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ABSTRACT

This book is one in a 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) "The Balance in Environment"; (2) "Water Environment"; (3) "Toxic Substances in the Environment"; (4) "The Air Environment"; (5) "Energy Sources and Uses"; and (6) "Future Sources of Energy". (KHR)

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THE DELICATE BALANCE AN ENERGY AND THE ENVIRONMENT CHEMISTRY MODULE

Glen Gordon William Keifer

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THE DELICATE BALANCE: AN ENERGY AND THE ENVIRONMENT CHEMISTRY MODULE

GLEN GORDON

Glen Gordon grew up on a farm in western Illinois. He received his bachelor's degree from the University of Illinois and his doctorate from the University of California at Berkeley. Glen taught at the Massachusetts Institute of Technology for nine years before assuming his current teaching position at the University of Maryland in 1969.

Glen has always been concerned with the quality of teaching and the content of science courses at the high school and college levels. He has contributed to college curricula by writing, with Professor William Zoller, Chemistry in Modern Perspective and, with several coauthors, Experiments in the Chemical Environment. He has made similar contributions to the chemistry curricula in high schools through the IAC program. Dr. Gordon is currently conducting research on the sources of air pollutants in United States cities.

Although teaching responsibilities and research projects keep Glen quite busy, he does find time to relax by pitching an occasional game of softball and keeping his yard full of healthy azaleas.

WILLIAM KEIFER

Bill Keifer grew up near the coal mines and steel mills of western Pennsylvania. He received his bachelor's degree from the University of Pittsburgh, his master's degree from the University of Wisconsin, and his doctorate from the University of Maryland.

Bill taught chemistry at the University of Pittsburgh at Johnstown for five years before completing his doctoral work. In his college teaching Bill developed a water-chemistry laboratory program designed for college freshmen. This program coordinated chemical and biological water-pollution studies. The main emphasis of Bill's teaching methods has been in developing student interest through the use of applied chemistry.

Dr. Keifer is presently a staff member at the Meteorology Institute, Inc., in Santa Rosa, California, where he conducts aircraft measurements of large-scale air-pollution problems throughout the United States.

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.

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with α is a set of α . The component α

© 1966 by Piet Hein

Piet Hein*

I'D LIKE I'd like to know what this whole show

is all about before it's out.

بالمراد والبابع الاستناقاتي

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

Marjorie Gardner Director, 1976-79 Interdisciplinary Approaches to Chemistry

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Our Environment: What Is the Balance?

In December 1968 three American astronauts, Frank Borman, James Lovell, and William Anders, piloted the first flight to a close orbit of the moon aboard Apollo 8. As they looked back at Earth, they saw a water-blue planet, covered with swirling, wispy white clouds, that looked like an illuminated glass marble suspended in the black of night. It must have been a beautiful sight!

Earth as seen from Apollo 8 as the spacecraft passed over the moon's surface.

An "Earth-rise" as seen from the moon.

E-1 Earth: Its Delicate Balance

When the *Apollo 8* crew returned from their first flight to the vicinity of the moon, Astronaut Anders made this statement concerning his observations from space:

The Earth looked so tiny in the heavens that there were times during the Apollo 8 mission when I had trouble finding it. If you can imagine yourself in a darkened room with only one clearly visible object, a small blue-green sphere about the size of a Christmas tree ornament, then you can begin to grasp what the Earth looks like from space. I think all of us subconsciously think that the Earth is flat or at least almost infinite. Let me assure you that, rather than a massive giant, it should be thought of as the fragile Christmas tree ball which we should handle with considerable care.

As far as we know, Earth is unique among the nine planets and the many satellites of the solar system in its ability to support life of the kind that we know. Earth has just the right temperature, the needed oxygen and carbon dioxide in its atmosphere, the water of its oceans, and all the other conditions that are necessary to sustain life. These conditions exist in a thin layer that extends from about 10 km (kilometers) beneath the surface of the ocean to about 30 km into the sky.

There is a *delicate balance* among natural forces that maintains the conditions necessary for life within this fragile veneer. Life is dependent upon a balance between the warmth of the sunlight striking the Earth and the heat that the Earth radiates back into space, between the water in the oceans and the clouds in the sky, and between the oxygen produced by green plants and that consumed by humans and animals.

Many complex relationships among the organisms of the biosphere (the living matter of Earth's veneer) are essential for the maintenance of life. This becomes evident as we observe the various cycles on the Earth: the energy transfer from the Sun to plants and animals and back into space; the flow of chemical nutrients from soil, water, and air through plants and animals and eventually back to soil, water, and air; the constant and necessary competition between predators and prey.

Many human activities have acted as disruptive forces on the natural environment. This force might seem small in comparison with great natural forces such as earthquakes, volcanoes, hurricanes, and tornadoes. However, during the thousands of years that we have used agricultural methods to grow our own food, we have stripped vast areas of land of their natural ground cover in order to introduce new crops into the soil. We have also removed vast areas of forest for wood to build our homes and for paper to produce our books. The overgrazing of land by herds of cattle and sheep has caused areas that were once fertile to become deserts.

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The natural environment of the Earth has been disrupted by the clearing of land of trees for farmland, by the mining of natural resources for fuel and manufacturing, and by the extensive development of towns and cities. Have you noticed similar changes in the area where you live? Are there other forms of environmental disruption in your area? How do you think these will affect the balance in the environment?

TIME MACHINE

- 1790 In the first U.S. census, population is estimated to be 3,929,214.
- 1793 Eli Whitney invents the cotton gin.
- 1795 The French devise and adopt the metric system.
- 1798 Thomas Malthus publishes Essay on Population, the first discussion of population pressures.
- 1809 Abraham Lincoln is born.
- 1810 U.S. population reaches 7,239,881.

Over the years the effects of these alterations of the natural environment were hardly noticed. Changes came gradually, but during the past several decades the rate of change has increased sharply because of both the enormous growth of the human population and the massive growth of technology. As we have tried to improve our standard of living, we have also altered our environment. Now it seems quite possible that we are capable of disturbing the delicate balance that makes life possible on our small planet.

E-2 Maintaining the Balance

Because of the damage we have done to our environment, some people have suggested that we halt all activities that might further alter the balance of nature. But such a step is no longer possible, if it ever was. There are just too many of us!

Although people have lived on Earth for thousands of years, it wasn't until about A.D. 1820 that the population reached 1 billion. During the next century it doubled, reaching 2 billion in 1920. By 1977, only 57 years later, it had doubled again, to about 4 billion. By the year 2000 it is estimated that the Earth's population will have increased to about 6 billion people or more!

In a population of 4 billion, about one-third of the world's people are inadequately fed and another one-third have barely adequate food and other resources. The remaining one-third—mainly in the technological nations of North America and Europe and in Japan live in relative affluence. The human population is already so large that we cannot provide the necessary food, shelter, and heat for our survival without causing some disturbance of nature. Our challenge is to find ways of providing a decent living standard for everyone on Earth while minimizing the harmful effects on our environment.

E-3 The Population Explosion

How has the Earth's population gotten out of control? Why do we seem to be running out of oil and many other resources? Much of the problem results from exponential growth. This type of growth occurs whenever a quantity increases from one year to the next by a fixed fraction of the amount present.

A dramatic example of exponential growth is described in a story told by George Gamow in his book One Two Three . . . Infinity.* According to an old legend, King Shirham of India wanted to reward his grand vizier for inventing the game of chess. The king

^{*}George Gamow, One Two Three . . . Infinity (New York: Bantam Books, 1971).

allowed the vizier to decide what the reward should be. The vizier's wish seemed very modest: he asked the king to place one grain of wheat on the first square of the chessboard, two grains on the second square, four grains on the third, and so forth, doubling the number for each succeeding square until all sixty-four squares of the board were covered.

The king was delighted to honor this simple desire and sent for a bag of wheat to fulfill the request. Then he put one grain on the first square, two on the second, four on the third, and so forth. But he was surprised to find that his bag was empty before he got to the twentieth square. The king soon realized that it would take more than all of the wheat in the kingdom to complete the sixty-fourth square! That would have required 18 466 744 073 709 551 615 grains. If 1 bushel of wheat contains 5 million grains, about 4000 billion bushels of wheat would be needed. Since the world production of wheat is now about 10 billion bushels per year, it would take a four-hundred-year supply of the world's wheat to fulfill the vizier's request!

We might call exponential growth "sneaky," since a quantity can double several times in the beginning before it is noticed, and then suddenly it increases by enormous steps. King Shirham was a victim of exponential growth, in this case a 100 percent increase of

area where you live? What do you think your area will look like in the future?

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wheat from one square to the next. We call this exponential growth because we can express the number of grains on a square as a number, in this case 2, raised to a power, here $n-1$, where n is the number of the square. In this example the number of grains of wheat on a square is expressed as 2^{n-1} . A graph of any quantity that is increasing exponentially will eventually appear to curve almost straight up.

