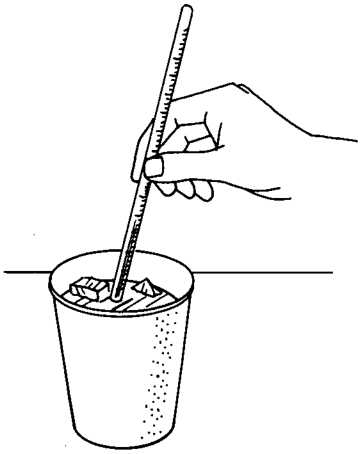


The thermal energy may also increase because chemical energy changes into thermal energy *within* the community, or the thermal energy may decrease because it is changed into chemical energy. In the next three experiments, you will carry out processes in which such changes of thermal energy and chemical energy take place. Naturally, when the thermal energy changes, the temperature also changes. The temperature change is actually a result of the change in the chemical energy caused by the molecular reorganization.

You will start by investigating the melting of a solid. When a certain amount of a solid melts, the change in the chemical energy is called the *heat of fusion*. The specific heat of fusion refers to the melting of a unit mass of the solid; and the molar heat of fusion refers to the melting of an amount of solid containing one mole of molecules.

EXPERIMENT

P-25 The Heat of Fusion of Ice



By using a device called a *calorimeter*, you will measure the specific heat of fusion and the molar heat of fusion of ice. A calorimeter is simply a container which is insulated to prevent heat from entering or leaving. A Styrofoam thermal cup makes a good calorimeter.

Using a graduated cylinder, measure exactly 100 cm³ of room temperature water. Pour it into a Styrofoam cup. Record the temperature of the water to the nearest 0.1°C.

Obtain two or three ice cubes which have partially melted, so that their temperature is 0°C. Dry them with a towel to remove excess liquid, and add them to the cup.

Gently stir the ice and water mixture with the thermometer. Observe the temperature as it goes down. When the temperature becomes constant, record the final temperature to the nearest 0.1°C. (The thermometer may not read exactly 0.0°C because it may be inaccurate or because heat may slowly enter the calorimeter.)

Remove the remaining ice, and shake as much water as possible back into the cup. Measure and record the volume of water remaining in the cup. Subtract 100 cm³ from this volume to get the volume of the water that melted from the ice. Since the mass of 1 cm³ of liquid water is 1 g, you can find the mass of the ice that melted.

Use a table similar to the following for your data:

initial water temp. (t_1) = ___ °C
final water temp. (t_2) = ___ °C
$t_2 - t_1$ = ___ °C
initial vol. of water = ___ cm³
final vol. of water = ___ cm³
vol. of water melted = ___ cm³
mass of ice melted = ___ g
thermal energy change = ___ cal
chemical energy change = ___ cal
specific heat of fusion = ___ cal/g
amount of ice melted = ___ mol
molar heat of fusion = ___ cal/mol

The 100 cm³ of water cooled from room temperature to the final temperature. Calculate the change in the thermal energy of this water by using the formula in the preceding section. You may assume that 1 cm³ of liquid water has a mass of 1 g.

The thermal energy lost by the 100 cm³ of water changed into an equal amount of chemical energy. Thus the change in the chemical energy is equal to minus the change in the thermal energy. Calculate the specific heat of fusion of the ice (in calories per gram). Compare your results with those obtained by your neighbors. Did you calculate the same value or different values for the change in chemical energy? What about the value for the specific heat of fusion? You would expect everyone to obtain the same value for only *one* of these two quantities. Which one and why?

The molar mass of H_2O is 18.0 g/mol. Calculate the amount of ice which melted (in moles):

$$\text{amount} = \text{mass/molar mass}$$

Now calculate the molar heat of fusion of ice. This is the change in the chemical energy per amount (moles) of solid melted:

$$\text{molar heat of fusion} = \frac{\text{chemical energy change}}{\text{amount of solid melted}}$$

You will need this value for comparison with later experiments.

Is the molar heat of fusion positive or negative? What are the correct units?

P-26 Endothermic and Exothermic

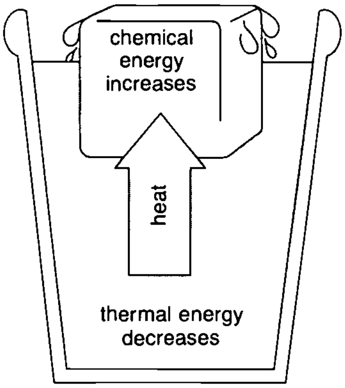
What happened to the thermal energy which left the water as it cooled? It could not flow out of the calorimeter as heat because the calorimeter was insulated. (Besides, heat always travels from warmer to cooler places.)

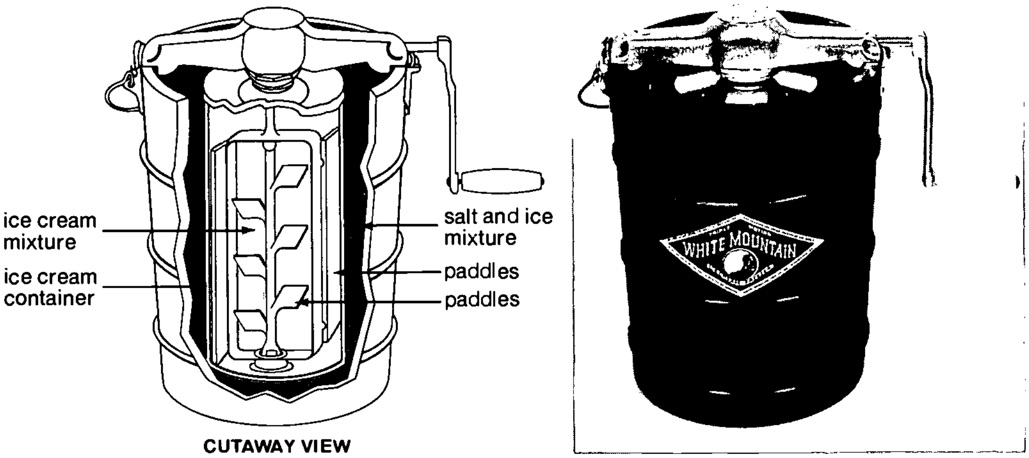
The thermal energy lost by the water must have changed into chemical energy. One way to look at the change is to say that the thermal energy entered the ice in the form of heat, and in the ice it changed into an equal amount of chemical energy which was gained by the water as it melted from the ice. Thus we can see that liquid water has more chemical energy than an equal mass of ice. The additional chemical energy goes into breaking hydrogen bonds in the ice and into weakening the other attractive forces between the H_2O molecules in the ice.

A process such as this, in which the chemical energy increases, is called an *endothermic process*. The melting of a solid and the vaporization of a liquid are always endothermic processes because they involve the breaking or weakening of the attractive forces between molecules. It requires an increase in chemical energy to pull one molecule away from another against the attractive pull, just as it requires energy to lift a weight up against the pull of gravity.

Home ice cream freezers take advantage of the endothermic process you have just studied to freeze and harden ice cream. To use an ice cream freezer, you place the ice cream container in a bucket filled with crushed ice, water, and salt. With ice and water only, the

ENERGY CHANGES IN MELTING ICE





CUTAWAY VIEW

This old-fashioned ice cream freezer operated on the principle of the endothermic process. The ice cream mixture is placed in the inner container; salt and ice are placed around this container. Handcranking the machine is easy until the ice cream begins to freeze, and then it becomes a difficult job.

temperature would not go below 0°C. But the salt dissolves in the water, causing some of the ice to melt without the need for heat from the outside (see *P-18 Antifreeze: Cure for the Common Cold*). Since melting is an endothermic process, the chemical energy increases. The thermal energy therefore decreases, and the temperature of the ice, water, and salt mixture drops to about −21°C.

A breeze makes moist skin feel cool because vaporization is also an endothermic process. The breeze speeds up the vaporization of moisture from the skin, causing the thermal energy of the skin to decrease and the skin temperature to go down.

Some processes are the opposite of endothermic processes. In an *exothermic process,* the chemical energy decreases. Usually most or all of the chemical energy changes into thermal energy, and the

ENDOTHERMIC

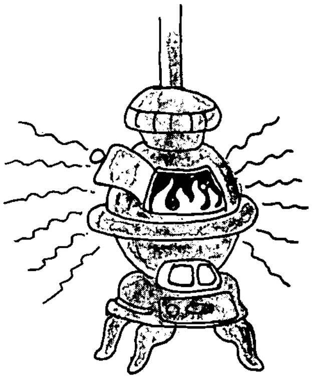
thermal energy → chemical energy

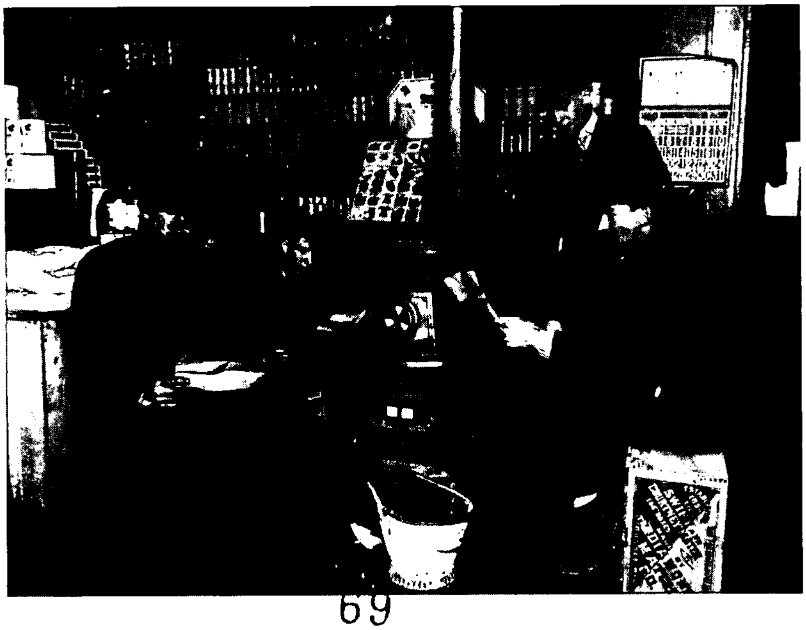
temperature drops

EXOTHERMIC

chemical energy → thermal energy

temperature rises





temperature rises. Combustion (burning) reactions and many other chemical reactions are exothermic. We make use of an exothermic combustion reaction in a furnace which burns oil or another fuel. In the furnace, the chemical energy of the fuel and of the oxygen in the air are converted into thermal energy to heat our homes.

P-27 Heat of Solution

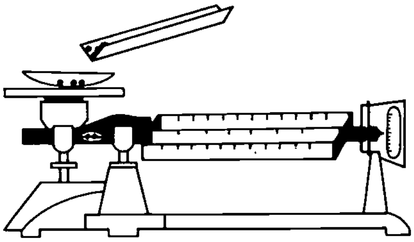
EXPERIMENT

The *molar heat of solution* of a substance is the change in the chemical energy when one mole of the substance is dissolved in a solvent. In this experiment, you will measure the molar heats of solution of two different ionic solids dissolved in water.

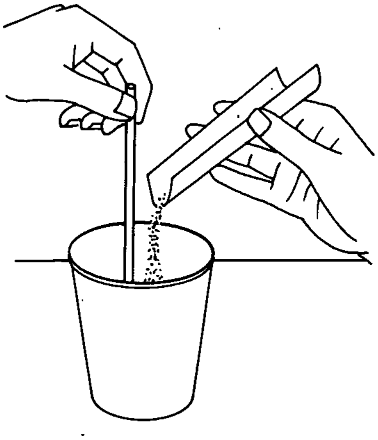
Using a graduated cylinder, measure 100 cm^3 of room temperature water. Pour the water into a Styrofoam cup. Weigh out approximately 25 g of sodium thiosulfate pentahydrate [photo hypo ($Na_2S_2O_3 \cdot 5H_2O$)]. Record the actual mass used. Record the temperature of the water in the cup to the nearest 0.1°C. Add the solid to the water and stir until it is completely dissolved.

Use a table similar to the following for the data you will obtain:

		$Na_2S_2O_3 \cdot 5H_2O$:	NaOH:
mass of solid	=	___ g	___ g
amount of solid	=	___ mol	___ mol
t_1	=	___ °C	___ °C
t_2	=	___ °C	___ °C
$t_2 - t_1$	=	___ °C	___ °C
thermal energy change	=	___ cal	___ cal
chemical energy change	=	___ cal	___ cal
molar heat of solution	=	___ cal/mol	___ cal/mol



Measure the temperature again, and record it to the nearest 0.1°C. Is this solution process endothermic or exothermic? Calculate the thermal energy change. Since the solution contains mostly water, the value of the specific heat capacity is about the same as for water, so you may use $C = 1.00$ cal/°C · g for your calculation.



Assume that no heat entered or left the cup, so that the chemical energy change was equal to minus the thermal energy change. Calculate the chemical energy change.

Calculate the amount (moles) of sodium thiosulfate pentahydrate which dissolved. (The molar mass of this substance is 248 g/mol.) Then calculate the molar heat of solution of sodium thiosulfate pentahydrate.

Now, repeat the experiment by dissolving approximately 4 g of sodium hydroxide (NaOH) in water. This time, is the solution process endothermic or exothermic? Repeat the calculations to obtain the molar heat of solution of sodium hydroxide. (The molar mass is 40.0 g/mol.)

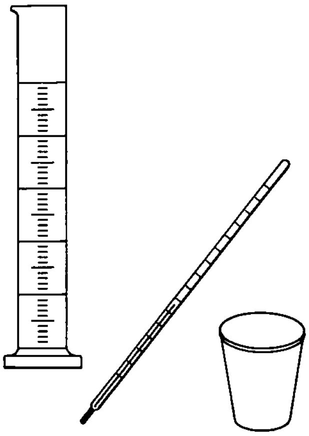
As you have seen, the solution process can be either endothermic or exothermic, depending upon the solid. This variation can be understood by realizing that attractive forces exist in *both* the solid and the solution. If the attractive forces between the molecules or ions in the solid are stronger than the attractive forces in the solution, a net increase in the chemical energy occurs when the solid dissolves; and therefore the dissolving process is endothermic. On the other hand, if the forces between the solute and the solvent are larger, the dissolving process is exothermic.

Think back to miniexperiment *P-16 Supersaturation*. You found that, when solid sodium thiosulfate pentahydrate precipitates from a solution, the temperature rises and therefore the process is exothermic. Since in the present experiment you carried out the *reverse* process, dissolving, you would predict the reverse change in chemical energy. Is this what you found?

"Instant" cold packs and hot packs which work through heats of solution are available for first aid. The packs contain a solid in a thin-walled bag which is sealed inside a plastic pouch. The pouch is filled with water. When you knead the pouch, the interior bag breaks, allowing the solid to dissolve. The pack becomes either hot or cold.

EXPERIMENT

P-28 Heat of Reaction



The *molar heat of reaction* is the change in the chemical energy per mole of product produced in a chemical reaction. Let's investigate the molar heat of reaction for the production of water from hydrogen ions and hydroxide ions:

$$H^+ + OH^- \rightarrow H_2O$$

This reaction is called neutralization.

Using a graduated cylinder, measure 50 cm³ of 2.0 M hydrochloric acid (HCl). Pour the hydrochloric acid into a Styrofoam cup.