Every quantity that grows exponentially has a certain doubling time. For the chessboard the doubling "time" was one square. As another example, \$100 in a savings account doubles to about \$200 in 10 years if the account draws 7 percent interest compounded annually. If exponential growth continues at the same percentage per year, the doubling time remains the same. After 20 years the account would be worth nearly \$400, in 30 years \$800, and so on.

Now let's relate this to the problem of *population explosion*. The enormous growth of population is in part a problem of exponential growth. If the population increases at 1 percent per year, it will double in 70 years. Exponential growth of the population would be serious enough, but the world population has been increasing even faster than that; as noted in section E-2, the doubling time has been getting shorter. It took about a century for the population to double from 1 billion to 2 billion people, whereas it took only about 57 years for it to double to 4 billion people in 1977.

10 11 Why has the doubling time shortened in recent years? The rate of population growth is determined by birth rates and death rates. In '1973 the birth rate in the United States was 15 births per 1000 people per year, and the death rate was 9.4 deaths per 1000 people per year. Thus the rate of population growth was 15 minus 9.4, or 5.6 per 1000 per year: an increase of 0.56 percent per year. This corresponds to a doubling time of about 125 years. Continued decreases in birth rates since 1973 have lowered the birth rate to the point at which the United States would eventually reach a stable population of probably 280 million people sometime in the mid-twenty-first century.

The main reason for the worldwide population explosion is the high rate of population increase in developing nations. Some countries in Central and South America, Africa, and the Far East have growth rates of 2 to 3 percent per year, which corresponds to a doubling time of 26 to 35 years. Think of what this means: about every 30 years these countries must double all of their resources such as food, shelter, and energy—just to keep even with population growth.

The major reason for the high rate of population increase in these countries is that death rates have been lowered because of modern medicine, the use of pesticides, and, in some cases, better nutrition. But birth rates have stayed nearly the same. Years ago families

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in most developing nations had large numbers of children principally to ensure that some children would survive. Now many more children are surviving, yet parents often continue to have large families.

E-4 The Limits to Growth

In view of our discussion of the population growth in developing nations, you might wonder if those nations are the major drain on the Earth's resources.

The use of some resources does increase at about the same rate as the population increases. For example, the energy content of the food people eat varies somewhat between technological and developing countries. But roughly speaking, the world food-energy requirement increases at approximately the same rate as the population increases.

If we consider most other resources, however, especially those associated with industry and a high living standard, each of us in the technological nations uses far more than the average person in a developing nation. For example, the United States has onlyabout 6 percent of the world's population but uses about one-third of the world's natural resources. This means that each of us is using nearly six times (33 percent divided by 6 percent) our share of the world's material assets!

Most people in the world obtain nearly all of their food energy from grain or other plants. In the developed countries we feed much of the grain to animals, and we eat the animals. This indirect intake of the food energy of plants results in a food-energy loss of about 80 percent (section $E-21$).

Because of the combined effects of population growth, increasing standards of living in the developed nations, and technological change, almost all of the Earth's resources follow a use pattern of exponential growth, the doubling times depending on the resource.

A brilliant, although highly controversial, book, The Limits to Growth,* explores the implications of continued exponential growth of population and the use of resources. Every renewable resource has a certain carrying capacity. A renewable resource is something that is always being replaced, such as sunlight, rain, or plants. The carrying capacity is the rate of use that the renewable resource can support. For example, food is a renewable resource. If we take good care of the farmlands and the oceans, these resources will maintain a certain carrying capacity (the number of people who use the food from those sources will remain fairly constant). *D. H. Meadows et al., The Limits to Growth, 2nd ed. (New York: Universe Books, 1974).

As the population continues to increase, so does the need for more food. Farmers and scientists must find more efficient ways to grow and harvest crops and to transport them to food-processing centers. In order to avoid clearing more and more of our landscape, we must use existing farmland wisely and efficiently.

When the use rate of a resource is far below the carrying capacity, we are not concerned with the constant doubling of the use rate just as the king was not concerned with the doublings of wheat on the first few squares of the chessboard. We become alarmed only during the doubling that moves the rate above the carrying capacity. This happened to the king when his sack was empty before the twentieth square! We don't know for sure what the Earth's carrying capacity is for food. Although some people are starving today, it is probable that by using the most efficient methods of farming and equitable distribution of food we could adequately feed all of the world's people. It is also probable, but less certain, that the estimated 8 billion people living in the year 2034 could be fed. But it is quite certain that population doubling cannot continue indefinitely—there simply will not be enough food!

The situation is even more serious for other kinds of resources. Billions of years ago in the Earth's history, rich deposits of iron, copper, lead, and other mineral resources were formed. These minerals lie near enough to the surface that they can be dug up, purified, and used. In addition, over hundreds of millions of years, the decaying remains of plants and animals covered by rocks and soil were slowly transformed into fossil fuels-coal, gas, and oil. Since the Industrial Revolution we have been digging up these deposits and using them at an exponentially increasing rate. These, however, are nonrenewable resources, which were formed so slowly by the Earth's processes that there won't be any more available when we use up the existing deposits.

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To determine how many years a particular resource will last, geologists estimate the total amount of the resource that can ultimately be recovered, or, in other words, the reserve of that resource. They then divide the reserve by the current use rate per year to get an estimate of how long it will be before the resource is used up. This calculation is known as the static index. For example, the reserve for lead is about 90 million metric tons. The annual world consumption of lead is about 3.5 million metric tons. Therefore, the static index is 90 million metric tons divided by 3.5 million metric tons per year, or about 26 years. An important point,made in The Limits to Growth is that we shouldn't calculate the index this way. Instead, we must realize that the use rate for most resources increases exponentially. Therefore, we should not only consider the current use rate but also look at the past to determine how rapidly the use rate is increasing. From this viewpoint, an exponential index can be calculated.

The exponential index is a measure of how long a resource will last at an exponentially growing rate of use. In general, the exponential index is shorter than the static index. The consumption of lead has been increasing at about 2 percent per year, yielding an exponential index of 21 years versus the static index of 26 years. The world is in immediate danger of running short of other resources such as copper, silver, aluminum, gas, and petroleum, although resources such as iron and coal should last for many years.

Because of our increased energy needs, land is left scarred by the mining of nonrenewable resources such as coal (above), oil (below), and copper (below left).

'Calculated in number of years.

This postage stamp commemorates the first 100 years of the petroleum industry by depicting the first oil well, drilled by E. L. Drake in Titusville, Pennsylvania.

TIME MACHINE Energy Resources

- 1859 E. L. Drake drills the first oil well in Titusville, Pennsylvania.
- 1865 William Stanley Jerons writes The Coal Question, dealing with the fact
- that coal supplies are exhaustible. 1886 Aluminum is first prepared by electrolysis by Charles Hall.

In the past, calculated estimates of resources have often been grossly low. For example, even before the turn of this century there was great concern that the supply of oil was about to run out. Since that time huge oil fields have been discovered throughout the world; so estimates of reserves have been upwardly revised. To account for the possibility of newfound reserves, the last column in the table shows how long each resource would last if the reserve were five times greater than it is now believed.

 $\tilde{\mathbf{S}}$ fuel energy results in problems caused by strip mining, oil slicks, Not only does each of us in a technological nation use more than our share of resources, but we also cause greater environmental disruption. As we shall see, most resource use involves the release of pollutants into the environment. For example, the use of fossilair pollution, and the release of carbon dioxide $(CO₂)$ into the atmosphere. Just as our resource use tends to grow exponentially, so also does the pollution associated with that use.

Technological nations also have developed products that lead to entirely new kinds of pollution. The propellants that once were used in aerosol spray cans, chlorofluoromethanes (CFMs-commonly referred to as fluorocarbons), were thought to destroy the ozone layer in the stratosphere, which protects us from the Sun's ultraviolet radiation. After extensive studies of this problem, the type of propellant was changed to prevent further damage to the ozone layer. Synthetic pesticides have performed miracles in our fight against insects that spread disease and destroy crops. But the use of some pesticides has endangered certain species of birds, and some pesticides cause cancer. Plastics have been a boon to our "disposable" society, but they too have caused problems in the environment. As one example, several workers in plants that make one of the most widely used plastics have died from a rare form of cancer (section E-25).

It's easy to point your finger and say, "It's your fault! You're causing all the environmental problems!" We are quick to point to

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electric companies, chemical plants, steel mills, automobile manufacturers, and oil companies. But stop for a minute and think- who uses the products from these companies?

E-5 Energy Watch miniexperiment

During your work in this module, devise a project to find out how much energy you and your family use. Work with your teacher to establish guidelines to determine this amount.

If you live in a house, calculate the energy your family uses. If you live in an apartment building, you may wish to determine the energy use of the entire building. Or you may wish to determine the energy use of your school. In doing so, you will have to determine the kinds of energy use you will need to monitor and the kinds of records you will need to keep.

Near the end of this module you will be asked to compute and summarize your findings, to compare them with national averages, and to make suggestions for instituting better energy savings.

E-6 How Is Chemistry Involved?

Because environmental problems affect biological systems, you may wonder why chemists and chemistry are involved. The fact is that chemical reactions play a role in nearly every environmental problem. Every biological organism is a small, highly complex bibchemical factory that takes in thousands of chemical compounds every day. Many of these are essential nutrients, but others are pollutants that cause trouble within the biological systems. Most pollutants are products of chemical reactions and therefore can be controlled only by chemical methods.

Chemists are often able to identify and study environmental problems by means of chemical analysis. Over the past twenty to thirty years vast improvements have been made in the chemical methods used to analyze substances. Extremely sensitive analytical methods are needed to detect and study toxic pollutants. These pollutants pose a problem when they are present in the environment, even in minute concentrations-termed parts per million (ppm) or parts per billion (ppb) by mass. A concentration of 1 ppm means that there is 1 g (gram) of pollutant per metric ton, 1000 kg (kilograms), of sample. Therefore, a concentration of 1 ppb means that there is 1 g of pollutant per 1000 metric tons of sample.

In many cases no one was aware of an environmental problem until chemists developed analytical methods sensitive enough to detect pollutants at these very low concentrations. The following substances are some of the pollutants that have been found.

- **EXECUTE:** ronment and cause similar problems. Polychlorinated biphenyls (PCBs) are used in electrical insulation, transformers, and noncarbon reproducing paper, which has a special coating to replace carbon paper. PCBs behave much like the pesticide DDT (dichlorodiphenyltrichloroethane) in the envi-
	- Pesticides such as DDT have been found in human and animal tissues.
	- Mercury has been found in fish.
	- Lead, sulfur dioxide, and polynuclear aromatic hydrocarbons (PAHs) have been found in the atmosphere.

Besides detecting pollutants, chemists are investigating the removal of sulfur from coal and oil to prevent sulfur dioxide pollution of the atmosphere. They are also developing methods for converting coal to cleaner gas or liquid fuels.

We have also been plagued with massive amounts of wastes from our technological society. Chemists and chemical engineers are devising ways to treat and reuse these wastes by converting them into useful materials—a process known as recycling. Equally important are their contributions to the search for new materials and resources that will benefit us but not harm the environment. Environmental chemistry is not simply the study of pollution. In a broad sense it is a branch of chemistry concerned with providing a more pleasant, yet safe, environment for all of the Earth's inhabitants.

PROBLEM (

Look around your home, in stores, and in advertisements for products that are convenience items. Make a list of some of these items. How many present potential problems to the environment? How many cause air pollution? How many cause pollution to our waterways? How many result in additional waste? How many use coal, oil, gas, or electricity? Think about what your life would be like with and without these products. How many could you live without if that would ensure a better environment?

Now let's take a closer look at one familiar product. Everyone enjoys the convenience of clean clothes and dishes. Because of the problem of hard water in many regions of North America and the mineral deposits that settle out, detergents containing phosphates were developed as a substitute for soaps. However, the element phosphorus, found in phosphates, promotes the growth of algae in bodies of water. These algae can cause an environmental problem (section E-10).

Phosphorus is required for a living organism to carry out normal metabolic functions. To illustrate this concept, you will be preparing several nutrient diets for algae. For this experiment you will

need several weeks to collect the necessary data. You should start now so that you will be able to review the results during the discussion of water pollution.

Algae growth on this pond (left) is caused by freshwater algae such as Spirogyra, shown reproducing by conjugation (right).

E-7 Don't Feed the Algae

First you will need to obtain some algae. Most pond water contains algae; if you live near a river or a stream you may wish to use it as your source. Otherwise you can take a sample from an aquarium, or your teacher will provide you with a culture of algae.

The class can be divided into four groups, each of which will grow algae in a different nutrient culture. One of the cultures will have all the nutrients required for growth. Each of the remaining cultures will lack a particular nutrient. Seven solutions containing chemicals for nutrient growth will be available. Use the following to make up your cultures.

Solution 1: KNO₃, MgSO₄, KH₂PO₄ Solution 2: H_3BO_3 , MnCl₂, ZnSO₄, CuSO₄, MoO₃, Ca(NO₃)₂, CoCl₂ Solution 3: Iron(III) citrate, citric acid Solution 4: KCI, MgSO₄, KH₂PO₄ Solution 5: KNO₃, MgSO₄ Solution 6: 5-10-10 fertilizer $(N/P₂O₅/K₂O)$ **Solution 7: Solution 2, with CaCl₂ substituted for Ca(NO₃)₂**

In addition to the nutrients, the algae require carbon dioxide and light for all photosynthesis to occur. To allow carbon dioxide to diffuse into the test tubes, stopper each tube loosely with a wad of cotton. Finally, label the test tubes and place them under a source of light-either near a window or under a fluorescent lamp.

EXPERIMENT

Group 1: Complete Nutrient Culture. To a test tube add 10 cm³ (cubic centimeters) Solution 1, 0.1 cm³ Solution 2, and 1.0 cm³ Solution 3. Swirl the test tube to mix the three solutions thoroughly; then add 0.5 cm³ algae culture.

Group II: Low Nitrogen Culture. To a test tube add 10 cm³ Solution 4, 0.1 cm³ Solution 3, 1.0 cm³ Solution 7. Swirl the test tube to mix the three solutions thoroughly; then add 0.5 cm^3 algae culture.

Group III: Culture Lacking Phosphate. To a test tube add 10 cm³ Solution 5, 0.1 cm³ Solution 2, 1.0 cm³ Solution 3. Swirl the test tube to mix the three solutions thoroughly; then add 0.5 cm^3 algae culture.

Group IV: 5-10-10 Fertilizer Culture. To a test tube add 10 cm³ Solution 6; then add 0.5 cm^3 algae culture.

Periodically check the level of liquid in the test tubes. In order to compensate for evaporation, which will occur under the light, you need to add distilled water periodically. Mark the outside of the test tube with a wax pencil at the original level of the liquid and keep it filled to this mark.

Observe all the test-tube cultures and record the results of the algae growth in your notebook. You will discuss your results in experiment E-11.

PROBLEMS **F**

- 1. List the environmental effects that are associated with the production and use of each of the following commodities you use daily: air conditioner, radio, paper goods, home heating, clean clothes, gasoline, and hair dryer. (By the time you finish this module, you may be able to add other environmental effects that you are not aware of now.)
- 2. Water from a river is found to contain 50 ppb of mercury (Hg).
	- a. What is the Hg concentration in parts per million?
	- b. How much pure water would have to be added to 1 liter of this contaminated water to reduce the Hg concentration to 2 ppb?
- 3. Suppose that you have just learned that you are the only living heir of a person who deposited \$100 in a savings account in a bank in Philadelphia in 1776.
	- a. At 5 percent interest, compounded annually, what is the doubling time of the account?
	- b. To the nearest doubling, what is the value of your account today?
- 4. The population of a developing nation is about 600 million people.

a. If the population grows at a rate of about 2.5 percent per year, how many people will be added to the population in 1 year? in 5 years? in 10 years? in 50 years?

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- b. What problems would this country face as a result of such increases in population?
- 5. Try to determine what the population of your town or city was 5 years ago, 10 years ago, and 50 years ago. What is it now? What do you think it will be in the year 2000?
- 6. Identify some resources that were mined or produced in your area 50 years ago. What are they now? How have these activities affected your environment? Predict what industries might be in your area 50 years from now. What effects might these industries have on the environment in the future?
- 7. Indicate which of the following resources are renewable, which are nonrenewable, and why you think so.

da adii saaxay xaabada ah dadka ah dalka ah dal

- a. uranium d. coal b. hydroelectric e. paper power f. iron
- c. wheat

The Water Environment

Water is almost everywhere in our environment: over two-thirds of the Earth is covered with it, and most land areas receive it in the form of abundant rainfall. But the amount of water available for people, animals, and plants is limited. Some bodies of water have become so polluted that they are almost "dead." What is happening to our available water?

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 $\mathcal{L}^{(2)}$ and $\mathcal{L}^{(2)}$

Water, water everywhere And all the boards did shrink. Water, water everywhere, Nor any drop to drink.

> Samuel Taylor Coleridge "The Rhyme of the Ancient Mariner"

Distribution of Water Per Square Centimeter of Earth's Surface

E-8 Water, Water Everywhere

We use water every day—much of it without our even realizing it. Although the average person drinks only a liter or two (about six to eight glasses) of water a day, the total amount of water used per person per day is about 64 000 liters. Of this amount, 57 000 liters are channeled through hydroelectric plants and used for the production of electricity, and 7000 liters are used for other purposes. The latter include industrial uses (57 percent), irrigation of farmland (35 percent), and public water supplies (7 percent).