Record the temperature of the HCl solution to the nearest 0.1°C.

Use a table similar to the following for your data:

temp. of HCl solution = ___ °C
temp. of NaOH solution = ___ °C
average initial temp. (t_1) = ___ °C
highest temp. reached (t_2) = ___ °C
$t_2 - t_1$ = ___ °C
thermal energy change = ___ cal
chemical energy change = ___ cal
amount of product formed = ___ mol
molar heat of reaction = ___ cal/mol

Rinse out the graduated cylinder and measure 50 cm³ of 2.0 M sodium hydroxide (NaOH). Rinse the thermometer and check the temperature of the NaOH solution while it is still in the cylinder.

If the temperature is different from the temperature of the HCl solution, record the *average* temperature of the two solutions (the temperature midway between).

Pour the NaOH solution into the cup and stir. Observe the temperature as it rises. Record the highest temperature reached to the nearest 0.1°C. Calculate how many moles of H^+ ions (from the HCl) and OH^- ions (from the NaOH) were present in your mixture. (Remember that 2.0 M means 2.0 moles in each liter, or 1000 cm^3.) Assuming that all of the H^+ ions and OH^- ions reacted, how many moles of product (H_2O) were produced? Now calculate the molar heat of reaction for the neutralization reaction. This is also called the *molar heat of neutralization.*

Now you have measured a molar heat of fusion, two molar heats of solution, and a molar heat of reaction. Compare your values. What kind of process seems to cause the largest chemical energy change per mole?

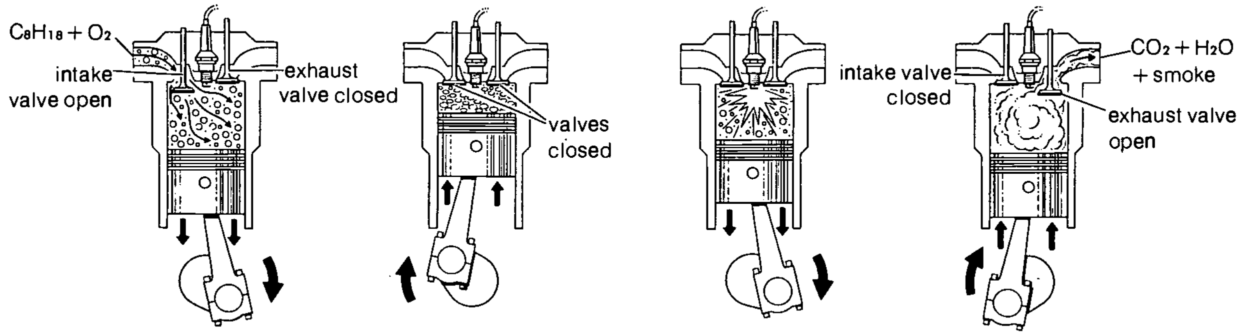
We can usually explain why a particular chemical reaction is endothermic or exothermic by the bonds that break and form. The chemical energy increases when a bond breaks, whereas it decreases when a bond is formed.

In the neutralization reaction, no bonds are broken, but a covalent bond is formed (between H^+ and OH^-). It is therefore understandable that the chemical energy should decrease, making this reaction exothermic.

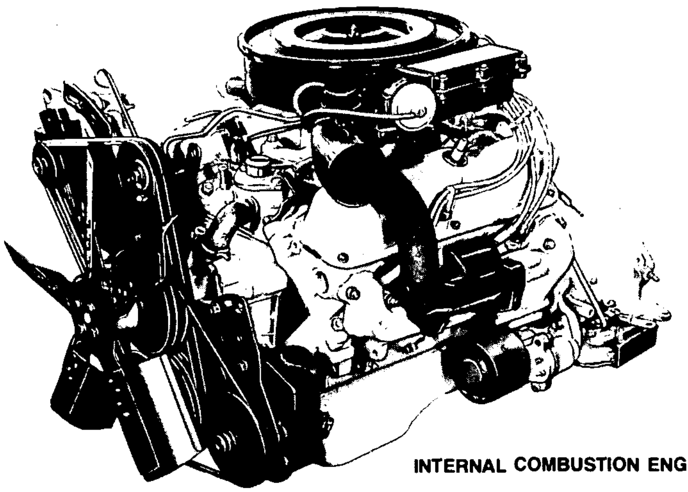
P-29 The Power of Thermal Energy

The temperature changes caused by chemical reactions have many important applications. Let us consider the question posed at the beginning of the module about how a gasoline engine produces energy to move an automobile. In the cylinder of the engine, a spark from the spark plug ignites a mixture of air and gasoline vapor. The components of the gasoline mixture burn to form carbon dioxide and water vapor.

In these diagrams of a cylinder of an automobile engine, you can see how the chemical change in fuel starts the piston moving. This causes the driveshaft to turn, the wheels to move, and the car to accelerate. When fuel in one of the cylinders does not burn properly, a premature explosion occurs causing "engine knock." We will discuss this further in section *P-32.*



Intake Stroke   Compression Stroke   Power Stroke   Exhaust Stroke



INTERNAL COMBUSTION ENGINE

For instance, the combustion reaction for octane is

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

The reaction of every two octane molecules requires the breaking of 14 carbon-carbon bonds, 36 carbon-hydrogen bonds, and 25 oxygen-oxygen bonds; and the formation of 32 carbon-oxygen bonds and 36 oxygen-hydrogen bonds. (Draw the structural formulas of the molecules in the reaction and see if you agree with these numbers.) More bonds are broken than are formed, so you might think that there would be a net increase in the chemical energy. However, the $C=O$ bonds which form in CO_2 are much stronger than any of the other bonds. Consequently, on balance, chemical energy changes into thermal energy, and the reaction is exothermic. Burning gasoline is hot!

Two changes occur as the gasoline ignites in the cylinder:

1. The number of molecules increases. Notice that in the octane reaction, for every twenty-seven molecules of reactants that disappear, thirty-four molecules of products appear. Since these molecules are in the gas phase, the increased number of molecules hitting the cylinder walls and piston causes the pressure to go up.
2. The gas gets extremely hot (up to about 1200°C) because the reaction is exothermic. As a gas heats up, its pressure increases.

Both changes cause the gas pressure in the cylinder to become very high. The temperature effect is the most important one. The force of the high pressure drives the piston, and mechanical energy is produced which moves the automobile. Only about one-third of the chemical energy that changes into thermal energy in the cylinder is converted into mechanical energy. The remainder ends up as waste heat in the exhaust system and cooling system.

A stamp issued to honor Nikolaus Otto, who was credited with building the first modern internal combustion engine.

TIME MACHINE

1873	Leo Tolstoy publishes *Anna Karenina.*
1874	First exhibit of "Impressionist" paintings, shown in Paris, includes Cezanne, Monet, and Pissarro.
1875	First Kentucky Derby run.
1875	Georges Bizet sees his last opera, *Carmen*, panned by audiences and dies soon after.
1876	**Nikolaus Otto, German engineer, builds the first modern internal combustion engine.**
1876	Mark Twain publishes *Tom Sawyer.*
1877	Thomas A. Edison invents the phonograph.
1878	Gilbert and Sullivan present *H.M.S. Pinafore.*

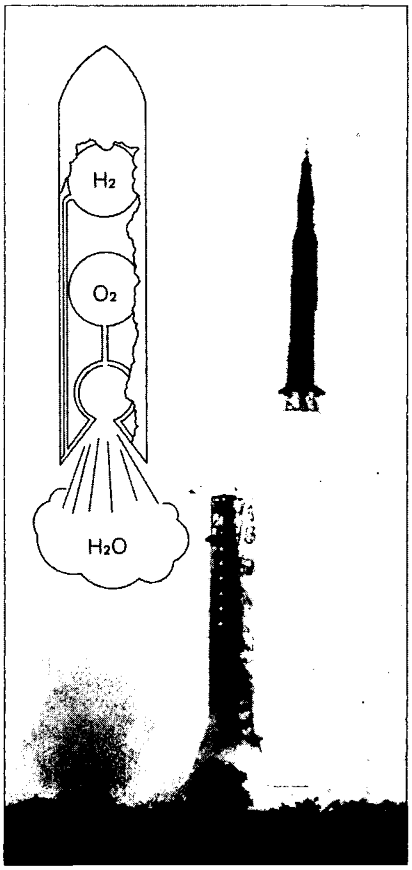
Rocket engines and jet aircraft engines also rely on exothermic chemical reactions for their propulsion. For instance, second and third stage Saturn V rocket engines burn hydrogen with oxygen:

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

This reaction, like all combustion reactions, is exothermic. The resulting high temperature causes the water-vapor product to have a high pressure in the rocket combustion chamber. The vapor leaves through the nozzle at a high speed, providing thrust for the rocket.

Exothermic reactions are used in the self-heating hair dyes and shave creams (hot shave) which now are on the market. One brand of hot shave contains hydrogen peroxide (H_2O_2) in a small sack inside the aerosol can, separated from the shave cream. When the cream is squirted out, this compound mixes and reacts with an organic compound in the shave cream to warm up the mixture.

Weight watchers and dietitians are interested in a certain kind of exothermic reaction involving foods. When you read that one tablespoon of sugar contains about 50 Calories, this means that the heat of combustion of one tablespoon of sugar is 50 000 cal. (The dietetic Calorie is written with a capital C to indicate a large calorie or one thousand of the calories used by chemists.) The heat of combustion of food is a measure of how much energy the body can derive from the chemical energy of food by biochemical reactions.



QUESTIONS

1. What is the change in the thermal energy and the change in the chemical energy for each of the following processes?
   (a) 400 g of water are heated from 25°C to 31°C.
   (b) 200 mol of liquid water at 100°C are boiled at 1 atm pressure until 20 mol of liquid are left. (The molar heat of vaporization of water is 9.7×10^3 cal/mol.)
   (c) 5.85 g of sodium chloride are dissolved in 400 cm^3 of water in an insulated calorimeter. The temperature drops by 0.32 degrees Celsius.
2. Calculate the molar heat of solution of sodium chloride (NaCl) from the information in question 1(c).
3. The accepted value of the molar heat of neutralization is -1.336×10^4 cal/mol. Suppose you were to take 100 cm^3 of 1.0 M KOH solution and 100 cm^3 of 2.0 M HNO_3 solution (nitric acid), with both solutions at 25.0°C, and mix them in a calorimeter. What do you predict the final temperature would be? (Hint: What is the amount of water that can be produced by the neutralization reaction? What is the total mass of water that changes temperature?)

Rates of Chemical Reactions

When we mix two or more substances, we often find that they begin to react to form new substances. Some reactions are fast and are completed almost instantly, such as the neutralization reaction you just studied. Others, such as the rusting of the iron, are slow reactions that may continue for decades or centuries. The *rate* of a reaction is usually measured by the amount of product produced per unit time in a certain volume.

The chemical reactions of blasting agents help clear an island waterway, making a safe channel for shipping.

P-30 Time to React

EXPERIMENT

In this experiment you will see how the rate of a particular reaction is affected by the concentrations of the reactants, by the temperature, and by a catalyst. You will investigate the rate of the reaction of iodide ions with peroxydisulfate ions

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

by measuring the time needed for a certain amount of iodine (I_2) to be produced. The first amount of I_2 to be produced in the reaction will very rapidly react with a small amount of thiosulfate ion ($S_2O_3^{2-}$) present in the reaction mixture:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

As soon as the thiosulfate ion is used up by reacting with the I_2, you will be able to detect the next molecules of I_2 that are produced. These molecules will react with some starch, also present in the reaction mixture, to form an easily visible blue material. You will determine how long it takes for the *first* blue color to appear.

Four solutions will be available: *Solution 1, Solution 2, Solution 3,* and a *Catalyst Solution.*

Solution 1 contains 0.10 M potassium iodide (KI), a source of I^- ions, and some starch.

Solution 2 contains 0.0025 M sodium thiosulfate ($Na_2S_2O_3$), a source of $S_2O_3^{2-}$ ions.

Solution 3 contains 0.10 M ammonium peroxydisulfate [$(NH_4)_2S_2O_8$], a source of $S_2O_8^{2-}$ ions.

The *Catalyst Solution* contains 0.01 M copper(II) sulfate, a source of Cu^{2+} ions.

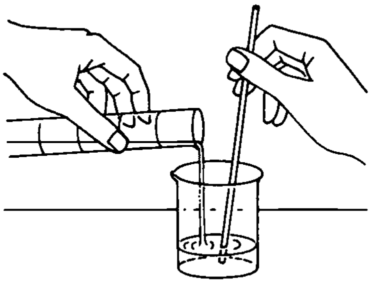
It is important in this experiment to measure the volumes accurately, and to rinse the glassware before each use to avoid contamination.

Part 1: Effect of Concentration

Measure 20.0 cm³ of *Solution 1,* using a 50-cm³ or 100-cm³ graduated cylinder. Pour the solution into a clean 150-cm³ beaker. Measure 10.0 cm³ of *Solution 2* in a 10-cm³ graduated cylinder, and add this solution to the same beaker. Put a glass stirring rod into the beaker.

Measure 20.0 cm³ of *Solution 3* in a clean 50-cm³ or 100-cm³ graduated cylinder. One partner will mix this solution with the solution in the beaker, and another partner will time the reaction.

When the timer gives the signal, the mixer should pour *Solution 3* from the graduated cylinder into the beaker and immediately stir the mixture.



The timer should watch for the first sign of the blue color and record exactly how many seconds it takes from the time the solution is poured into the beaker until the first blue color appears.

Next, empty and rinse the glassware and repeat the experiment. This time, start with a mixture of 10.0 cm^3 *Solution 1,* 10.0 cm^3 *Solution 2,* and 10.0 cm^3 water in the beaker. Add 20.0 cm^3 of *Solution 3* from a graduated cylinder when the timer gives the signal. The starting concentration of the I^- ion is now half what it was before. Do you agree? What effect does this change have on the reaction time?

Repeat the experiment a third time. This time start with a mixture of 20.0 cm^3 *Solution 1,* 10.0 cm^3 *Solution 2,* and 10.0 cm^3 water in the beaker. Add 10.0 cm^3 of *Solution 3* when the timer gives the signal. The starting concentration of the $S_2O_8^{2-}$ ion is now half what it was in the two preceding trials. How does this affect the reaction time?

Part 2: Effect of Temperature
Repeat the experiment at a different temperature. Place 20.0 cm^3 of *Solution 1* in a small flask, and warm or chill the solution until it is about 25 degrees Celsius higher or lower than room temperature. Do not let water or ice get into the solution. Put the solution into a 150-cm^3 beaker and add 10.0 cm^3 *Solution 2.* Add 20.0 cm^3 *Solution 3* when the timer gives the signal. The temperature of the mixture will be about 10 degrees Celsius above or below room temperature. What effect does this change in temperature have on the reaction time?

Part 3: Effect of a Catalyst
Repeat the experiment at room temperature. Use a mixture of 20.0 cm^3 *Solution 1* and 10.0 cm^3 *Solution 2.* Add four drops of the *Catalyst Solution* to 20.0 cm^3 *Solution 3* and add this mixture to the beaker when the timer gives the signal. What effect does the presence of the *Catalyst Solution* have on the reaction time?