Most of the water used for these purposes is not actually "used up"; it is usually returned to a river or lake. Some uses leave the water almost unchanged—for example, passage through a hydroelectric plant. But in many cases the water is changed by the addition of heat, chemicals, or sewage. About 8 percent of all the water used is ultimately "consumed," or lost to further use.

If water covers nearly three-quarters of the Earth's surface, why are the future supply and quality of our water endangered? To begin with, most of the Earth's water is inaccessible: it is in underground streams, in oceans, and in the atmosphere as water vapor. Ocean water, composed of salt water, is unfit for human consumption. The fresh water that we drink comes from rivers, lakes, and streams. It also comes from rain that falls on land, soaks into the ground, and becomes part of the groundwater that supplies underground wells and springs.

In the final analysis, only about 0.03 percent of the Earth's water is fresh and in the liquid state. But even this fresh water is now endangered because pollutants from both industries and homes are poured into it.

16 IST COPY AVAILABLE 25

PROBLEM

Are there any bodies of water in or near your community? If so, describe their appearance. Would you swim in the water? Are the shorelines clean or filled with debris? Have factories or homes been built near the water? How do they use the water? Does the community's sewage empty into this body of water? How do you think the body of water looked 100 years ago? How do you think it will look 100 years from now?

Millions of liters of fresh water per minute flow over the Cumberland Falls in Kentucky.

E-9 The Effects of Industrial Pollutants

Many industries dump their manufacturing wastes directly into bodies of water or into city sewage systems that release their effluent (the treated-water part of sewage) into bodies of water. As industrial development and production grow, so does water pollution from industrial wastes. These wastes contain a variety of chemicals, many of which are known poisons, such as arsenic (As), lead (Pb), and various organic chlorine compounds. But the poisonous nature of some chemical wastes becomes evident only after disasters occur. For instance, during the late 1950s the deaths of more than forty people who had consumed fish from Minamata Bay in Japan brought attention to the danger of compounds that contain methyl mercury. It was found that certain mercury compounds used as fungicides are readily absorbed into the body, and are very poisonous. These compounds were being discharged into the Japanese waters by a nearby factory and had concentrated in the fish.

Wastes have been pouring into lakes, rivers, and streams ever since industrial cities were built near bodies of water. Even if the dumping of wastes were to be stopped entirely, it would still take many years to restore those bodies of water to their natural state. Constant surveillance and testing by city and government agencies will help restore our waters for future use.

In 1970 there was a mercury "scare" in the United States. Fish from some waters were declared unfit for human consumption because they contained more than the limit of 0.5 ppm Hg set by the Food and Drug Administration (FDA). Industrial plants that were releasing large amounts of mercury into the water were forced to halt those releases. But the mercury problem still exists. Because most inorganic forms of mercury are quite insoluble, much of the mercury dumped into lakes and rivers is still present in the bottom sediments. Some organisms that inhabit these sediments are able to convert the mercury compounds into the more mobile and toxic methyl mercury. In this form the mercury gets into the bodies of fish, which animals or people may eat.

Besides toxic metals, modern chemical industries have dumped thousands of organic chemicals into bodies of water. Many of these are synthetic chemicals that are toxic to people, animals, and vegetation. Over the years these highly toxic wastes have been disposed of by being placed in storage containers and buried. But some of the containers have leaked toxic chemicals into the ground. Today we are only beginning to understand how serious is the threat that these chemical dumps may pose.

A scientist works with a simulated streambank to determine the effects of mercury poisoning on the environment (above). Toxic chemicals from a spill (below) can seep into the groundwater and eventually pollute our drinking water.

These chloroplasts contain the chlorophyll necessary for photosynthesis-the energy-storing process in plants. By studying chloroplasts, scientists have learned the complex chemistry involved in photosynthesis. Research is being done to develop fuels such as hydrogen gas from the photosynthetic energy produced by algae.

PHOTOSYNTHESIS

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E-10 Eutrophication and Overfed Lakes

Bodies of water follow a natural aging process and have a natural life expectancy. Both features are dependent upon the size of the body of water, its width and depth, the climate, and the surrounding terrain. A lake's lifetime may be from one thousand years to one hundred thousand years, if there is no outside interference. However, the effects of technology and our current life-style have shown up clearly in many bodies of water. Industrial wastes, municipal sewage-plant effluents, and runoff from agricultural land have been added to water. These wastes contain both toxic materials and life-supporting nutrients. Plants and fish must have nutrients to live, but an oversupply can be harmful.

A serious water-pollution problem results from the overfeeding of nutrients into lakes-a process known as eutrophication. Overfeeding encourages the growth of algae. Like all green plants, algae are *photosynthetic*—that is, with the aid of chlorophyll and the energy of sunlight, they combine water, carbon dioxide, and other nutrients to make food for themselves. In simplified form, the basic reaction of photosynthesis is

The energy of sunlight is used to convert carbon dioxide and water into glucose, a simple sugar, which can be bound together in long chains to form starch, food that is stored, or cellulose, the material that helps to give a plant its shape. This basic photosynthesis equation ignores many other nutrients required for plant growth as well as the formation of other compounds, such as amino acids-the building blocks of proteins. Plants also synthesize these other materials. Thus, algae and other plant life produce both essential organic materials and the oxygen required by animal life.

 $_{\mathrm{O_2}}$ beneficial, is reversed. The decomposition of dead algae uses up 'After a time, however, the algae die and sink to the bottom of the lake. At this point the photosynthetic process, which had been oxygen-essentially the reverse of the photosynthesis equation. This would not be a serious problem if the lake were shallow and the water well stirred by winds. Oxygen from the air would dissolve in the water and mix throughout the lake, replacing the oxygen that the decaying algae had used up. In the summertime, however, deep lakes often develop layers of water of different temperatures—a situation that prevents oxygen from reaching the deeper parts of the lakes.

As an example, let's look at Lake Erie, one of the most severely polluted bodies of water in the United States and Canada. During the summer, cold, dense water at the bottom of deep portions of

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the lake is separated from the warmer, less dense surface water by a thermocline. This invisible barrier, where the water's temperature changes sharply with depth, prevents water and dissolved materials from mixing between the upper and lower layers. When a thermocline is present, dissolved oxygen in the upper layer cannot enter the lower layer to replace oxygen used up by the decaying algae. In this way the lower layer becomes deficient in oxygen during the middle and late summer.

Water saturated with oxygen contains about 10 mg (milligrams) of oxygen per liter, whereas the most economically desirable species of fish require an oxygen concentration of about 5 mg of oxygen

LAKE ERIE

TIME MACHINE

artificial satellite, Explorer 1.

As you examine this map of Lake Erie and the land surrounding it (above), note the large industrial cities that are situated on the lake. How does this affect the problem of eutrophication in the lake? The numerals indicate typical concentrations of dissolved oxygen in bottom waters during August. A profile of Lake Erie (below) provides a cutaway or side view of the lake, indicating areas of the lake that are affected by thermoclines.

Algae growing on a lake eventually die and accelerate the depletion of the water's oxygen content.

per liter. During the summer the oxygen concentration in large areas of the bottom layer of Lake Erie, particularly in its large central basin, drops to the range of 0 to 2 mg of oxygen per liter, making it impossible for desirable fish to survive. Several years ago such species of fish as the cisco, the walleye, and the blue pike virtually disappeared from the lake and were replaced by hardier "trash" fish, which can live on decayed matter and sewage and can survive with far less oxygen. Although toxic chemicals and eutrophication are major problems for Lake Erie, the disappearance of some fish may also have been caused by overfishing and the opening of canals (which would allow predatory species of fish from other bodies of water to enter the lake).

Besides using up the oxygen, the decay of algae and other plant life releases nutrients for further plant growth. If we were to continue to dump excess nutrients into the water of a lake, plant life would completely take over, and the decaying matter and sediments would fill the bottom of the lake. Eventually, as the process continued, the lake would become a swamp and then completely disappear. Lakes typically exist for ten thousand to one hundred thousand years before being filled with sediments and vegetation. However, it has been estimated that because of human interference Lake Erie has aged as much in fifty years as it would have in fifteen thousand years without human interference.

Throughout this discussion we have emphasized the problems of Lake Erie, but its condition is just one dramatic, familiar example of the results of pollution. It is by no means the only body of water to suffer from the effects of human activities. Many lakes and rivers have similar problems.

Once so much damage has been done to a body of water such as Lake Erie, is there any way to reverse the process and clean up the water? It can be done, but not easily or quickly.