P-31 Rates and Concentrations

In the experiment you found that halving the concentration of either of the reactants, I^- or $S_2O_8^{2-}$, roughly doubled the reaction time. The reaction time in the experiment is the time needed for certain fixed amounts of the products to form. Therefore, your results indicate that when you halve the concentration of a reactant, the reaction rate is also halved. In other words, in the reaction you studied the rate is *proportional* to the concentration of either reactant.

To understand why this should be the case, you must visualize what happens in the molecular world. The molecules or ions of the reactants must collide with one another before a chemical reaction can take place. Once the proper particles have collided, they interact with one another through various forces. They can break and reform covalent bonds to produce molecules or ions of the products. The more particles of a particular reactant there are in each cubic centimeter of the solution, the greater the number of collisions per second and so the greater the reaction rate.

The reaction you studied in the experiment can be written:

$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Looking at this reaction, you might assume that three ions must collide simultaneously: two I^- ions and one $S_2O_8^{2-}$ ion. But it is only very infrequently that three particles happen to collide at the same time.

Actually, the reaction just discussed occurs in two successive steps:

$$I^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4I^- \text{ (slow)}$$
$$SO_4I^- + I^- \rightarrow SO_4^{2-} + I_2 \text{ (fast)}$$

These steps are known as *elementary steps*. They describe the particles which actually collide. Notice that in each elementary step, only two ions need to come together. Many other reactions also take place in a series of elementary steps, usually involving the collision of only two molecules or ions at a time.

The rate of each elementary step is proportional to the concentration of each reactant involved in the collision. Halving the concentration of either reactant halves the rate at which the ions of this reactant collide with ions of the other reactant.

It happens that the rate of this first elementary step is much slower than the rate of the second. The slow step is known as the *rate-determining step* because the rate of this step is the rate of the overall reaction. It's like cars backed up at a bad traffic bottleneck on an otherwise fast highway. It may take each car 30 minutes to get past the bottleneck, and only 1 minute for it to travel an additional mile on the fast part of the highway. The bottleneck is the rate-determining step in reaching the end of this mile.

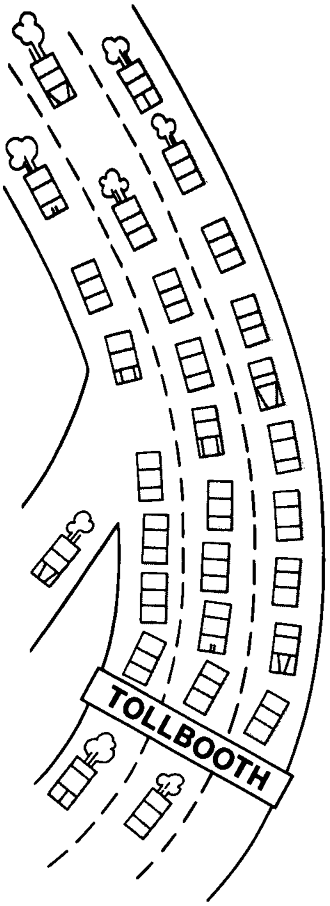
Since the slow elementary step is rate determining, and since it involves the collision of one I^- ion with one $S_2O_8^{2-}$ ion, we can understand why the *overall* rate is proportional to the concentrations of I^- and $S_2O_8^{2-}$. We may express this concept in the algebraic equation

$$\text{rate} = k[I^-][S_2O_8^{2-}]$$

Here, k is a constant called the *rate constant* for the reaction. The square brackets are used to indicate concentrations.

TIME MACHINE

1951	Ralph Ellison publishes *The Invisible Man*, a novel about being black in America.
1952	First jet airline passenger service begins.
1953	**Manfred Eigen, German physical chemist, measures the rate constant of the neutralization reaction.**
1953	Edmund Hillary and Tensing Norkay reach the top of Mount Everest.
1954	J. R. R. Tolkien publishes *The Lord of the Rings*.



Cars backed up at a tollbooth are an example of a *rate-determining step.*

P-32 Rates and Temperature

Since molecules move faster at higher temperatures than at lower temperatures, we expect more frequent collisions as the temperature is raised. Thus, the rate of a reaction should increase along with an increase in temperature. This is what you observed in experiment *P-30 Time to React.*

Actually, we cannot explain the increase in the rate of a reaction just on the basis of collision rates. The rate of a reaction typically doubles when the temperature is raised 10 degrees Celsius. Is this what you found in the experiment?

The explanation for this big rate increase is that when two molecules collide, their chances of reacting depend upon how hard they hit. They have to have a certain minimum kinetic energy in order to allow bonds to break. This minimum energy is called the *activation energy.* If two colliding reactant molecules have less kinetic energy than the activation energy, they don't react during the collision. But when the temperature is increased, the average kinetic energy of the molecules is greater and a collision has a greater chance of causing a reaction.

The concept of the activation energy explains why many reactions never occur at all until the temperature is raised. A mixture of air and gasoline vapor does not react at room temperature. However, if you toss in a lighted match or fire a spark plug, some of the organic molecules and oxygen molecules acquire enough kinetic energy to break their bonds and initiate combustion. Thereafter, the increase in

ACTIVATION ENERGY

SOME REACTIONS REQUIRE AN INPUT OF ENERGY TO GET THEM STARTED.

thermal energy as the mixture burns raises the temperature of the remaining mixture to the point where it also will burn.

In the cylinder of a gasoline engine, the gasoline-air mixture starts burning at the spark plug. The maximum mechanical energy is obtained when a "flame front" of hot, burning gas sweeps rapidly but smoothly towards the other end of the cylinder. Under certain conditions, however, the high temperature gets ahead of the flame front and the gasoline-air mixture reacts too rapidly. A rapid exothermic reaction taking place everywhere at almost the same time is called an *explosion*. In the case of a car engine, we call this explosion reaction "engine knock." Knock can be prevented by using higher octane gasoline mixtures or by adding gasoline additives such as tetraethyl lead, which unfortunately can pollute the atmosphere with lead compounds.

The rate of many exothermic reactions depends on whether the heat that flows out is able to heat up the unreacted material. Some common examples of this effect can be observed. If you start a wood fire, you find that it is difficult to keep it burning with only one log. You need several logs placed close together, so that the heat coming from each burning log will help the other logs to burn. The same is true of charcoal briquets in a grill. A small oily rag is unlikely to start burning by itself, but a pile of oily rags may slowly rise in temperature because of oxidation until the whole pile bursts into flame (spontaneous combustion).

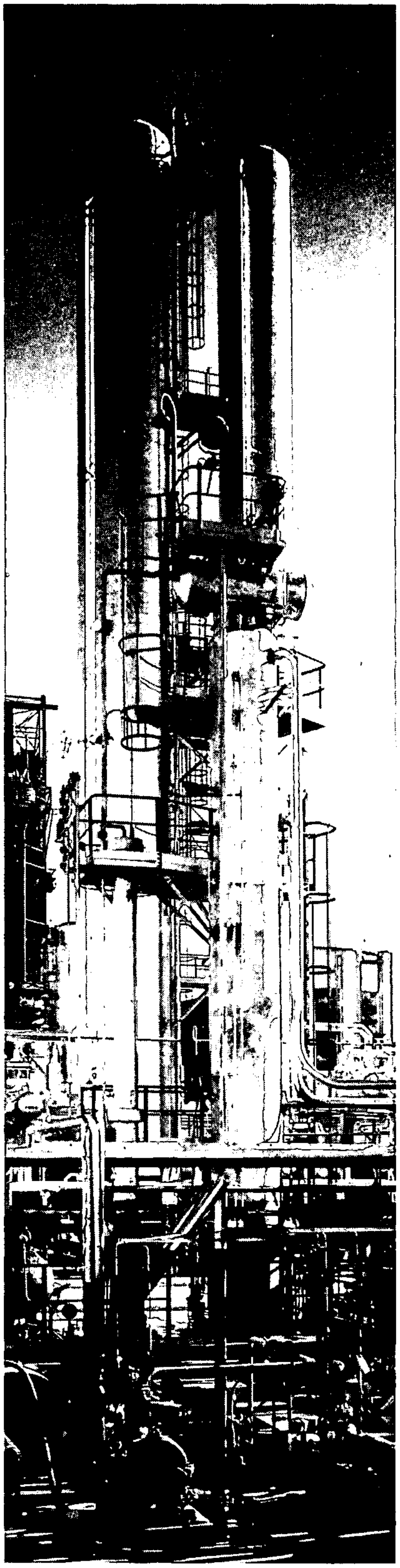
One of the most dramatic examples of the temperature effect is a dust explosion. A small pile of dust or flour is difficult to light and will slowly smolder. However, a large cloud of the dust or flour in the air will explode if it is ignited by a match or a spark. Each dust particle can be freely reached by oxygen, and the heat flowing from one burning particle raises the temperature of neighboring particles until they ignite.

Refrigeration slows down food spoilage because reaction rates decrease as the temperature is lowered. At the low temperature in a refrigerator, reactions in food caused by bacteria and mold are slowed down considerably (see *Molecules in Living Systems: A Biochemistry Module*).

P-33 Catalysts: Essential for Life

As we have seen, one way to increase the rate of a chemical reaction is to increase the concentration of one of the reactants. Another way is to raise the temperature. For some reactions there is a third way. We may be able to add a compound or a material which speeds up the reaction without being consumed. This is called a *catalyst*, and the increase in rate is called *catalysis*. In experiment *P-30 Time to React* you added copper(II) ions (Cu^{2+}) which served as a catalyst.

Can you discuss the rate of exothermic reactions that are involved in a forest fire?



A catalyst is not used up in the reaction it catalyzes. It works by allowing one of the elementary steps to take place with a lower activation energy. Then more of the molecular collisions cause bonds to break, and the reaction is speeded up.

Catalysts are important in many industrial processes. One example in petroleum refining is called *catalytic cracking*. In this process, some of the hydrocarbon molecules from petroleum which are too large to be used in gasoline are converted to high octane gasoline. To accomplish this, the molecules are heated to about 500°C and passed as a vapor through beads or a powder made of claylike material (zeolite) in huge catalytic towers or "cat crackers." The surface of the clay is a catalyst for a reaction in which the molecules are broken up into smaller ones with a high octane rating. Without the catalyst, much higher temperatures would be required for any appreciable rate of reaction.

Life would be impossible without catalysts. Your body contains thousands of different kinds of protein molecules called *enzymes*. Each kind of enzyme catalyzes a particular chemical reaction that is essential for life (see *Molecules in Living Systems: A Biochemistry Module*). If the enzyme were not present, the rate of reaction would be too slow to permit you to live.

QUESTIONS

1. List three factors which can increase the rate of a reaction.
2. (a) The equation given at the end of section *P-31* may be rearranged to give

$$k = \text{rate}/[I^-][S_2O_8^{2-}]$$

Calculate the value of the rate constant k using your data from the first measurement in Part 1 of experiment *P-30 Time to React*. For this calculation, you need the following information: the rate is equal to the amount of I_2 produced per unit volume when the blue color appeared (2.5×10^{-4} mole/liter) divided by the time it took for the blue color to appear. The values of $[I^-]$ and of $[S_2O_8^{2-}]$ were both 0.040 mole/liter in this experiment. If time is expressed in seconds, the value of k will be in units of liter/mole · second.

(b) Now repeat the calculation for the other two measurements in Part 1. Remember that the concentrations of I^- or $S_2O_8^{2-}$ were halved in these measurements. Are your values of k in agreement?

(c) Using an average value of k, calculate the expected value of the rate (in mole/liter · second) if $[I^-]$ and $[S_2O_3^{2-}]$ are both equal to 0.020 mole/liter.

Chemical Equilibrium

The overall rate of any chemical reaction eventually slows down and stops, provided you do not keep adding reactants. The numbers of each reactant molecule and each product molecule become constant in the community of molecules. The community attains *chemical equilibrium.*

A research chemist passes an electrical discharge through a gas mixture in order to study possible chemical equilibrium conditions that existed in the earth's atmosphere before life began.

P-34 Equilibrium Constants

Like the other equilibria we have studied, in the vaporization and dissolving processes, a chemical equilibrium is a *dynamic* equilibrium. It occurs because the rates of two opposite chemical reactions become equal. By exploring this idea, we will be able to come up with a very useful concept called the *equilibrium constant.*

Every reaction that we can write down has the possibility of a reverse reaction. For instance, in experiment *P-28 Heat of Reaction* you studied the neutralization reaction:

$$H^+ + OH^- \rightarrow H_2O$$

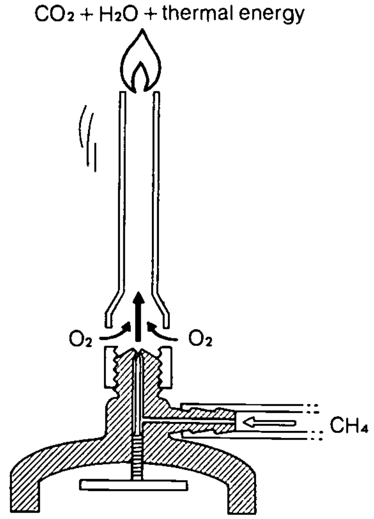
This is the forward reaction. H^+ and OH^- are the reactants and H_2O is the product. The reverse reaction is

$$H_2O \rightarrow H^+ + OH^-$$

Here H_2O is the reactant and H^+ and OH^- are the products. The forward and reverse reactions are said to oppose one another because the forward reaction produces water and the reverse reaction consumes it. The forward reaction together with the reverse reaction can be indicated by double arrows:

$$H^+ + OH^- \rightleftarrows H_2O$$

When a solution containing water is at chemical equilibrium, the forward and reverse reactions occur at the same rate. The H_2O molecules are produced at the same rate as they are consumed. You can tell that there is a chemical equilibrium by measuring the concentration of H^+ ions and finding that it does not change.



A STEADY STATE SYSTEM

Incidentally, in certain communities of molecules in which reactions are taking place, the amounts of the reactants and products are constant—yet there is no chemical equilibrium! These are called *steady state systems*. You can tell that they are steady state systems because reactants are continually added and products are continually removed. A Bunsen burner and a living person are two examples. Fuel or food enter, and combustion products or waste products leave. The amounts of each compound within a Bunsen burner or a living person stay approximately constant. However, these systems are not at chemical equilibrium because the rates of the various forward reactions producing the products are faster than the reverse reactions consuming the products. If the rates were equal, products could not continually be removed.

The neutralization reaction you studied in experiment *P-28 Heat of Reaction* is an example of an extremely rapid reaction. When you added a solution containing OH^- ions to a solution containing H^+ ions, the concentrations of these reactants very quickly decreased to their final equilibrium values. Chemical equilibrium was reached almost instantly. In a slower reaction, it takes longer for the equilibrium to be reached.

To develop the concept of an equilibrium constant, we will use a reaction you will study in the next miniexperiment. The forward reaction can be written

$$\mathrm{Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}}$$

Two ions (in a solution) collide and form a bond. This is the only elementary step.

The rate of the forward reaction can be expressed by the equation

$$\text{rate of FeSCN}^{2+}\text{ production} = k_1\,[\mathrm{Fe^{3+}}][\mathrm{SCN^-}]$$

Here k_1 is the rate constant for the forward reaction.