Most air pollutants remain airborne for just a few days (unless they reach the upper layers of the atmosphere). It would therefore be possible to clean up air pollution in cities in a few days if we halted the release of all air pollutants. By comparison, the time scale of pollution in lakes is much greater: a drop of polluted

water stays in Lake Erie an average of three years before leaving it, and in much larger Lake Superior the water may remain for two hundred years. Consequently, it would take many years, even with an all-out cleanup effort, to restore large bodies of water such as these to a reasonably clean condition. Such efforts have begun in areas around the Great Lakes, but it will take many years to complete the job.

How can we limit the growth of algae and put an end to the $\frac{1913}{1914}$ problem of eutrophication? We could stop feeding algae by removing all nutrients from the water that runs into the lakes. But this would be an enormous task, and it's probably not necessary or even desirable. Algae, like people, require a "balanced diet" for growth. For every 40 g of carbon in their diet, algae require about 7 g of nitrogen, 1 g of phosphorus, and smaller amounts of other essential elements such as calcium, sulfur, potassium,' iron, and manganese. When algae exhaust the supply of one essential nutrient, it doesn't matter how much of the other nutrients is present the algae can grow no further!

TIME MACHINE

Panama Canal is completed, linking the Atlantic and Pacific oceans.

E-11 How Did Your Algae Grow?

Look at the results of the algae cultures you started in experiment E-7. Did the algae grow equally well in all the test tubes? If not, why not? What was missing in the tubes in which the algae did not grow as well?

EXPERIMENT

E-12 Putting Algae on a Diet

We can control algae by limiting the amount of any one of the elements needed for their growth. Which element should we limit? Since algae need carbon more than anything else, we might try to limit carbon. But algae get most of their carbon through carbon dioxide, which is always available near the surface of the water because of both the contact with the atmosphere and the decay of vegetation. Could we limit the nitrogen? Compounds containing nitrogen are present in large amounts in municipal sewage and in the water that drains off farmland, either from animal wastes or from nitrogen fertilizers. Even if we could control those nitrogen inputs, some species of algae are able to utilize nitrogen from the atmosphere. Could we limit the minor essential elements? Probably not enough to solve the problem. In most bodies of water it would be impossible to reduce concentrations of these elements below the small amounts algae need.

This leaves phosphorus as the element scientists believe can be most easily reduced to limit the growth of algae. About 70 percent of the phosphorus compounds used in the United States goes into agricultural fertilizer and about 13 percent into household detergents. One might suppose that most phosphorus in water comes from the runoff of phosphate fertilizers from farmers' fields. Actually, unlike nitrates in fertilizers, phosphates are not very soluble in water. They stay on the soil; only very small amounts run off.

Most of the detergent phosphates in wash water are dumped into sewer systems. Unfortunately, most municipal sewagetreatment plants remove only one-half or less of the phosphates

To increase crop yields sufficiently to feed the world's growing population, billions of dollars are spent each year on fertilizers used on farmlands. The use of these chemicals accounts for about one-fourth of all crop production. The main elements supplied by fertilizers are nitrogen, potassium, and phosphorus. These nutrients can be applied to the land in the form of a powder (right), sprayed as a liquid (page 25, top), injected into the soil, or added to

irrigation water (left).

from the water before it is released into a river or lake. An estimated 50 to 60 percent of the phosphates in both Lake Erie and the Potomac River, in Maryland, are from detergents.

The idea of limiting the growth of algae by reducing the amount of phosphates released into bodies of water was a highly controversial issue during the early 1970s. Since then, the reduction of phosphate drainage into lakes has improved the quality of water in many of them, and now there is little doubt that the method is effective. For example, during the middle 1950s Lake Washington, near Seattle, was beginning to have eutrophication problems. During the early 1960s, sewage from Seattle, which had been supplying about 60 percent of the total phosphorus input, was diverted to another body of water where it would have a less harmful effect. Although the concentration of dissolved carbon dioxide stayed about the same and nitrates decreased only 20 percent by 1969, the concentrations of both phosphorus and algae decreased by 80 percent. These reductions have stopped the eutrophication of Lake Washington and have restored the water to good condition.

It appears, then, that water quality in most areas would be improved if phosphate levels in detergents or in the effluents from sewage-treatment plants were reduced. In some areas laws have been passed that require reduction or removal of the phosphate content of detergents. Through this action the quality of the water in these areas has been improved.

PROBLEM

Check the regulations in your state or municipality regarding the sale of detergents containing phosphates. Also check the packages of detergents in your supermarket for phosphate content.

How much phosphate is present in various natural waters in your area and in the detergents used in your household? An analysis that determines the phosphate content in water and detergents is described in the following experiment.

First, collect samples of water from sources such as streams, ponds, and lakes. Keep each sample in a clean, chemically inert container, such as a polyethylene bottle. Also, bring in samples of detergents used in your home and analyze them for their phosphate content.

EXPERIMENT **553 E-13**

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 special precautions in addition to those discussed in Appendix I.

17 - 17 **Phosphate in Water and Detergents**

To determine the amount of phosphate in a sample of water or detergent, you will be comparing your sample with a series of standards, that is, other samples that contain known amounts of phosphate.

First, prepare a series of standard solutions that contain 10, 7.5, 5, and 2.5 ppm of phosphate. Then treat the standards with a reagent that causes the phosphate to be converted to a colored compound.

ascorbic acid (vitamin C) $\mathsf{PO_4^{3-}} \quad + \quad \{ \text{ ammonium molybdate, } (\mathsf{NH_4})_2\mathsf{MOO_4} \quad \} \quad \longrightarrow$ sulfuric acid, $\rm H_2SO_4$ colored compound

You will use the same procedure with your unknown sample and compare the intensity of its color with the intensity of the colors of the standards. You will then be able to make a fairly good estimate of the concentration of phosphate ions in your unknown sample.

Preparing a standard series:

- 1. Measure one of the assigned amounts* $(40 \text{ cm}^3, 30 \text{ cm}^3, 20 \text{ cm}^3, \text{ or }$ 10 cm3) of standard phosphate and pour it into a 250-cm3 Erlenmeyer flask.
- 2. Increase the volume of your sample to 40 cm3 by adding distilled water to the flask. (After step 3 your solution will contain 10, 7.5, 5, or 2.5 ppm of phosphate, depending on which standard phosphate volume you were assigned.)
- 3. Put 4.0 cm^3 of ammonium molybdate–sulfuric acid solution directly into your flask from the dispensing buret.
- 4. Add a few crystals of ascorbic acid to your flask.
- 5. Heat the solution to boiling. What color do you observe?
- 6. Cool the flask in an ice bath. Transfer the cooled solution to a test tube, label it, and place it in a test-tube rack.

*You will need four standards for comparison. This task may be divided among groups in the class, with each student preparing one of the standards.

Determining the amount of phosphate in a water sample:

- 1. Place about 40 $cm³$ of your water sample in a 250-cm³ Erlenmeyer flask.
- 2. Follow steps 3 through 6 of the standard-series procedure.
- 3. Match the color of your water sample to one of the standard solutions. Estimate the phosphate ion concentration in your water sample. Compare your results with those of others in the class.

Determining the amount of phosphate in a detergent sample:

- 1. Place a 1.0-g sample of detergent in a 600- to 1000-cm3 beaker.
- 2. Add 500 cm3 of distilled water and dissolve the sample by stirring.
- 3. Place 10 cm³ of the solution prepared in step 2 in a 600- to 1000-cm³ beaker and add enough water to bring the level to 500 cm3.
- 4. Measure 40 cm³ of the solution from step 3 with a graduated cylinder and place the solution in an Erlenmeyer flask.
- 5. Follow steps 3 to 6 of the standard-series procedure.
- 6. Match the color with the standard series and estimate the concentration of phosphate ions.

Calculating the percentage of phosphate in the detergent:

From step 6 you estimated the parts per million of phosphate in the 40-cm3 solution. Let's call this concentration y. In step 3 you diluted 10 cm³ of the original solution to the 500-cm³ solution you made in step 2. This solution has a phosphate concentration of 50y. The mass of phosphate in step 2 was

50y ppm \times 500 g (of solution) \times 10⁻⁶ = 2.5 \times 10⁻² (y) g PO₄³⁻

This amount is the mass of PO₄³⁻ present in the gram of detergent you started with. The percentage of phosphate (by mass) in the detergent is

percent PO₄³⁻ =
$$
\frac{\text{mass of phosphate}}{\text{mass of determined}}
$$
 × 100
= $\frac{2.5 \times 10^{-2}(y) \text{ g PO}_{4}^{3-} \times 100}{1 \text{ g}}$
= 2.5(y)% PO₄³⁻

Compare the percentage of phosphate in your detergent sample with the results found by others in your class. How do your results compare with the manufacturer's statement of content?

E-14 Why Phosphates in Detergents?

The water in most municipal water supplies is hard-that is, it contains large amounts of dissolved minerals. As water passes over rocks and through soil, it dissolves metal ions such as calcium $(Ca²⁺)$ and magnesium $(Mg²⁺)$, along with anions (negative ions) such as carbonate (CO_3^2) and bicarbonate (HCO₃⁻). When detergents are added to the water, the metal ions form insoluble precipitates with the detergent molecules.

The formation of precipitates interferes with the cleansing action of a detergent. When you use a detergent to wash clothes, the formation of precipitates uses up detergent molecules, which are then no longer available to float particles of grease and dirt off the clothes. The precipitates are then deposited on the clothes, leaving them gray instead of white. This deposit is similar to the "bathtub ring" that shows up after you bathe with soap.

Manufacturers prevent the formation of precipitates in detergent solutions by adding compounds of sodium and phosphates to the detergent. Some commonly used compounds are trisodium orthophosphate (Na₃PO₄); tetrasodium pyrophosphate (Na₄P₂O₇); and pentasodium tripolyphosphate, STPP ($\text{Na}_5\text{P}_3\text{O}_{10}$). Instead of reacting with the detergent molecules, metal ions such as calcium form strongly bound, soluble, complex ions with the phosphates. In this way the phosphates prevent the formation of precipitates.

To find out more about this, you will do an experiment to determine the hardness of water. But first you will investigate the effects of soaps and detergents on hard and soft water.

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RING AROUND THE BATHTUR 77

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E-15 Ring Around the Bathtub

What causes a "ring" around the bathtub? Why do some people use water softeners? Why are detergents more popular than soaps? This activity will help you answer these questions.

First, clean and dry four test tubes. Place about 10 $cm³$ of distilled water in each of two test tubes and label them "soft water."

Place about 10 cm³ of hard water—well water, river water, or even unsoftened tap water-in each of the other two test tubes and label them.

Your teacher will supply a solution of bathing soap and a solution of laundry detergent. Place a few drops of bathing-soap solution into one of the "soft-water" tubes and the same amount into one of the "hard-water" tubes and label them.

Place a few drops of laundry-detergent solution into the other two test tubes and label them. Allow the test tubes to remain undisturbed for a few minutes; then record your observations.

Finally, shake all four test tubes vigorously for 1 minute and again allow the tubes to remain undisturbed for a few minutes. Record your observations.

QUESTIONS:

- 1. In what way do hard and soft water react differently with soap?
- 2. What is a "bathtub ring" and how does it form when you bathe in hard water?
- 3. What is the difference between a soap and a detergent?

You have just observed the effects of using soap and detergents with soft and hard water. Now let's check the hardness of water that comes from your local water supply. Start by collecting a water sample from the tap in your home. If you live in an area where all the water is supplied by one source, the samples obtained by some of your classmates may be alike. If you are able to obtain water samples from a local stream, a recent rainfall, or a well, these can also be tested.

E-16 How Hard Is the Water? EXPERIMENT

Titration of the water sample: Place 50 cm³ of the collected sample in a 250-cm³ Erlenmeyer flask. Add 10 cm³ of $NH₃-NH₄Cl$ buffer. Check the pH with litmus paper. If the solution is not basic, add more buffer. Finally, add a few drops of either Eriochrome Black T or Calgamite indicator.

Fill a buret with standard ethylenediaminetetraacetic acid (EDTA) solution and record the initial buret reading. Now titrate the water sample with the standard EDTA solution. The end point is reached when the last traces of pink color disappear from the blue solution. The best way to check the end point is to place a piece of white paper unde'r the sample. As you approach the end point, the blue color will persist for longer periods of time when the solution is swirled. Be careful: some samples have very little "hardness" and will reach the end point quickly. Once you have reached the end point, record the final buret reading and calculate the volume of standard EDTA needed for the titration. This volume, $V_{\rm so}$, will be used later when you calculate the water hardness of your sample.

The distilled water blank: Since all water contains some "hardness," the chemical solutions used in the titration process also contain "hardness." When you titrated your water sample, you determined the "hardness" in both the sample and the chemical solutions. To determine the net hardness of the samples, you will need to subtract a "blank" value from the total hardness. The "blank" value is the hardness indicated by titrating a distilled water sample using all the chemicals and following the same procedure as before. Buffer and indicator must be added before titration. Record the volume of EDTA necessary to titrate the "blank," V_{bl} . This value will be used in later calculations.

Standardization of EDTA: Measure exactly 5.0 cm³ of standard calcium carbonate (CaCO₃) solution. Add this solution to 45 cm³ of distilled water in a 250-cm3 Erlenmeyer flask. Titrate this standard in the same manner as before. Be sure to add the buffer, and check the pH before adding the indicator to this standard solution. Record the volume of EDTA used to reach the end point, V_{std} . Your teacher will tell you the concentration of. the standard $CaCO₃$ solution (C $_{CaCO₃}$).

Calculations: First calculate the concentration of the EDTA solution (C_{EDTA}) in terms of the amount of calcium carbonate that reacts with each cubic centimeter of EDTA solution.

$$
C_{EDTA}
$$
 (mg CaCO₃/cm³) = C_{caCO₃}(mg/cm³) × $\frac{(5.0 \text{ cm}^3)}{V_{std}(\text{cm}^3)} - V_{bi}(\text{cm}^3)$

Now you can compute the equivalent $CaCO₃$ hardness of the water sample.

hardness (mg CaCO₃/cm³) =
$$
\frac{V_{sp} (cm^{3}) - V_{bl} (cm^{3})}{50 cm^{3}}
$$

$$
\times C_{EDTA} (mg CaCO_{3}/cm^{3})
$$

Since the value of water hardness in terms of milligrams per cubic centimeter is generally a small number, it is often more convenient to express the answer in terms of parts per million by mass. One milligram of material dissolved in 1000 cm³ (about 1000 g) of solution is approximately 1 ppm. To obtain hardness in parts per million, then, we must multiply the preceding answer by 1000.

hardness (ppm $CaCO₃$) = hardness (mg $CaCO₃/cm³$) × 1000

Interpretation: Use the Table of Relative Water Hardness to determine the quality of your water sample.

QUESTIONS:

- 1. Compare the results obtained from your water samples with those obtained by other members of the class. If all the tap water samples came from the same central supply, is there good agreement in values?
- 2. What did you find out about the water samples collected from local streams? Are there great variations between them? If so, what might cause such variations?
- 3. How do rainwater samples compare with samples collected from streams? Can you explain the differences?

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- 4. If anyone brought in water softened by a home water softener, how does it compare with other samples of water in terms of hardness?
- 5. Can you explain the source of the residue or scale found inside tea kettles, coffeepots, and pans used consistently for boiling water?

It might be interesting to compare your experimental values with those observed in various regions of the country. Because of differences in the chemical composition of soil and rocks, there are variations in water hardness from one area to another. Natural waters of the southeastern states from Texas to Virginia (exduding Florida), the New England states, and the far northwestern states (Oregon and Washington) are usually soft. The hardness of these waters is 60 ppm $CaCO₃$ or less. Waters of the midwestern states (Ohio, Indiana, Illinois, Iowa, Nebraska, Kansas, and Missouri) are generally much harder-up to 180 ppm or greater.

E-17 Detergents: The Phosphate Dilemma

If the phosphates from detergents contribute to the eutrophication of our nation's water, what can be done to help reduce the problem? There is no clear answer. Makers of detergents have tried to develop substitutes for phosphates—compounds that would keep the water basic and form complex ions with calcium $(Ca²⁺)$ and other ions. Several companies considered replacing the phosphates ¹ with sodium nitrilotriacetate (NTA). But before NTA was intro-
duced tests showed that in combination with metal ions such as duced, tests showed that in combination with metal ions such as

0-55 ppm 55-120 ppm 120-250 ppm 250+ ppm

Pollution in this river was caused by nonbiodegradable soaps and detergents (pre-1965) in waste water. The problem of surface foam on water was solved through the use of biodegradable detergents.

TIME MACHINE **Detergents**

- 1933 Synthetic detergents are introduced commercially. Their main use was for washing dishes, since they were not successful in cleaning laundry.
- 1939 Lake Winnebago, Wisconsin, experiences an "algae population explosion." Algae numbered in the millions per "glassful."
- 1946 Synthetic detergents capable of handling most household-cleaning problems are introduced.
- 1950s First phosphate-based detergents are introduced.
- 1965 U.S. detergent industry changes to readily "biodegradable" materials LASs (linear sodium alkyl benzene s ulfonates).
- 1970 A ban on the sale of detergents containing more than 20 percent phosphates goes into effect in Canada.
- 1977 Suffolk County, Long Island (New York), bans the sale of most laundry detergents containing phosphates.

mercury (Hg²⁺) and cadmium (Cd²⁺) the NTA caused birth deformities and prenatal deaths in rats. NTA itself has extremely low toxicity, but it causes tumors when massive doses are given to test animals over long periods. However, NTA has been used in detergents in Canada and other countries for several years, so far without obvious detrimental effects. It is broken down fairly rapidly after release into the environment.