The reverse reaction is

$$\mathrm{FeSCN^{2+} \rightarrow Fe^{3+} + SCN^-}$$

The reverse reaction is simply the breaking of a bond. The bond is weak and can easily be broken by collisions with the solvent molecules in the solution. The rate of the reverse reaction can be written

$$\text{rate of FeSCN}^{2+}\text{ consumption} = k_2[\mathrm{FeSCN^{2+}}]$$

Here k_2 is a different rate constant for the reverse reaction. The reason that the rate is proportional to $[\mathrm{FeSCN^{2+}}]$ is that the more $\mathrm{FeSCN^{2+}}$ ions there are in each cubic centimeter of solution, the more bonds there are that will break every second.

At chemical equilibrium, the forward and reverse rates are equal. There is no *net* production or consumption of $\mathrm{FeSCN^{2+}}$ ions. Thus we can state that at equilibrium

$$\text{rate of FeSCN}^{2+}\text{ production} = \text{rate of FeSCN}^{2+}\text{ consumption}$$

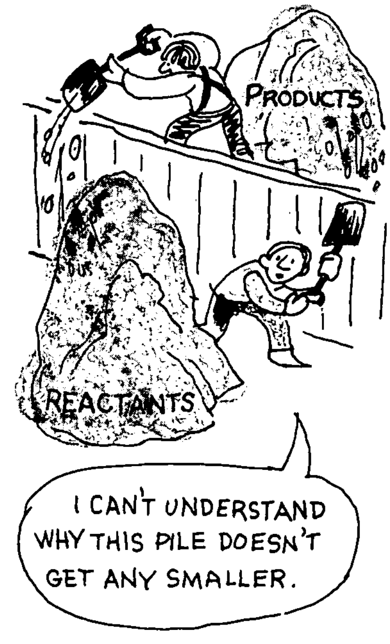
We can substitute into the equation the expressions in the preceding equations. We then obtain the equation

$$k_1[\mathrm{Fe^{3+}}][\mathrm{SCN^-}] = k_2[\mathrm{FeSCN^{2+}}]$$

When we divide both sides of this equation by $k_2[\mathrm{Fe^{3+}}][\mathrm{SCN^-}]$, we obtain

$$\frac{k_1}{k_2} = \frac{[\mathrm{FeSCN^{2+}}]}{[\mathrm{Fe^{3+}}][\mathrm{SCN^-}]}$$

Since k_1 and k_2 are constants, having values which do not depend on the concentrations, the ratio k_1/k_2 must also be constant. The



equation therefore states that a *concentration quotient* written in the following form

$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

is equal to a *constant* at chemical equilibrium. This constant is called the *equilibrium constant.*

The equilibrium constant for this particular reaction has been found to have the value 138 liter/mole at 25°C. Thus the concentrations of the reactants and products at equilibrium, whatever values they may happen to have, must satisfy the equation:

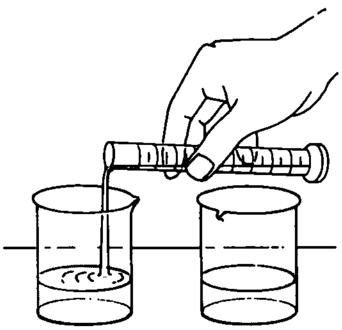
$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = 138 \text{ liter/mole}$$

An experiment will enable you to see what happens to the concentration of the product in this reaction when you change the amounts of the reactants. The reactants are iron(III) ion (Fe^{3+}), which is almost colorless, and thiocyanate ion (SCN^-), which is completely colorless. You will be able to detect the presence of the product, the $FeSCN^{2+}$ ion, by its red color:

$$\underset{\substack{\text{almost}\\ \text{colorless}}}{Fe^{3+}} + \underset{\text{colorless}}{SCN^-} \rightleftharpoons \underset{\text{red}}{FeSCN^{2+}}$$

miniexperiment

P-35 Shifting an Equilibrium



Obtain two 150-cm^3 beakers. Measure 80 cm^3 of water and place it in one of the beakers.

Measure 10 cm^3 of 0.01 M potassium thiocyanate solution (KSCN) with a small graduated cylinder and add it to the water. The solution contains K^+ ions and SCN^- ions.

Rinse out the small graduated cylinder. Use it to measure 10 cm^3 of 0.01 M iron(III) nitrate solution [$Fe(NO_3)_3$]. This solution contains Fe^{3+} ions and NO_3^- ions. (The solution also contains some nitric acid to prevent the formation of ions such as $Fe(OH)^{2+}$, which would be colored, so handle the solution carefully.) Add this solution to the water also.

Divide your mixture equally between the two beakers (50 cm^3 in each beaker).

Add 5 cm^3 of the 0.01 M KSCN solution to the mixture in one beaker. Then add 5 cm^3 of the 0.01 M $Fe(NO_3)_3$ solution to the mixture in the other beaker. Rinse your graduated cylinder after each measurement. Notice carefully what change occurs with each addition. Compare the appearance of both mixtures after you are finished.

Interpret the changes that you saw. The following discussion will help you.

Did you notice that the color changes occur instantaneously—at least to the extent that the eye can see? This is because both the reaction and the reverse reaction have very fast rates. Chemical equilibrium is reached almost as soon as the solutions are mixed. This is often true of reactions between ions.

The first time you mixed the Fe^{3+} ions and the SCN^- ions, the equilibrium concentrations in your mixture were

$$[Fe^{3+}] = 8.9 \times 10^{-4} \text{ mole/liter}$$
$$[SCN^-] = 8.9 \times 10^{-4} \text{ mole/liter}$$
$$[FeSCN^{2+}] = 1.1 \times 10^{-4} \text{ mole/liter}$$

These are the only values of the concentrations that could be obtained from the amounts of Fe^{3+} and SCN^- which you added and which make the concentration quotient equal to 138 liter/mole:

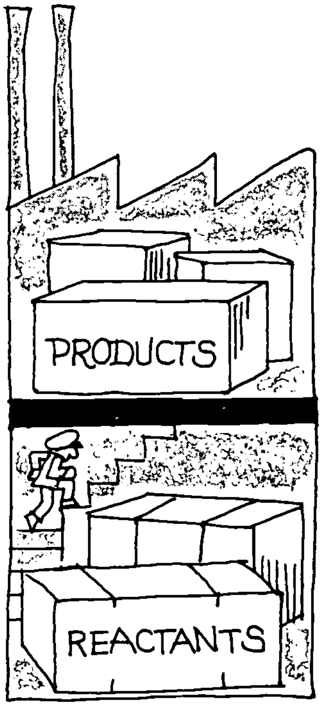
$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{1.1 \times 10^{-4} \text{ mole/liter}}{(8.9 \times 10^{-4} \text{ mole/liter})(8.9 \times 10^{-4} \text{ mole/liter})} = 138 \text{ liter/mole}$$

The K^+ ions and the NO_3^- ions were not involved in the reaction.

When you added more SCN^- ions, what happened to the $FeSCN^{2+}$ concentration? Did this addition make the Fe^{3+} and SCN^- concentrations change? What about the step in which you added more Fe^{3+} ions?

In general, what can you say about the change that will occur in the product concentration when more of a reactant is added? A change in the equilibrium concentration of a product is called a *shift* in the equilibrium. What do you think would have happened if you could have *added* more product to the solution? What if you could *remove* product from the solution?

For even the most complicated chemical reaction, with any number of elementary steps, we can write down an expression for the concentration quotient just by knowing the overall reaction. First, we write down the completed chemical equation for the reaction. Next, we write the concentration quotient with the concentration of each reactant downstairs (in the denominator) and the concentration of each product upstairs (in the numerator). If there is more than one concentration in the denominator, they should be multiplied together. Similarly, more than one concentration in the numerator are multiplied together. At equilibrium, this concentration quotient is equal to the equilibrium constant.



The concentration of every molecule that is a reactant or a product in the reaction has to be included in the concentration quotient, even if this means that some concentrations are repeated. For instance, in the gas phase reaction

$$2NO_2 \rightleftarrows N_2O_4$$

two molecules of NO_2 are needed as reactants. The correct concentration quotient for this reaction is therefore

$$\frac{[N_2O_4]}{[NO_2][NO_2]} \text{ or } \frac{[N_2O_4]}{[NO_2]^2}$$

(Concentration quotients work just as well for a reaction in a gas phase as for reactions in a liquid phase.)

Some conditions affect the value of the equilibrium constant of a reaction, and some do not. Adding a catalyst does *not* change the value of the equilibrium constant. This is because the catalyst increases the rates of *both* the forward and reverse reactions, by equal percentages, so that the equilibrium concentrations do not change. However, changing the temperature usually *does* change the value. When we give the value of an equilibrium constant, we usually refer to the reaction taking place at room temperature. Otherwise, we have to specify what the temperature is.

P-36 The Importance of Size

The equilibrium constants of some reactions have very large values. For instance, the combustion reaction of methane (the main constituent of natural gas) is

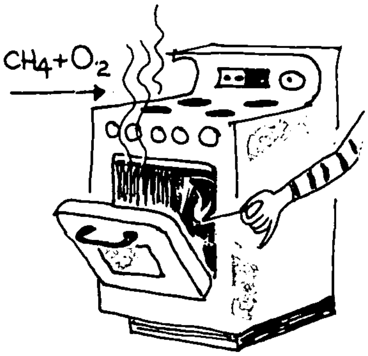
$$CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O$$

The equilibrium constant (at room temperature) has the enormous value of 10^{140}. This means that at equilibrium

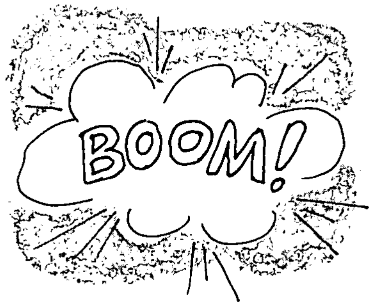
$$\frac{[CO_2][H_2O]^2}{[CH_4][O_2]^2} = 10^{140}$$

This equation tells us that at equilibrium at least one of the reactant concentrations must be extremely small in order to make the concentration quotient so enormous. (Another way the concentration quotient could be very large is for a product concentration to be very large, but this is not possible in a gas.) Thus at equilibrium one or both of the reactants is almost completely used up. A very large equilibrium constant means that the reaction goes practically to *completion* at equilibrium.

For instance, suppose that 1000 cm^3 of a gas mixture at one atmosphere of pressure, consisting of methane and oxygen molecules in a 1 to 2 proportion, is allowed to burn. It can be calculated from the equilibrium constant that the equilibrium gas mixture should contain 2×10^{-73} mol of methane molecules and 4×10^{-73} mol of oxygen molecules. Since one molecule is about 10^{-23} mol, there would be much less than one molecule of the reactants at equilibrium! Actually, what this calculation means is that methane and oxygen molecules are present only very infrequently in the equilibrium mixture.



The methane combustion reaction illustrates another phenomenon. Methane (or natural gas) and oxygen (or air) if mixed together at room temperature do not react. Even though the amounts of the compounds do not change, the mixture is *not* at chemical equilibrium. If you supply the necessary activation energy by striking a match, the reaction proceeds explosively and equilibrium is quickly attained.



Any reaction with a very *small* equilibrium constant has only small concentrations of the products present at equilibrium. The reaction proceeds to only a small extent. For instance, acetic acid (CH_3COOH) in water can produce ethyl alcohol (CH_3CH_2OH) by the reaction

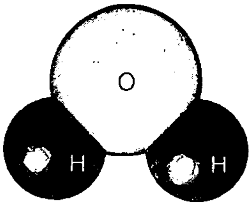
$$CH_3COOH + H_2O \rightleftharpoons CH_3CH_2OH + O_2$$

The equilibrium constant for this reaction is about 10^{-82}. This extremely small value suggests that very little wine is formed from vinegar. It also suggests that wine turns almost completely into vinegar in the presence of oxygen.

P-37 Hydrogen Ions: The Acid Test

Some of the most important applications of equilibrium constants involve acids and bases. An *acid* is a compound which produces hydrogen ions (H^+) when dissolved in water. A *base* (or alkali) is a compound which produces hydroxide ions (OH^-) in water.

Chemists believe that in water H^+ ions are attached by polar attractions to one or more water molecules. Some chemists write the formula of the ion as H_3O^+ and call it a "hydronium ion." We will refer simply to a hydrogen ion, written H^+, without worrying about the exact structure.



Pure liquid water is neither acidic nor basic; it is neutral. However, it contains small concentrations of both hydrogen ions and hydroxide ions resulting from the ionization reaction

$$H_2O \rightleftharpoons H^+ + OH^-$$

At equilibrium, the concentration quotient is equal to the equilibrium constant as expressed in this equation:

$$\frac{[H^+][OH^-]}{[H_2O]} = K$$

The symbol K stands for the equilibrium constant.

If H_2O is a product or reactant of a reaction occurring in liquid water, it is customary to omit $[H_2O]$ from the numerator or the denominator of the concentration quotient. The reason is that the concentration of H_2O in liquid water is so high (55 M, as you can easily figure out) that it cannot change appreciably during the reaction. Therefore, the concentration quotient with $[H_2O]$ omitted is still equal to a constant at equilibrium.

We can use the ionization reaction to illustrate how $[H_2O]$ may be omitted. When we multiply both sides of the preceding equation by $[H_2O]$, we obtain a new equation:

$$[H^+][OH^-] = K[H_2O]$$

This equation states that the concentration quotient, with $[H_2O]$ omitted, is equal to $K[H_2O]$. Since $[H_2O]$ is practically a constant (equal to 55 M), $K[H_2O]$ is a constant also and may be treated as a new equilibrium constant. This particular equilibrium constant is called the *ion product* of water. Its value is found to be 10^{-14}(mole/liter)^2.

In other words, at equilibrium we can write

$$[H^+][OH^-] = 10^{-14}\ (\text{mole/liter})^2$$

Since the ionization of one H_2O molecule produces one H^+ ion and one OH^- ion, the concentrations of both ions must be equal in pure water. (The concentrations are *not* equal if you add an acid or a base.) The correct value of the ion product is obtained with the following equal concentrations:

$$[H^+] = 10^{-7}\ \text{mole/liter}$$
$$[OH^-] = 10^{-7}\ \text{mole/liter}$$

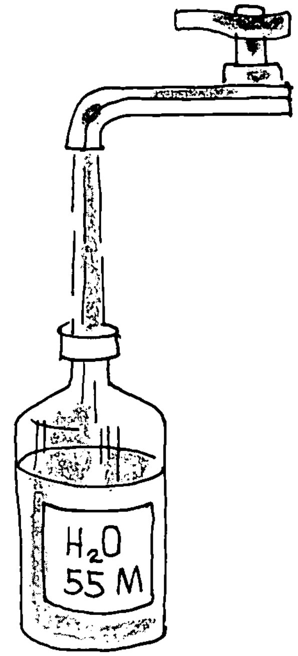
Therefore the concentration of H^+ in a neutral solution is 10^{-7} M. An acidic solution has a higher concentration of H^+ than 10^{-7} M, and a basic solution has a lower concentration of H^+ than 10^{-7} M.

Chemists find it convenient to describe the hydrogen ion concentration (in units of moles per liter) by giving the power of ten without the minus sign. By this method the value is called the pH of the solution. Thus a neutral solution has a pH of 7.