Other compounds have been tried as phosphate replacements: polycarbonates, metasilicates, and perborates. Often, instead of forming soluble compounds with hard-water ions, these substances form granular precipitates that sink to the bottom of the wash water rather than deposit on the clothes. These phosphate substitutes, however, have the problem of being very caustic because they hydrolyze in water; that is, they react with water to release hydroxide ions.

> CO_3^{2-} + H_2O \longrightarrow HCO_3^{-} + $OH^$ carbonate bicarbonate hydroxide

Currently there doesn't seem to be an easy solution to the phosphate-detergent problem. In time there may be municipal sewage plants that have been modified so that they can remove phosphates from waste water before it is released into the environment. Processes for removing phosphates have been developed, but the installation of the equipment in sewage plants throughout the country will be a long and expensive operation. In the meantime, perhaps, we should go back to using soap and ignore the precipitates.

E-18 Out of Sight-Not Out of Circulation

When you pour waste down the drain, where does this material go? As far as you're concerned, it's gone. But we never really throw anything away. The material always persists in some form as atoms and molecules somewhere else in the environment. The disposal of waste materials determines the quality of water in streams, the safety of drinking water, and the eutrophication of lakes.

Some diseases are transmitted from one person to another through intestinal wastes. At the turn of this century, many diseases, such as cholera, typhoid, and dysentery, were spread by pathogenic (disease-causing) bacteria in untreated sewage. It is easy to see how this could happen, since waste water discharged into a river by one community is often reused as drinking water by communities downstream. Mainly to prevent the spread of diseases, most communities in the United States installed facilities for the treatment of sewage and drinking water. These measures have virtually eliminated diseases transmitted by pathogenic bacteria, but the diseases still occur in many areas of the world that have poorer sanitation facilities.

Most communities are served by municipal plants employing *pri*mary or secondary sewage treatment. Sewage is about 99.9 percent water and about 0.1 percent other materials. In primary treatment, sewage passes through a screen that removes large solids before $\begin{bmatrix} -\text{BOD} \\ \text{removal} \end{bmatrix}$ entering a settling tank where finer solids settle out and a film of grease is skimmed off the top. Chlorine is added to kill pathogenic bacteria before the water (effluent) is discharged into the receiving water (lakes, rivers, and streams).

Primary sewage treatment helps prevent the spread of diseases, but the effluent still contains large amounts of organic material. After the effluent is released into a body of water, microorganisms decompose the remaining organic material, which is made up of compounds that contain carbon, hydrogen, oxygen, nitrogen, sulfur, and phosphorus. These elements are oxidized to form carbon dioxide, water, and other minor products, just as in the case of dead algae (section E-10). This biological decay uses oxygen from the lake or stream in which the effluent is released. The water may become so depleted of oxygen that it cannot support desirable aquatic life forms. In extreme cases the bottom waters may become so deficient in dissolved oxygen that only anaerobic bacteria can survive. These bacteria, which derive their energy needs from chemical reactions that do not involve oxygen, release smelly, sulfurous gases. When this happens, the body of water eventually becomes unusable.

An indicator commonly used to determine the amount of organic material released in waste water or in water in streams or lakes is

PRIMARY AND SECONDARY WASTEWATER TREATMENTS

Sewage treatment at this water-pollution control plant (top left) begins at the screen house (top right). Here large pieces of debris are removed and smaller particles settle in grit channels (foreground). Suspended solids are removed at the primary settling tanks (bottom left). Sludge from these tanks is concentrated, heated, and then pumped to digesters (bottom right, the circular tanks in the background). The action of anaerobic bacteria in the digesters makes the sludge less toxic.

the biological oxygen demand (BOD) of the water. BOD is a measurement of the amount of dissolved oxygen used up by chemical and biological processes during the decay of organic wastes over a period of time.

Using 300-cm3 sample bottles, collect water samples for measurement of BOD. Bring the samples back to the laboratory as soon as possible so that the measurement can be started before much oxygen decay occurs. Don't stopper the sample bottles too tightly, since the water needs oxygen for aerobic (with oxygen) decomposition to take place. If no oxygen is present, anaerobic bacteria will take over and cause decomposition of the organic material. Since it is the aerobic decomposition we want to measure, we must let the sample have oxygen until the BOD test begins.

E-19 Testing for the BOD

Because of the time necessary to perform numerous titrations, the quantitative (answering the question, How much is present?) BOD test used in sewage treatment would be impractical here. Instead, you will be performing a qualitative (answering the question, What is present?) BOD analysis. This analysis is based on the amount of time necessary for a sewage sample to remove the oxygen in a water sample and change the color of an indicator. The shorter the time, the greater the BOD of the water sample.

The indicator to be used in this experiment is methylene blue. In addition to your water sample, some simulated sewage will also be tested. Powdered milk will be used to represent sewage, and yeast will be used to represent the bacteria in the sewage. Label and fill five test tubes with the appropriate volume of each ingredient listed in the table.

Used as a control to illustrate the effect of the yeast solution.

Next, with a pipet add 1 cm³ of methylene blue solution to each test tube, after having placed the pipet tip deep into the sample solution. (Wash the pipet thoroughly with distilled water before reuse or use a clean pipet each time.) Using the pipet in this way will reduce the amount of air

EXPERIMENT

 \Diamond

pickup by the methylene blue solution. Record the time at which the methylene blue was added. Make observations; then set the tubes aside for later inspection.

Check the test tubes daily to see when the blue solution turns clear. From the amount of time that is necessary for the dissolved oxygen in the sample to be used up, you can obtain an estimate of the BOD of the sample.

Questions: Which sample had the highest BOD-the water sample or one of the samples of simulated sewage? Is this what you expected? Why? Can you account for the differences noted in the other samples?

E-20 Lowering the BOD

Although many communities use only primary sewage treatment, the high BOD levels of the effluent can cause such serious oxygen depletion in the receiving waters that it is desirable for cities to use secondary sewage treatment. After mechanical removal of solids and grease, the sewage water is placed in aeration tanks containing aerobic bacteria, organisms that use oxygen to decompose organic material. Air is pumped through the water (aeration) to supply the oxygen. After aerobic digestion, the water is transferred to a settling tank to allow the bacterial sludge to settle for return to the aeration tanks. Then the water is treated with chlorine and released.

Secondary treatment is more effective than primary treatment. Primary treatment removes about 32 percent of the BOD and 36 percent of the suspended solids. Primary followed by secondary

Wastewater treatment at the Northeast Water Pollution Control Plant in Philadelphia, Pennsylvania, includes the aeration process (left), in which aerobic bacteria lower the BOD. Bacterial sludge settles out in the final tanks (right) and is returned to the aeration tanks for further use.

treatment removes about 85 percent of each. In this way, secondary treatment removes most of the material that would directly cause depletion of oxygen from receiving water.

But even secondary treatment doesn't solve the eutrophication problem. Sewage-treatment plants remove less than half of the nitrogen and phosphorus from waste water before discharging it. The problem is that the aerobic bacteria in the aeration tanks, just like algae, need a balanced diet. Sewage contains an excess of nitrogen and phosphorus relative to the amount of carbon in the diet of aerobic bacteria. These leftover elements (and other minor nutrient elements) are released into the receiving water and "fertilize" the algae. Out in the stream or lake, carbon dioxide from the air supplies the "missing" carbon.

What can be done about the release of phosphorus and nitrogen into water? For some years it was felt that "tertiary" treatment should be used—the addition of cleanup steps after primary and secondary treatments. It now appears that it would be better to replace the whole process, including the biological secondary treatment, with an entirely nonbiological set of processes called independent physiochemical treatment (IPCT).

In the IPCT process, large solids in the waste water are filtered out and ground up. But instead of simply allowing the remaining solids to settle, the treatment requires the addition of chemicals called coagulants, which cause fine particles to come together to form larger ones that settle out rapidly. These coagulants include lime (CaO), iron, aluminum salts, and synthetic polymers. Whereas only about half of the solids settle out in conventional primary treatment, coagulation and settling remove 95 to 99 percent of the solids. Other materials are removed by filtration and contact with

The sludge removed during sewage treatment is being processed for use as fertilizer. A by-product of bacterial action on sludge is methane gas, which can be used as a fuel.

TIME MACHINE

Floating barriers are used to trap oil and debris that pollute bodies of water.

activated charcoal, which has an unusual ability to collect material that comes into contact with its surface. The use of activated charcoal is one of the most important steps because it removes large quantities of organic materials. In contrast, when chlorine is added to water containing organic ions, organic chlorine compounds are formed, many of which can cause cancer.