An acidic solution in which $[H^+] = 10^{-6}$ M has a pH of 6. A solution with $[H^+] = 10^{-9}$ M (a basic solution) has a pH of 9. In general

$$\text{pH} = -\log[H^+] \quad \text{or} \quad [H^+] = 10^{-\text{pH}}$$

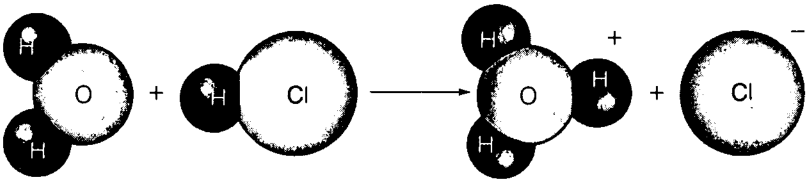
Solutions with a pH less than 7 are acidic. Solutions with a pH greater than 7 are basic.

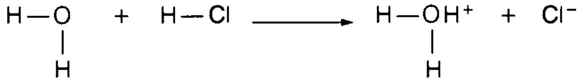


TIME MACHINE

1905	NCAA becomes rulemaking body for U.S. intercollegiate sports.
1906	Congress passes Federal Food and Drug Act.
1908	Henry Ford produces the first Model T automobiles.
1909	**Søren Sørensen, Danish biochemist, invents the term pH—power of hydrogen.**
1910	A Memphis dance band introduces the blues.
1911	Irving Berlin composes "Alexander's Ragtime Band."
1912	S. S. *Titanic* sinks on her maiden voyage.

The compound hydrogen chloride (HCl) is a molecule in the gas phase, but in water it ionizes completely into the ions H^+ and Cl^-.





$$\underset{\textstyle H}{\overset{}{H{-}\underset{|}{O}}} + H{-}Cl \longrightarrow \underset{\textstyle H}{H{-}\underset{|}{O}H^+} + Cl^-$$

A water solution of HCl is called hydrochloric acid. Those acids that ionize completely, such as hydrochloric acid, are called *strong acids*. Some other important strong acids are sulfuric acid (H_2SO_4) and nitric acid (HNO_3). (Only one H^+ ion ionizes completely from H_2SO_4.)

If one mole of HCl is dissolved in 1000 cm^3 of water, a solution containing one mole of H^+ ions per 1000 cm^3 is produced. Therefore $[H^+]$ equals 1 M. Most of the OH^- ions that were present in the water before the HCl was added are neutralized by the added H^+ ions. The concentration of H^+ is so high that the neutralization changes this concentration very little, but the OH^- ion concentration decreases. In fact, it decreases until $[OH^-] = 10^{-14}$ M in order to make the ion product equal to 10^{-14} (mole/liter)^2:

$$[H^+][OH^-] = (1\text{ mole/liter}) \times (10^{-14}\text{ mole/liter}) = 10^{-14}\text{ (mole/liter)}^2$$

pH	$[H^+]$	$[OH^-]$	
0	1 M	10^{-14} M	MORE ACIDIC
1	10^{-1} M	10^{-13} M	
2	10^{-2} M	10^{-12} M	
3	10^{-3} M	10^{-11} M	
4	10^{-4} M	10^{-10} M	
5	10^{-5} M	10^{-9} M	
6	10^{-6} M	10^{-8} M	
7	10^{-7} M	10^{-7} M	NEUTRAL
8	10^{-8} M	10^{-6} M	MORE BASIC
9	10^{-9} M	10^{-5} M	
10	10^{-10} M	10^{-4} M	
⋮	⋮	⋮	

Sodium hydroxide (NaOH) is an ionic solid which dissociates completely into Na^+ ions and OH^- ions in water. Therefore, NaOH is a *strong base*. When NaOH is dissolved in water, $[OH^-]$ increases and $[H^+]$ decreases. The concentration of H^+ becomes less than 10^{-7} M, and the solution is therefore basic.

Acids and bases which do not ionize completely are called *weak* acids and bases. In a solution of a weak acid or base, there is a chemical equilibrium between ions and neutral molecules. For instance, acetic acid (the main constituent of vinegar) has the ionization reaction

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

Therefore, at equilibrium we can write

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = K_a$$

The equilibrium constant K_a is called the *ionization constant* of acetic acid. In the next experiment you will determine the value of K_a for acetic acid.

An example of a weak base is ammonia (NH_3). Its ionization reaction is

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

Can you write the concentration quotient for this reaction? Remember to omit $[H_2O]$.

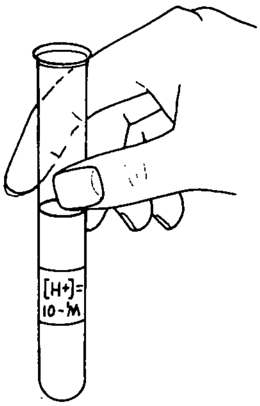
EXPERIMENT

P-38 Show Your Colors

In this experiment you will use certain dyes called *acid-base indicators.* The color of an indicator in a solution depends upon the hydrogen ion concentration of the solution. The color changes within a particular range of $[H^+]$ values, depending upon which indicator is used.

You will first prepare solutions of known $[H^+]$ values from hydrochloric acid. These solutions, with the indicator added, will serve as standards. You will use these standards to estimate the $[H^+]$ values in several solutions of acetic acid. From your results you will be able to calculate the ionization constant of acetic acid.

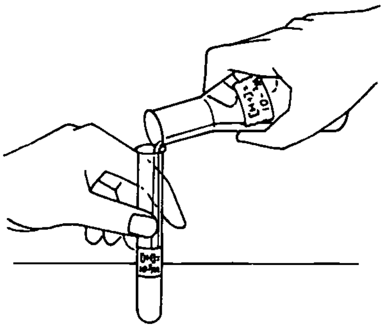
Note: *It is important in this experiment to use clean glassware. Rinse each graduated cylinder, flask, and test tube before use, and shake as much water out as possible.*



Part 1: Preparation of Standards

You will be provided with a solution of 0.10 M HCl. Place about 10 cm^3 of this solution in a clean test tube. Since hydrochloric acid is a strong acid which ionizes completely, the concentration of H^+ is the same as the concentration of the hydrochloric acid. Label the test tube $[H^+] = 10^{-1}$ M. What is the pH of this solution?

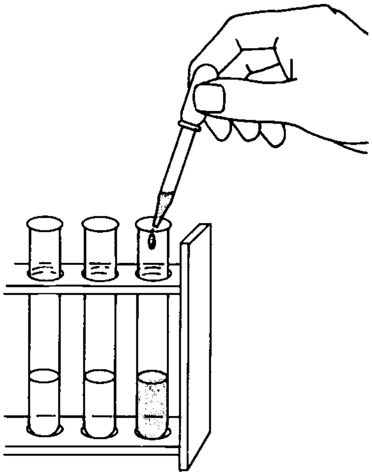
Prepare 10^{-2} M HCl by diluting 10 cm^3 of the 10^{-1} M HCl in a clean 100-cm^3 graduated cylinder. First, carefully measure exactly 10 cm^3 of the 10^{-1} M HCl in the graduated cylinder. Then slowly add water from a clean beaker or flask until the total volume is exactly 100 cm^3. Thoroughly mix the 100 cm^3 of solution by pouring it into a clean 125-cm^3 Erlenmeyer flask, then back into the cylinder, and finally into the flask again. Label the flask $[H^+] = 10^{-2}$ M. Pour about 10 cm^3 of this solution into a clean test tube. (Save the remaining solution.) Label the test tube $[H^+] = 10^{-2}$ M.



By the same method, dilute 10 cm^3 of the 10^{-2} M solution to prepare 100 cm^3 of 10^{-3} M HCl. Then dilute 10 cm^3 of this 10^{-3} M solution to prepare 100 cm^3 of 10^{-4} M HCl. Finally dilute 10 cm^3 of the 10^{-4} M solution to prepare 100 cm^3 of 10^{-5} M HCl. Be sure to save about 10 cm^3 of each of these solutions in labeled test tubes.

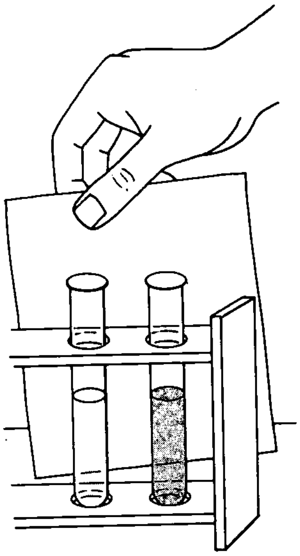
You should now have five test tubes containing different HCl solutions. Line them up in order of decreasing concentration. What are the pH values of these solutions?

Prepare another set of five, clean test tubes and label them exactly as you did the first set. Pour half of the contents of each test tube in the first set into its corresponding test tube in the second set.



Two indicators will be available. Add one drop of one of the indicators to each of the five test tubes in the first set of standards. Add one drop of the other indicator to each of the test tubes in the second set. Observe the colors. Do the two indicators change color in the same range of pH? Save the standards for *Part 2.*

Part 2: Acetic Acid Solutions
You will work with a solution of 0.10 M acetic acid, a weak acid. Place about 5 cm^3 of the 0.10 M acetic acid in each of two clean test tubes. Add a drop of one indicator to one test tube and a drop of the other indicator to the second test tube. Carefully compare the colors with your standards. It helps if you view the test tubes in front of a well-lighted sheet of white paper. If acetic acid dissociates completely, the colors should match the colors of the standards labeled $[H^+] = 10^{-1}$ M. Do they match? Explain.



Pick the standards having the same $[H^+]$ which give the closest match in colors to the two acetic acid solutions. Record the concentration of the acetic acid and the concentration of H^+ as you have estimated it from the standards.

Carefully measure 1 cm^3 of the 0.10 M acetic acid in a clean 10-cm^3 graduated cylinder. Pour the acetic acid into a clean 100-cm^3 graduated cylinder and add water until the total volume is 100 cm^3. Mix in the same way as in *Part 1.* The concentration of the acetic acid in this solution is 10^{-3} M. Do you see why? Again determine $[H^+]$ and record it.

Part 3: Ionization Constant of Acetic Acid
The reaction for the ionization of acetic acid is

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

You may assume that all of the H^+ ions present in your acetic acid solution were produced by this reaction. (The only other source of H^+ ions is H_2O, but the amount of ionization of H_2O molecules is insignificant compared to the ionization of the acetic acid.) Each molecule of CH_3COOH that ionizes produces one H^+ ion and one CH_3COO^- ion. Therefore there are equal concentrations of H^+ ions and CH_3COO^- ions:

$$[CH_3COO^-] = [H^+]$$

You may also assume that in each of your solutions $[CH_3COOH]$ is equal to the total concentration of the acetic acid. By looking at the $[H^+]$ values you determined, you will see that only a small fraction of the acetic acid is ionized in each solution.

Remembering that $[CH_3COO^-]$ is equal to $[H^+]$, and that $[CH_3COOH]$ is equal to the total acetic acid concentration c, we find that the concentration quotient

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

is equal to $[H^+]^2/c$. Calculate $[H^+]^2/c$ for your two acetic acid solutions. Is the concentration quotient a constant in your solutions?

Use a table similar to the following for your data:

$[CH_3COOH] = c = 10^{-1}$ mole/liter:
$[H^+] =$ ___ mole/liter
$[H^+]^2/c =$ ___ mole/liter

$[CH_3COOH] = c = 10^{-3}$ mole/liter:
$[H^+] =$ ___ mole/liter
$[H^+]^2/c =$ ___ mole/liter

How does an acid-base indicator work? An indicator is itself a weak acid or a weak base. The indicator has two chemical forms which we can represent by the formulas HIn and In^-. These forms react as follows:

$$HIn \rightleftarrows H^+ + In^-$$

The HIn form is called the acid form (because it is the only form present in very acidic solutions), and the In^- form is called the basic form. These two forms may have different colors, or in some instances, one form is colored and the other colorless. The colors reveal the H^+ concentration and the pH.

To use an indicator, you add it to a solution in such a small amount that it cannot affect the H^+ concentration. At equilibrium we can write

$$\frac{[H^+][In^-]}{[HIn]} = K_{ind}$$

where K_{ind} stands for the indicator equilibrium constant. The equation may be rearranged to

$$\frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_{ind}}$$

This equation shows that when $[H^+]$ is much larger than K_{ind}, $[HIn]$ is much larger than $[In^-]$. The solution has the color of the acid form of the indicator HIn. When $[H^+]$ is much smaller than K_{ind}, it is $[In^-]$ that is large and the solution has the color of the basic form of the indicator. The intermediate situation is when

$[H^+] = K_{ind}$. Then the acid and basic indicator forms have equal concentrations, and the color is a combination of the colors of the two forms.

Different indicators change their colors at different values of $[H^+]$, depending upon the value of K_{ind}. Many different indicators are available, which is fortunate, since this allows you to select an indicator which changes color at the H^+ concentration you are interested in.

Some natural materials contain indicators. Tea becomes pale when lemon juice (containing citric acid) is added. Red cabbage juice, beet juice, and many flower dyes change colors when acids or bases are added.

QUESTIONS

1. An example of a chemical reaction is

$$\underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+ \rightleftarrows \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$$

If more H^+ is added to the solution, will the solution become more yellow, more orange, or remain the same color? Explain.

2. The compounds A and B react to form compounds C and D, according to the reaction

$$A + B \rightleftarrows C + D$$

One liter of a solution at equilibrium is analyzed and found to contain 0.010 mol of A, 0.020 mol of B, 0.010 mol of C, and 0.040 mol of D. What is the value of the equilibrium constant? If a new solution is prepared which has the equilibrium concentrations of A, B, and C all equal to 0.010 M, what will be the equilibrium concentration of D?

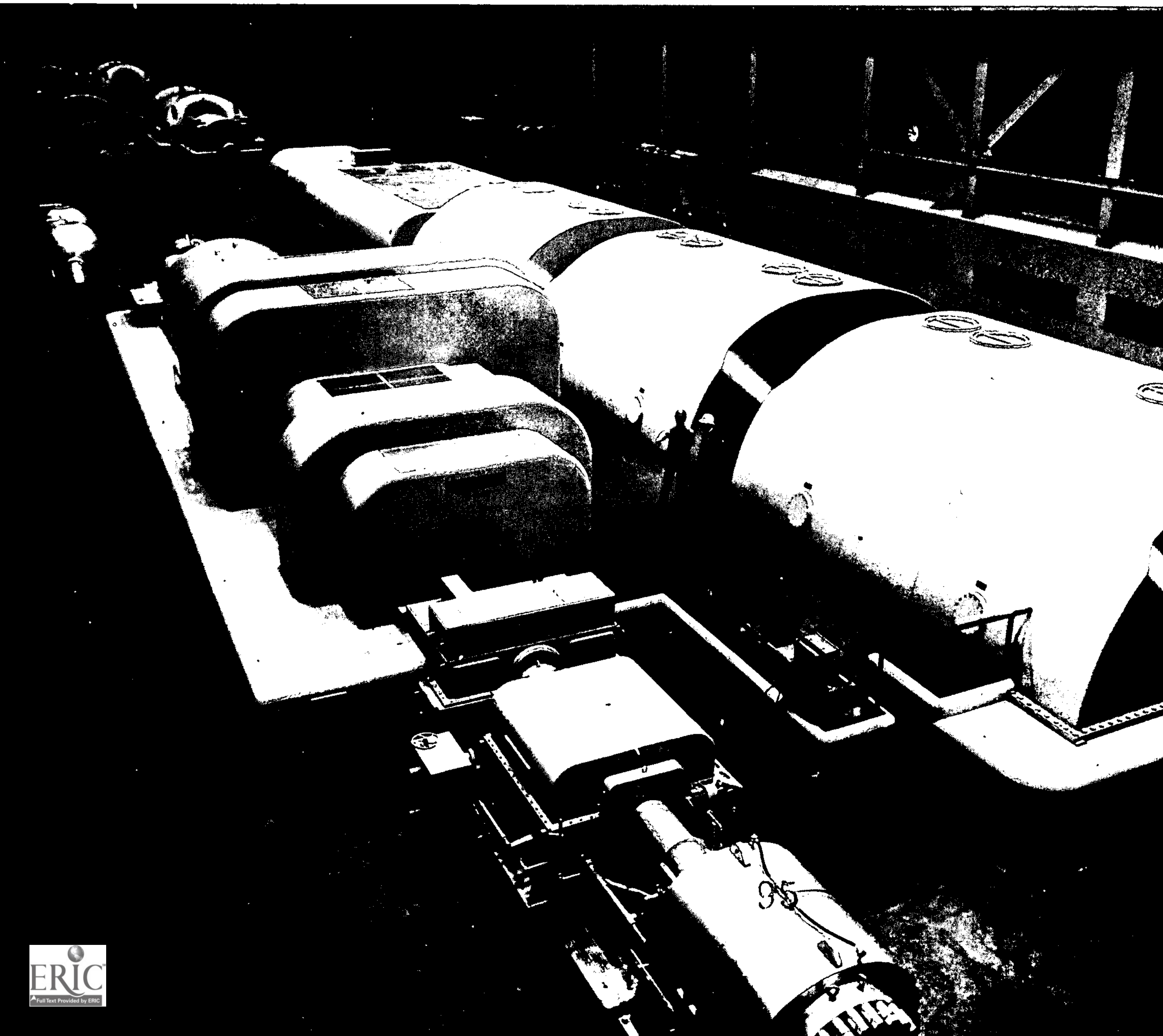
3. For a solution of methyl red, an acid-base indicator, the equilibrium constant has the value $K_{ind} = 6 \times 10^{-6}$ M. The reaction is

$$\underset{\text{red}}{HIn} \rightleftarrows H^+ + \underset{\text{yellow}}{In^-}$$

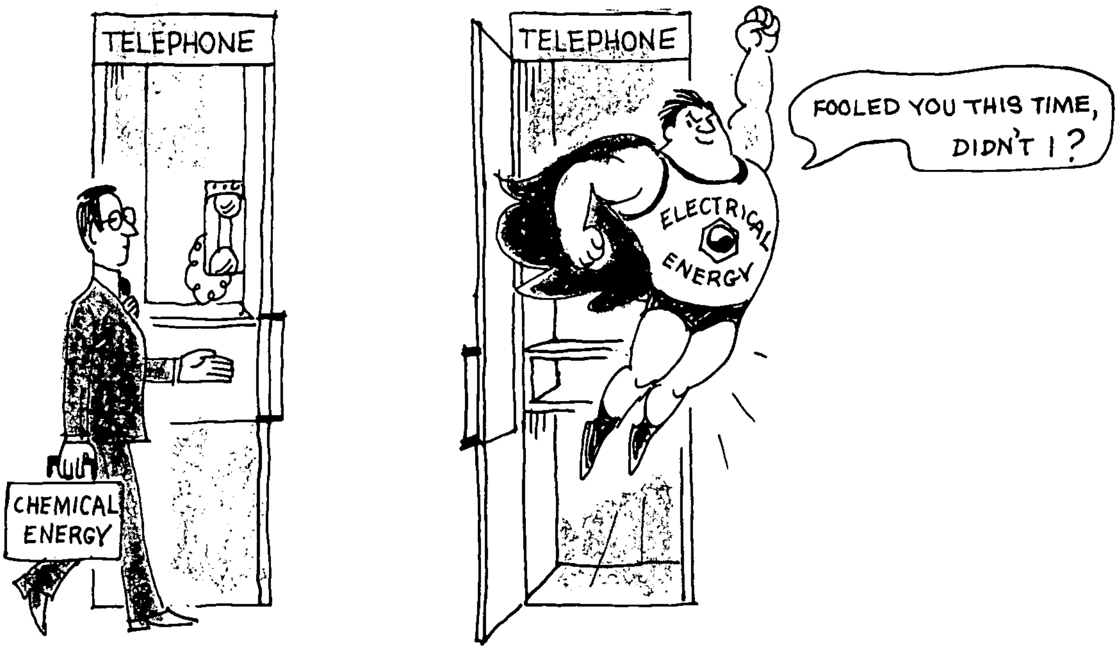
Which form of the indicator will have the larger concentration at pH = 2? How many times larger is this concentration? What about at pH = 5 and at pH = 8? Predict the color of each of these solutions.

Electrochemistry

Electricity is a form of *energy,* just as thermal energy and chemical energy are. The electrical energy coming through wires into your home and your school probably is produced at a steam generation power station. At the power station, coal, gas, or oil is burned. This is an example of an exothermic reaction in which chemical energy is converted into thermal energy. The thermal energy is used to produce steam from water. The steam drives the turbines which turn the electric generators. It sounds complicated, doesn't it?



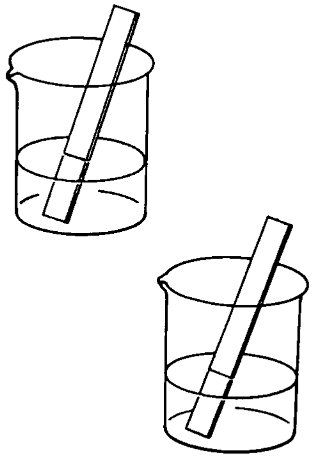
An electrochemical cell is a less complicated way of harnessing a chemical reaction to produce electrical energy. No thermal energy is involved in the operation of a cell. Chemical energy is converted directly and efficiently into electrical energy. The main drawback is that only certain reactions can be harnessed in this way. Among other things, the reaction must be a kind of reaction called an oxidation-reduction reaction. You will study such a reaction in the next miniexperiment.



P-39 Oxidation-Reduction Reactions

miniexperiment

Fill a 150-cm^3 beaker about one-third full of 0.5 M copper(II) sulfate ($CuSO_4$). Fill a second beaker about one-third full of 0.5 M zinc sulfate ($ZnSO_4$). The first solution contains Cu^{2+} ions and the second contains Zn^{2+} ions.



Place a zinc metal strip in the solution containing Cu^{2+} ions, and a copper metal strip in the solution containing Zn^{2+} ions. Carefully observe what happens. Then remove the metal strips. Save the solutions and the metal strips for the next experiment.

Here are two possible reactions:

Reaction 1: $Zn\ (solid) + Cu^{2+} \rightarrow Zn^{2+} + Cu\ (solid)$
Reaction 2: $Zn^{2+} + Cu\ (solid) \rightarrow Zn\ (solid) + Cu^{2+}$

Notice that *Reaction 2* is the reverse of *Reaction 1.* Which of these reactions actually occurs?

TIME MACHINE

1797	John Adams becomes second president of the United States.
1798	Samuel Taylor Coleridge writes "Rime of the Ancient Mariner" and "Kubla Khan."
1799	Beethoven composes his First Symphony.
1800	**Physicist Alessandro Volta of Italy makes the first electrochemical cells.**
1801	John Marshall becomes first chief justice of U.S. Supreme Court.
1802	U.S. Military Academy opens at West Point on July 4.
1803	The United States purchases the Louisiana Territory from France.

When a molecule, ion, or atom *loses* electrons it is said to be *oxidized*. When it *gains* electrons it is said to be *reduced*. In *Reaction 1* in *P-39*, Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu. This kind of reaction is called an *oxidation-reduction reaction*, or *redox reaction* for short. You may think of it as a process in which electrons move from one substance to another. One substance is oxidized, and the other is reduced. If *Reaction 2* occurred, which substance would be oxidized and which substance would be reduced?

An oxidation-reduction reaction, like any other chemical reaction, will take place whenever the forward reaction has a faster rate than the reverse reaction. Electrons must be able to move from one of the reactants to the other. If we can arrange for the electrons to move through a wire during this process, we will have a source of electricity. The electrical energy of the electricity will come from the chemical energy of the reactants.

Fortunately, such an arrangement can often be devised. The arrangement is called an *electrochemical cell*. In the following experiment, you will make a cell utilizing the copper-zinc reaction.

EXPERIMENT

P-40 Copper-Zinc Cell

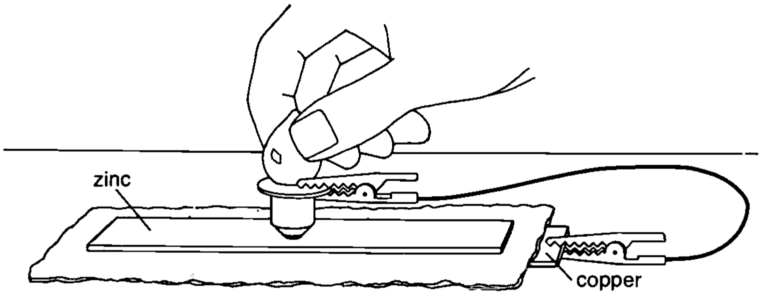
Rinse off the zinc and copper strips used in the preceding miniexperiment. Rub the copper coating from the zinc strip with a cloth, a paper towel, or steel wool.

Place the copper strip on the laboratory table or on another nonmetallic waterproof surface. Connect a wire from the end of the copper strip to the flange of a test light bulb.

Take a strip of cloth towel and dip it into the 0.5 M zinc sulfate solution used in the preceding miniexperiment. Cover the copper strip with the wet cloth strip. Place the zinc strip on top to make a sandwich with the cloth in the middle. Arrange the sandwich so that the two metal strips do not directly touch.

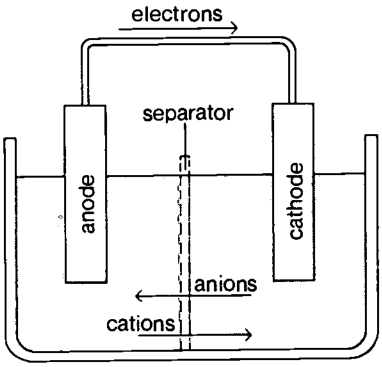
Touch the base of the test bulb to the zinc strip. Press down on the sandwich to insure good contact between the metals and the solution. Is there any electrical activity?

This postage stamp honors Alessandro Volta and his contribution to the chemistry of electricity—the first electrochemical cell.



Now take your sandwich apart and rinse and dry the metal strips. Put the cloth strip back into the beaker of zinc sulfate solution for use later. Repeat the experiment using a new cloth strip dipped into 0.5 M copper(II) sulfate solution. This time is there any electrical activity?

Do you find that the same solution which caused an oxidation-reduction reaction to occur in the preceding miniexperiment is necessary to make an electrochemical cell in this experiment?



ELECTROCHEMICAL CELL

The zinc and copper strips in your cell are called *electrodes*. There are two kinds of electrodes in any cell: the *anode* and the *cathode*. At the anode, oxidation occurs. The substance that is oxidized loses electrons, which enter the anode. Since electrons have a negative charge, the anode becomes negatively charged. At the cathode, reduction occurs. The substance which is reduced gains electrons from the cathode. Since the reduction removes electrons from the cathode, the cathode becomes positively charged.

The negative charge of the anode causes an electrical voltage between the two electrodes. Electrons move in the wire from the anode to the cathode. The electrical circuit is completed inside the cell by various ions moving through the solutions. The negative ions move toward the anode, and the positive ions move toward the cathode. Negative ions are called *anions;* positive ions are called *cations*.

It helps to understand how an electrochemical cell works if you write separate reactions for what happens at each electrode. These are called *half-reactions*. In your cell the half-reaction at the zinc electrode is

$$Zn \rightarrow Zn^{2+} + 2e^-$$

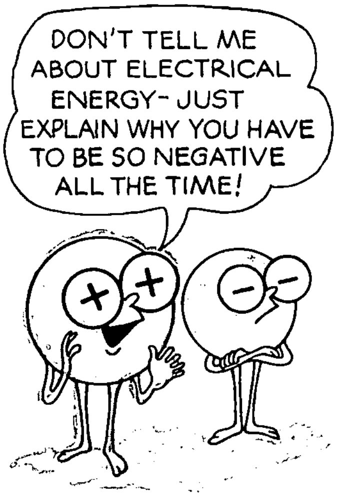
This means that a Zn atom (in the electrode) produces a Zn^{2+} ion (in the solution next to the electrode) and two electrons which go into the wire.

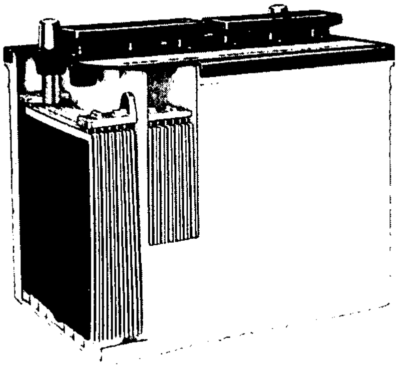
The half-reaction at the copper electrode is

$$Cu^{2+} + 2e^- \rightarrow Cu$$

This means that a Cu^{2+} ion (from the $CuSO_4$ solution) and two electrons from the wire produce a Cu atom.

A single half-reaction cannot take place to any measurable extent by itself. *Two* half-reactions always take place at the same time. One half-reaction is an oxidation reaction which produces electrons, and the other half-reaction is a reduction reaction which uses up the electrons. Which of the half-reactions in your cell is the oxidation





Cutaway view of an automobile lead storage battery showing two of the six lead-acid cells.

reaction and which is the reduction reaction? Which of the electrodes is the cathode and which the anode? Which way do the electrons move in the wire?

Write down the overall chemical change taking place. Is it the same as the oxidation-reduction reaction you observed in mini-experiment *P-39 Oxidation-Reduction Reactions*?

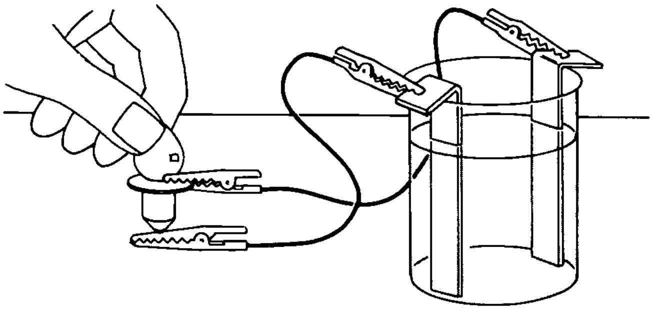
In the experiment that follows you will make a lead-acid cell, the kind found in automobile lead storage batteries. A battery is several cells connected together to give a higher voltage or more current. A lead-acid cell produces two volts of electricity. Therefore, a six-volt storage battery contains three cells and a twelve-volt storage battery contains six cells.

EXPERIMENT

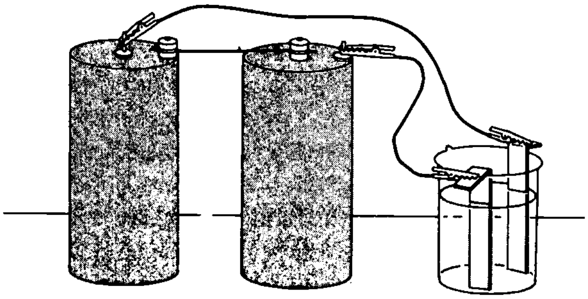
P-41 Lead-Acid Cell

Place two lead strips in a 150-cm^3 beaker. Bend the tops of the strips over the rim of the beaker so that they will stand against the sides. Clip a wire to each strip. Fill the beaker two-thirds full of 4 M sulfuric acid (H_2SO_4). **Caution:** *Use care—sulfuric acid is very corrosive!*

Test the cell for electrical activity by clipping one wire to a test light bulb and touching the bottom of the test bulb to the other wire.



Remove the test bulb and attach two dry cells in series to the lead strips, as illustrated.



Carefully examine the lead strips and note any changes. Leave the dry cells connected to the lead strips for at least 15 minutes.

The purpose of this step is to form a coating of lead dioxide (PbO_2) on one of the lead strips. Electrical energy from the dry cells is forcing two half-reactions to occur which would not otherwise take place; at the lead strip connected to the negative terminal:

$$2H^+ + 2e^- \rightarrow H_2 \text{ (gas)}$$

and at the lead strip connected to the positive terminal:

$$Pb + 2H_2O \rightarrow PbO_2 + 4H^+ + 4e^-$$

Compare the appearance of the two lead strips.

After 15 minutes, or longer if possible, remove the dry cells and again attach the test bulb to the wires. How long does the electrical activity last?

The half-reactions that are going on while the cell lights the bulb are as follows:

$$Pb \rightarrow Pb^{2+} + 2e^-$$
$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$$

Which of these half-reactions is the oxidation reaction and which is the reduction reaction?

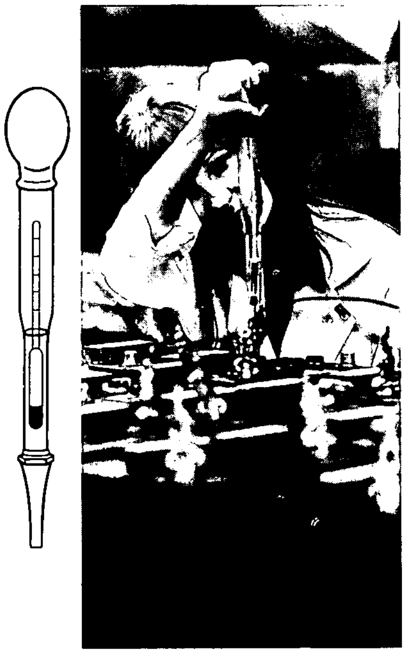
These are the half-reactions that occur in each cell of a car storage battery as it is delivering a current. Notice that Pb^{2+} ions are produced at both electrodes of the cell. By the following reaction, this ion forms an insoluble precipitate of lead sulfate ($PbSO_4$) that coats each electrode:

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$$

The SO_4^{2-} ions come from the sulfuric acid in the cell. As the battery runs down, sulfuric acid is used up. Since water is less dense than sulfuric acid (has less mass per unit volume), the solution in the cell becomes less dense. Measuring the density of the solution is one way to tell whether a battery needs recharging.

When a storage battery is charged by passing electricity through it, the half-reactions given previously occur in reverse. Pb^{2+} ions are converted to Pb and PbO_2, ready to be used again to produce electrical energy. The biggest advantage of a storage battery is that it can be recharged. The half-reactions of most electrochemical cells cannot be reversed in this way.

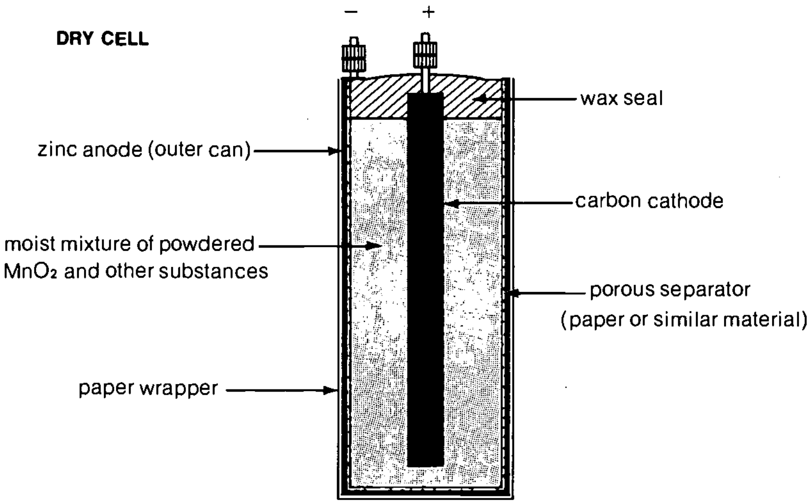
Testing storage batteries with a battery tester. The hydrometer in the tester measures the density of the sulfuric acid solution.



P-42 Practical Portable Power

Many useful kinds of electrochemical cells and batteries have been invented. (The so-called "battery" used in a flashlight is actually only a single cell.) Three interesting kinds of cells are dry cells, alkaline-manganese cells, and fuel cells.

The common *dry cell* or carbon-zinc cell, such as the ones you used in experiment *P-41 Lead-Acid Cell*, are usually constructed like this:



A "dry cell" is not really dry, but the contents are sealed to prevent them from leaking. Dry cells are often used in flashlights. The voltage of a fresh dry cell is about 1.5 V (volts). At the anode, the half-reaction is

$$Zn \rightarrow Zn^{2+} + 2e^-$$

At the cathode, the half-reaction is

$$2MnO_2 + Zn^{2+} + 2e^- \rightarrow ZnMn_2O_4$$

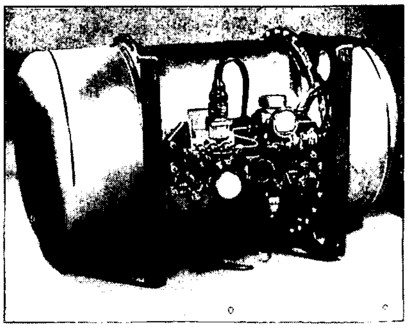
Alkaline-manganese cells, sometimes called alkaline cells, are also used in flashlights and in transistor radios. An alkaline-manganese cell may give two to eight times the useful service of a dry cell of the same size, but it is more expensive than a dry cell. The alkaline-manganese cell contains a zinc anode and a manganese oxide (MnO_2) cathode separated by a basic liquid solution, with half-reactions similar to the dry cell.

Fuel cells are exotic developments of current research. Unlike other electrochemical cells, they are steady state systems when in operation. They are continuously fed with chemical reactants so that they never run down. The only kind of widely used fuel cell utilizes the combustion reaction of hydrogen gas and oxygen gas to produce water and electricity. The overall chemical reaction is

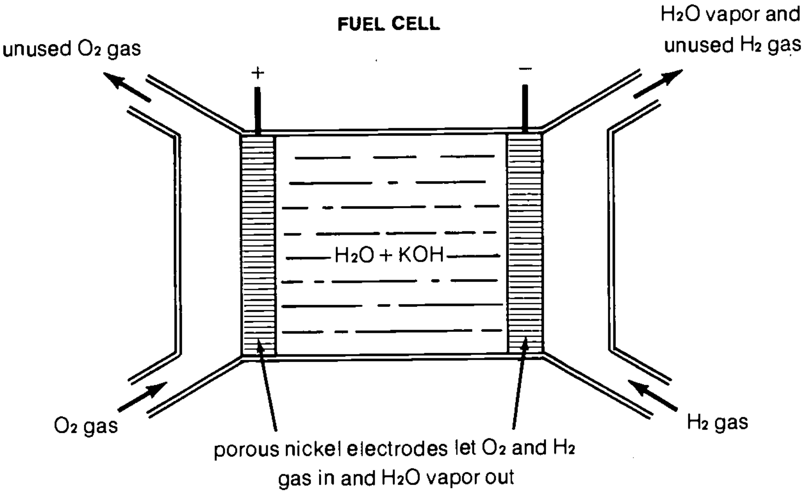
$$2H_2 + O_2 \rightarrow 2H_2O$$

The reaction is carried out in the fuel cell at temperatures up to 260°C. The ordinary rate of combustion of H_2 at this temperature is so slow that it cannot be measured.

The Apollo lunar spacecrafts contained thirty-one fuel cells of this type to provide electrical energy. The construction of each fuel cell is shown in the following illustration.



This fuel cell was designed for spacecraft use. It uses hydrogen and oxygen to produce one kilowatt of electricity along with one-half liter of pure water for each hour of operation.



The half-reactions are

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

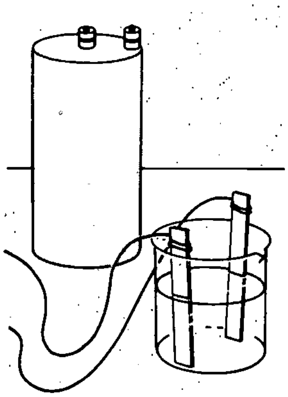
H_2O, the product of the reaction, is removed continuously as a vapor and is condensed to liquid water. The water was used as drinking water by the astronauts!

Hydrogen-oxygen fuel cells which are similar to this one are being tested as possible replacements for steam generation power plants. Coal, gas, or oil would be reacted with steam to form the hydrogen gas needed for the fuel cell, as well as carbon dioxide. The fuel cell would be able to produce more electrical energy from each gram of fuel, with much less air pollution, than if the fuel were burned in the usual power station process.

Electrochemical cells are a means of converting chemical energy into electrical energy. In miniexperiment *P-39 Oxidation-Reduction Reactions* you found that no reaction occurs when a copper strip is placed in a solution containing Zn^{2+} ions. In the final experiment, you will use the electrical energy from a dry cell to force a reaction to occur. The reaction deposits metallic zinc on the copper strip. In this process, electrical energy is converted into chemical energy. The process is an example of *electroplating*.

EXPERIMENT

P-43 Finishing Touches



Place a zinc strip and a copper strip in a beaker containing 0.5 M zinc sulfate ($ZnSO_4$). Keep the strips apart from each other. Does any reaction take place?

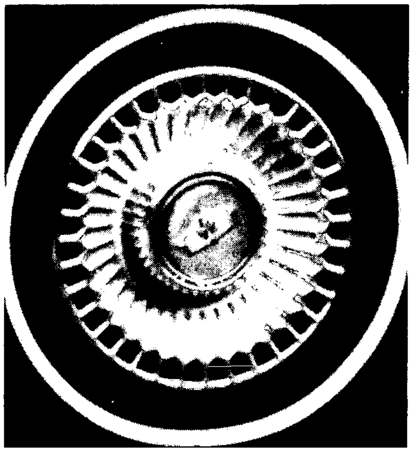
Now attach a wire to each strip, and connect the wires to a dry cell. You want the copper strip to be the *cathode* in this setup so that Zn^{2+} ions will be reduced there. Electrons, therefore, must come *into* the copper strip from the wire. Which terminal of the dry cell must you connect to the copper strip of the electroplating setup?

After the electroplating setup has run for awhile, inspect the two electrodes. What half-reaction has occurred at each electrode? Would these reactions have occurred if the dry cell had not been in the circuit?

Electroplating is used to deposit thin films of certain metals on metallic objects in order to protect the objects from corrosion, improve their appearance, and give them other desirable properties. For instance, coatings of zinc or cadmium are electroplated in ways similar to the experiment onto objects such as steel nails and screws in order to prevent them from rusting. Commercially, the electricity which is required is produced by a power station instead of an electrochemical cell. (Zinc coatings may also be made by the galvanizing process, in which steel is dipped into hot molten zinc.) "Tin cans" are really steel cans electroplated with tin to prevent rusting by the food contents.

Silverplated items have a base of copper and are coated with silver by the electroplating process.

Chromium plate gives car bumpers and other metal objects a shiny protective surface. It is sometimes called (incorrectly) "chrome plate." Because chromium is expensive, chromium plate is usually a very thin layer of chromium metal, less than 10^{-4} cm in thickness, deposited on a nickel underlayer. The nickel layer is first electroplated onto the metal object by this half-reaction at the cathode:

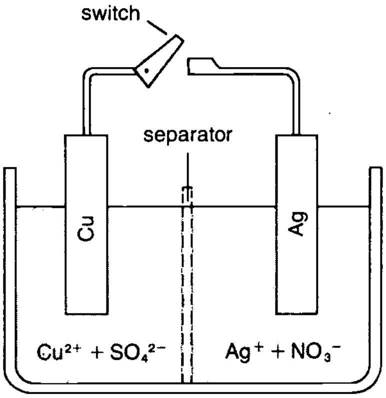


$$Ni^{2+} + 2e^- \rightarrow Ni$$

Then the chromium is electroplated from a solution of chromic acid (H_2CrO_4) by this half-reaction at the cathode:

$$H_2CrO_4 + 6H^+ + 6e^- \rightarrow Cr + 4H_2O$$

QUESTIONS



1. The diagram shows a simple electrochemical cell. When the switch is closed, electrons move through the wire from the copper electrode to the silver electrode.
   (a) Write the half-reactions for the electrodes.
   (b) Which of the electrodes is the cathode? Which is the anode?
   (c) Which electrode is the positive electrode? Which is the negative electrode?
   (d) Write the overall chemical reaction. One way to do this is to make sure that both of the half-reactions show the same number of electrons. (If they don't, multiply everything in one of the half-reactions by a constant to give the same number of electrons as the other half-reaction.) Then add the two half-reactions. The electrons will cancel. Check your overall chemical reaction to make sure it is balanced. There must be the same number of each kind of atom on both sides of the reaction, and the net charge must be the same on both sides of the reaction.
   (e) Judging from the overall chemical reaction, what do you think will happen if you place a copper metal strip in a solution containing Ag^+ ions? What about if you place a silver metal strip in a solution containing Cu^{2+} ions?
2. (a) Write the overall chemical reaction that occurs in a lead-acid cell as the cell delivers a current. Combine this reaction with the reaction for the precipitation of lead sulfate, in order to show lead sulfate as the product of the overall reaction.
   (b) Write the overall chemical reaction that occurs when a lead-acid storage battery is being charged. Show lead sulfate as the reactant. Use this reaction to explain why the density of the solution rises as the battery is charged.

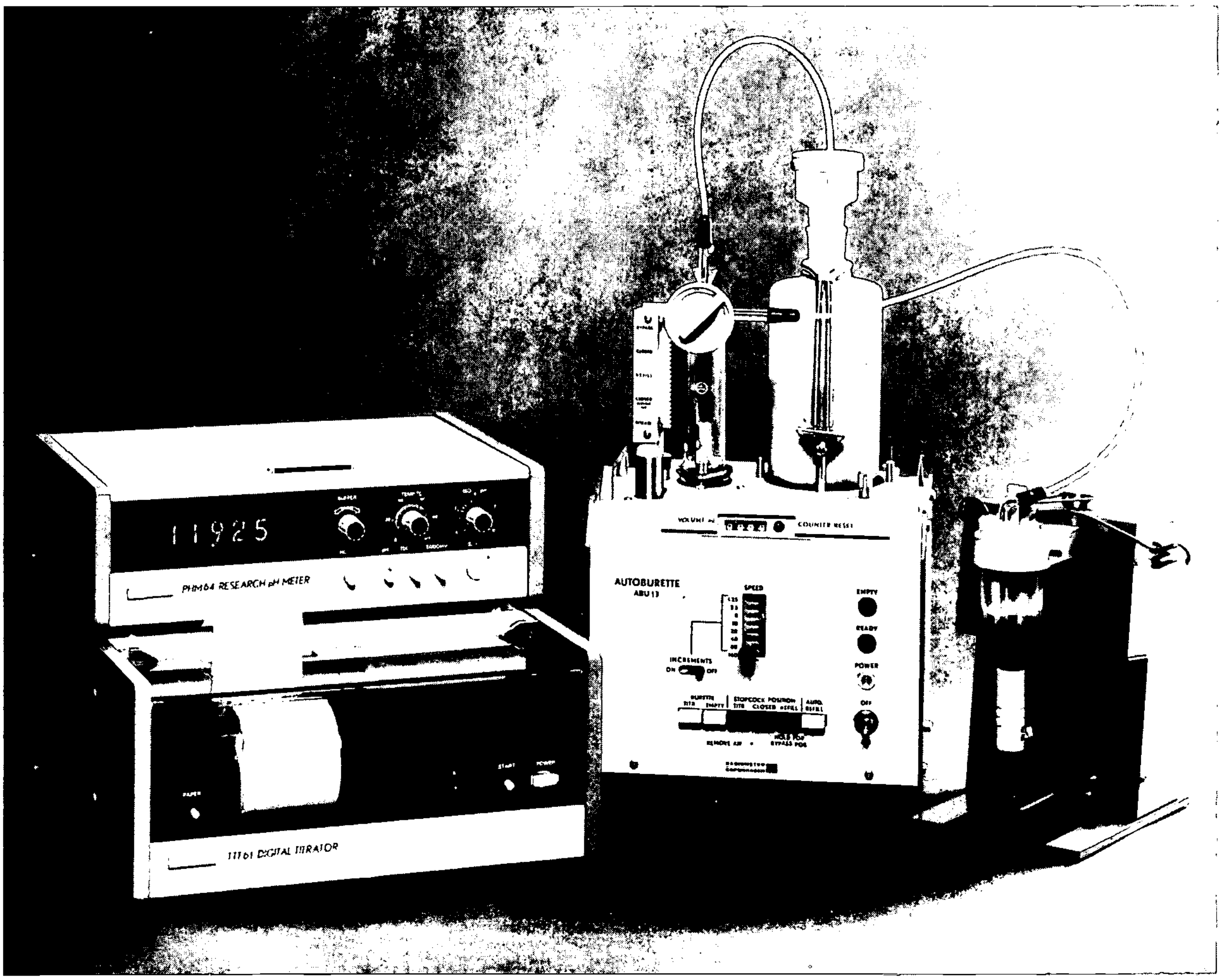
Summary

This module has introduced you to a wide variety of communities of molecules—some simple and some complicated, some familiar and others not, some in equilibrium and others changing in time, but all having properties explainable by the behavior of the restless particles contained in them.

As we've seen, physical chemistry is the branch of chemistry that attempts to measure and explain these properties of chemical systems. It is traditionally divided into three broad areas: the study of the precise arrangements of atoms in the molecular world (chemical structure); the study of how rapidly changes occur in these arrangements (chemical kinetics); and the study of energy changes and equilibrium (chemical thermodynamics). Each of these areas

has many specialized topics, and many of these topics are at present subjects of very active research.

Physical chemistry is not confined to any one kind of molecule or any one type of chemical system. Its theories and insights are useful to all of the other branches of chemistry—organic chemistry, environmental chemistry, biochemistry, and so on. Some of the current research topics in physical chemistry are aimed at solving problems in these other fields. An example related to both organic chemistry and environmental chemistry is the precise measurement of reaction rates of organic pollutants in the gas mixtures emitted from power plant smokestacks. An example of a different sort and related to biochemistry is the development of theories by which the three-dimensional shape of a large protein molecule can be predicted and calculated in detail by a computer. As you can see, physical chemistry is truly fundamental, relevant, and interdisciplinary.



Appendix I: Safety

SAFETY IN THE LABORATORY

Proper conduct in a chemistry laboratory is really an extension of safety procedures normally followed each day around your home and in the outside world. Exercising care in a laboratory demands the same caution you apply to driving a car, riding a motorbike or bicycle, or participating in a sport. Athletes consider safety measures a part of playing the game. For example, football players willingly spend a great deal of time putting on equipment such as helmets, hip pads, and shoulder pads to protect themselves from potential injury.

Chemists must also be properly dressed. To protect themselves in the laboratory, they commonly wear a lab apron or a coat and protective glasses. Throughout this course you will use similar items. Hopefully their use will become second nature to you, much as it becomes second nature for a baseball catcher to put on a chest protector and mask before stepping behind home plate.

As you read through a written experimental procedure, you will notice that specific hazards and precautions are called to your attention. Be prepared to discuss these hazards with your teacher and with your fellow students. Always read the entire experimental procedure thoroughly before starting any laboratory work.

A list of general laboratory safety procedures follows. It is not intended that you memorize these safety procedures but rather that you *use* them regularly when performing experiments. You may notice that this list is by no means complete. Your teacher may wish to add safety guidelines that are relevant to your specific classroom situation. It would be impossible to anticipate every hazardous situation that might arise in the chemistry laboratory. However, if you are familiar with these general laboratory safety procedures and if you use common sense, you will be able to handle potentially hazardous situations intelligently and safely. Treat all chemicals with respect, not fear.

GENERAL SAFETY GUIDELINES

1. Work in the laboratory only when the teacher is present or when you have been given permission to do so. In case of accident, notify your teacher immediately.
2. Before starting any laboratory exercise, be sure that the laboratory bench is clean.
3. Put on a laboratory coat or apron and protective glasses or goggles before beginning an experiment.
4. Tie back loose hair to prevent the possibility of its contacting any Bunsen burner flames.
5. Open sandals or bare feet are not permitted in the laboratory. The dangers of broken glass and corrosive liquid spills are always present in a laboratory.
6. Fire is a special hazard in the laboratory because many chemicals are flammable. Learn how to use the fire blanket, fire extinguisher, and shower (if your laboratory has one).
7. For minor skin burns, immediately immerse the burned area in cold water for several minutes. Then consult your teacher for further instructions on possible additional treatment.
8. In case of a chemical splash on your skin, immediately rinse the area with cold water for at least one minute. Consult your teacher for further action.
9. If any liquid material splashes into your eye, wash the eye immediately with water from an eyewash bottle or eyewash fountain.
10. Never look directly down into a test tube—view the contents of the tube from the side. (Why?)
11. Never smell a material by placing your nose directly at the mouth of the tube or flask. Instead, with your hand, "fan" some of the vapor from the container toward your nose. Inhale cautiously.
12. Never taste any material in the laboratory.
13. Never add water to concentrated acid solutions. The heat generated may cause spattering. Instead, as you stir, add the acid slowly to the water or dilute solution.
14. Read the label on a chemical bottle at least *twice* before removing a sample. H_2O_2 is not the same as H_2O.
15. Follow your teacher's instructions or laboratory procedure when disposing of used chemicals.

This symbol represents three of the common hazards in a chemistry laboratory —flame, fumes, and explosion. It will appear with certain experiments in this module to alert you to potential hazards.

Appendix II: Using Figures

SCIENTIFIC NOTATION

In science we often work with very large and very small numbers that are inconvenient to read and write because they have many zeros. These zeros may be avoided by expressing the number in *scientific notation*. To learn how to do this, it is first necessary to understand *powers of ten*.

A *power of ten* is the number 10 multiplied by itself any number of times:

10 is 1 power of ten, or 10^1
100 is 2 powers of ten, or 10^2
1000 is 3 powers of ten, or 10^3

and so on. Notice that the power written after 10 is the same as the number of zeros in the number.

Fractions of ten can be written as negative powers of ten:

1/10 or 0.1 is 10^{-1}
1/100 or 0.01 is 10^{-2}
1/1000 or 0.001 is 10^{-3}

and so on. The power written after 10 is the number of zeros in the fraction, with a negative sign.

Now that we have discussed powers of ten, it is easy to explain scientific notation itself. For example, instead of writing 5 200 000, it is easier to write 5.2×10^6. The rule for changing a *large* number into scientific notation is to move the decimal point to the *left* until there is one digit in front of the decimal point (5.2 in this example). Then multiply this smaller number by 10 raised to the number of positions you had to move the decimal point (10^6 in this example because the decimal point was moved 6 places to the left).

Another example: 0.000 000 43 is more easily written as 4.3×10^{-7}. The rule for changing a *small* number into scientific notation is to move the decimal point to the *right* to give one digit in front of the decimal point. Multiply this number by 10 raised to minus the number of places the decimal point was moved.

It is easy to multiply two powers of ten. Simply add the powers:

$$10^6 \times 10^{12} = 10^{6+12} = 10^{18}$$
$$10^6 \times 10^{-7} = 10^{6-7} = 10^{-1}$$

By extension of this rule, to multiply two numbers written in scientific notation, it is necessary to multiply the powers of ten and the numbers in front separately.

Examples:

$$(5.2 \times 10^6) \times (1.5 \times 10^{12}) = (5.2 \times 1.5) \times 10^{6+12} = 7.8 \times 10^{18}$$
$$(5.2 \times 10^6) \times (4.3 \times 10^{-7}) = (5.2 \times 4.3) \times 10^{6-7} = 22 \times 10^{-1}$$
$$= 22 \times 0.1 = 2.2$$

To divide by a number in scientific notation, change the sign of the power and multiply.

Examples:

$$\frac{5.2 \times 10^6}{1.5 \times 10^{12}} = \frac{5.2 \times 10^6 \times 10^{-12}}{1.5} = 3.5 \times 10^{-6}$$
$$\frac{5.2 \times 10^6}{4.3 \times 10^{-7}} = \frac{5.2 \times 10^6 \times 10^7}{4.3} = 1.2 \times 10^{13}$$

SIGNIFICANT FIGURES

Each digit in a number which is not used simply to locate the decimal point is called a *significant figure*. For instance, the number 5.2×10^6 has two significant figures, that is, 5 and 2. If you wanted to round off this number to one significant figure, you would write 5×10^6.

Another example: 4.30×10^{-2} has three significant figures, 4, 3, and 0. If you wrote this number as 0.043 0 instead, it would still have three significant figures. The first two zeros in 0.043 0 are not significant figures because they are used only to locate the decimal point.

When you multiply two numbers, or divide one number by another, you should round off the answer to have as many significant figures as the smallest number of significant figures in the numbers you multiplied or divided. Thus in the examples given of multiplication and division in scientific notation, the numbers have two significant figures and so the answers have been rounded off to have two significant figures also. (See *Appendix IV: Significant Figures and Rounding Off* in *Reactions and Reason: An Introductory Module.*)

Appendix III: Metric Units

PHYSICAL QUANTITY	SI BASE OR DERIVED UNIT		OTHER UNITS	
	NAME	SYMBOL AND DEFINITION	NAME	SYMBOL AND DEFINITION
length	meter*	m	kilometer	$1\ \text{km} = 10^3\ \text{m}$
			centimeter	$1\ \text{cm} = 10^{-2}\ \text{m}$
			nanometer	$1\ \text{nm} = 10^{-9}\ \text{m} = 10^{-7}\ \text{cm}$
area	square meter	m^2	square centimeter	$1\ \text{cm}^2 = 10^{-4}\ \text{m}^2$
volume	cubic meter	m^3	cubic centimeter	$1\ \text{cm}^3 = 10^{-6}\ \text{m}^3$
			liter	$1\ \text{l} = 10^3\ \text{cm}^3$
mass	kilogram*	kg	gram	$1\ \text{g} = 10^{-3}\ \text{kg}$
time	second*	s		
amount of substance	mole*	mol		
concentration	moles per cubic meter	mol/m^3	moles per liter	$1\ \text{mol/l} = 10^3\ \text{mol/m}^3$
			molar concentration (molarity)	$1\ \text{M} = \text{mol/l}$
Celsius temperature			degree Celsius	^0C
thermodynamic temperature	kelvin*	K		
pressure	pascal	$\text{Pa} = \text{kg/m} \cdot \text{s}^2$	centimeter of mercury	$1\ \text{cm Hg} = 1.333 \times 10^3\ \text{Pa}$
			atmosphere	$1\ \text{atm} = 1.013 \times 10^5\ \text{Pa}$
				$1\ \text{atm} = 76.0\ \text{cm Hg}$
energy	joule	$\text{J} = \text{kg} \cdot \text{m}^2/\text{s}^2$	calorie	$1\ \text{cal} = 4.184\ \text{J}$

*SI base unit, exactly defined in terms of certain physical measurements.

Selected Readings

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Interesting discussion on the chemistry of soap bubbles.

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Advanced topics in bond formation, kinetic theory, etc.

Faraday, Michael. *Chemical History of a Candle*. New York: T. Y. Crowell, 1957. Paperback.
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Holden, Alan, and Singer, Phylis. *Crystals and Crystal Growing*. New York: Anchor Books; Doubleday & Co., 1960. Paperback.
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In addition, discussions of new developments in chemistry relevant to the topics covered in this module will be found in *Chemistry*, *Journal of Chemical Education*, *Scientific American*, and *Science News*.

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TABLE OF INTERNATIONAL RELATIVE ATOMIC MASSES*

Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	227.0
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	12.0
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)
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(257)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
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	Lr	103	(260)
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	(258)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	237.0
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.0
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.0
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	231.0
Radium	Ra	88	226.0
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
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	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

*Based on International Union of Pure and Applied Chemistry (IUPAC) values (1975).

**Numbers in parentheses give the mass numbers of the most stable isotopes.

PERIODIC TABLE OF THE ELEMENTS

200.6 — atomic mass
Hg — symbol
Mercury — name
80 — atomic number

IA	IIA	IIIB	IVB	VB	VIB	VIIB	←	VIIIB	→	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1.008 **H** Hydrogen 1																	4.00 **He** Helium 2
6.94 **Li** Lithium 3	9.01 **Be** Beryllium 4											10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12											27.0 **Al** Aluminum 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulfur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybd'm 42	(97) **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Cesium 55	137.3 **Ba** Barium 56	138.9 **La*** Lanthanum 57	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.8 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	(209) **Po** Polonium 84	(210) **At** Astatine 85	(222) **Rn** Radon 86
(223) **Fr**† Francium 87	226.0 **Ra** Radium 88	(227) **Ac**** Actinium 69	‡ 104	‡ 105	‡ 106												

*	140.1 **Ce** Cerium 58	140.9 **Pr** Praseody'm 59	144.2 **Nd** Neodymium 60	(145) **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
**	232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	(242) **Pu** Plutonium 94	(243) **Am** Americium 95	(245) **Cm** Curium 96	(245) **Bk** Berkelium 97	(251) **Cf** Californium 98	(254) **Es** Einsteinium 99	(254) **Fm** Fermium 100	(256) **Md** Mendel'm 101	(254) **No** Nobelium 102	(257) **Lr** Lawrencium 103

†The most stable known isotopes are shown in parentheses.

‡The discovery of elements 104, 105, and 106 has been claimed by both American and Soviet scientists. The Americans have suggested the name *rutherfordium* and *hahnium* for 104 and 105; the Soviets have suggested the names *kurchatovium* and *nielsbohrium* for these same elements. No name has yet been proposed for element 106.

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