The IPCT plants are also able to help solve the detergenteutrophication problem by removing most phosphates and nitrogen from the water before it is released. Since more than 90 percent of the nitrogen in waste water is present as ammonium ions $(NH₄⁺)$ or ammonia (NH_3) , much of the nitrogen can be removed by making the water highly basic (through the addition of lime, CaO), which causes NH_4^+ to form NH_3 , most of which comes off as a gas.

$$
CaO(s) + H2O(l) \longrightarrow Ca2+(aq) + 2 OH-(aq)
$$

$$
NH4+(aq) + OH-(aq) \longrightarrow NH3(g) + H2O(l)
$$

Various combinations of these and other steps are now being used in IPCT plants. There are about thirty IPCT plants of a variety of designs currently operating in communities throughout the United States that provide large-scale practical tests of the various methods. So far the results have been quite encouraging, indicating that these plants release much cleaner water than the primaryplus-secondary treatment plants. In the next decade we will probably see a much wider implementation of IPCT processes.

Since it is very costly to build new plants for removal of nutrients from water, it is desirable to find a simpler solution to the nutrient problem. We could consider the nitrogen and phosphorus in waste water as resources-out-of-place. These are substances that are considered pollutants in their present locales, but would become valuable resources if handled properly. For instance, farmers and homeowners buy considerable amounts of fertilizers that supply the nitrogen, phosphorus, and potassium needed by plants. We could obtain the nitrogen and phosphorus for fertilizers from waste water. The "sludge" removed from sewage-treatment settling vats is already being used as a fertilizer and soil conditioner. Until further studies are completed, however, these materials can be used only on nonfood crops, because they contain toxic metals and viruses.

Here we conclude our brief discussion of water pollution, although it has been only an introduction. Besides the problems associated with eutrophication and sewage treatment, there are many other water-pollution problems: pollution by toxic metals, carcinogenic (cancer-causing) compounds, pesticides, oil slicks, asbestos, radioactivity, thermal pollution, and acidic water from coal mines. We will discuss some of these other areas in later sections.

An oil slick on the waters of New York City's Upper Bay can be seen in the foreground.

PROBLEMS **Sections**

- 1. Explain why, although algae scum on water is unpleasant, algae are chemically beneficial while they are alive. Then explain why they are detrimental after they die.
- 2. Secondary sewage treatment removes most of the bacteria and BOD from water, but it does not control eutrophication very well. Explain why, and suggest ways in which we could further reduce eutrophication.
- 3. The "fertilizer" elements in waste water nitrogen and phosphorus-are our first examples of resources-out-of-place. Make a list of other resources-out-of-place and explain your reasons for including each.
- 4. a. Calculate the mass fraction of phosphorus (P) in STPP, pentasodium tripolyphosphate $(Na_5P_3O_{10})$.
	- b. What is the percentage of phosphorus in a detergent that contains 35 percent STPP by mass?
- 5. a. Estimate the amount of detergent needed to tie up the Ca^{2+} ions in hard water. Assume that we add 250 g of detergent, containing 35 percent STPP (see problem 4), to 100 liters of wash water.
	- b. How many moles of STPP are in the added detergent? (Assume that the water has moderate hardness, or approximately 60 ppm $CaCO₃$.)
	- c. If all the hardness is due to $CaCO₃$, how many moles of Ca^{2+} are in the 100 cm³ of wash water?
- d. If each STPP ion can bind one Ca²⁺ ion, which is in excess-STPP or Ca^{2+} -and by what factor?
- 6. Assume that every family of four in a city of 100 000 people uses 500 g of detergent (35 percent STPP by mass) per week.
	- a. Calculate the mass of phosphate added to the streams in the area per year.
	- b. If ICPT plants were installed and they removed 99 percent of the phosphate, how much phosphate would be released per year?
- 7. On the average, each person adds about 15 kg of phosphorus to sewage every year.
	- a. How much phosphorus (in kilograms) is dumped into Lake Erie annually by the approximately 14 millon residents of the region surrounding the lake?
	- b. How many moles of $O₂$ are used up by the decomposition of the algae formed with the phosphorus, assuming adequate amounts of all other nutrients? (Each mole of phosphorus can produce enough algae to require 155 moles of $O₂$ for decomposition.)
	- c. How many moles of $O₂$ are contained in the lake when its 460-km³ volume of water is saturated? Recall that water saturated with oxygen contains about 10 mg O₂ per liter (or per cubic decimeter).
- 8. List the actions individuals could take to maintain or upgrade the quality of the water in their environment.

Toxic Substances in the Environment

The chemical industry has developed countless products designed for easier and better living-products that are inexpensive, durable, and convenient to use. But once in a while something goes wrong and we learn later, often too late, that some of these products have serious side effects because of the toxic substances they contain. How can we check the environmental safety of these products beforehand? How can we reap the benefits of modern chemistry without harming our environment?

For the past two decades, massive amounts of pesticides have been used to ensure high crop yields and to protect crops from diseases and insects. One way to distribute pesticides over farmland has been to use an airplane to spray blankets of toxic chemicals on large areas at one time.

 $\frac{1}{26}$. The zooplanktons. For the continuance of life in the ocean, the interdependence of the producers (phytoplankton and aquatic plants) and the consumers (zooplankton, fish and birds) is essential. Elimination of any one of these links in the food chain would threaten the survival of the others. Radiolaria (left) are among the smallest one-celled animals of

E-21 The Pyramid of Life

In order to understand the behavior of toxic substances in the environment, we need to learn how living organisms get their food. The energy contained in our food comes ultimately from the Sun. In the process of photosynthesis, through the action of sunlight, green plants combine water, carbon dioxide, and minerals to form high-energy organic compounds such as carbohydrates and proteins (section E-10). The green plants are called *producers* because they produce the high-energy compounds needed to sustain the animals that eat these plants. Those animals are called consumers.

In any ecosystem, such as a lake or a forest, there are food chains, with producers at the bottom of these chains. In a lake the producers may be phytoplankton (such as diatoms and algae). These phytoplankton may be consumed by microscopic animal life called zooplankton. These are in turn eaten by small fish, which are eaten by larger fish. Finally, a predatory bird, such as a pelican, may eat the large fish.

This example of a food chain consists of five "links," called trophic levels. The producers at the bottom of the chain are succeeded by four levels of consumers. The higher up the food chain a species is, the lower the total mass per level. The transfer of energy and nutrients from one level in a food chain to the next higher level is not efficient. For example, large fish of the fourth level retain in their bodies only about 10 percent of the energy and nutrients present in the bodies of the small fish of the third level, which the large fish consume.

As a result of the many chemical toxins in the environment, the bald eagle (left), the peregrine falcon (middle), and the California condor (right) are listed as endangered species. Only through careful methods of monitoring and control will these birds survive.

For a 1-kg fish in a lake to survive, there must be about 10 kg of smaller fish available for it to consume. For every kilogram of living matter at the fifth level there must be 10 000 kg of producer mass at the bottom of the chain.

Life in a natural ecosystem is rarely as simple as the diagrams used to describe it. In many cases species consume food from two or more levels and are themselves consumed by species at more than one higher level. Instead of a simple food chain, we frequently encounter a complex set of producers and consumers called a food web. For example, people obtain most of their food from the first and second trophic levels on land, but they also consume fish from the third and fourth trophic levels of the aquatic system. We are now prepared to see how these trophic relationships cause some toxic substances to become concentrated in species at higher levels of the food web.

FOOD WEB

E-22 Alien Substances in the Environment

Today one hears a lot about recycling as a way of helping to dispose of the mountains of trash that are produced, while conserving our valuable natural resources. Recycling is actually a very old process. Nature has been recycling resources since the beginning of time, and it is an activity that is essential to life on our planet. There are natural chemical mechanisms for breaking up every molecule in living organisms to form simpler substances that other living species can then use as nutrients. These breakdown mechanisms are complex biochemical reactions that are catalyzed by the enzymes in bacteria, fungi, and other organisms. We speak of these natural materials as being biodegradable. If there were no breakdown of certain kinds of living matter, all the nutrients required by other living species for further growth would eventually be stored in the bodies of these indestructible species, and life would come to a halt.

Our technological society has an impact on the environment. Recent advances in chemistry have resulted in the production of an assortment of substances that have never before existed in nature. Many of these products are valuable to our society, but some of them can cause problems when they are released into the environment. The chemical structures of these new substances are unfamiliar to the enzymes, bacteria, and fungi that have evolved to decompose substances naturally present in living systems. Synthetic materials are often resistant to breakdown by sunlight and by chemicals. They may persist for years without their molecules breaking down into simpler substances. Such long-lasting materials are called nonbiodegradable.

The disposal of over 200 million metric tons of trash each year has become a major problem in the United States. Cities are running out of space for such large masses of garbage. What other methods for the disposal of waste do you think will play a part in the future? In what ways could we put this trash to better use? Who should accept the responsibility for this

POLYETHYLENE $+$ CH₂CH₂ $+$ _n

Consider two kinds of solid waste generated in sizable quantities by our society-newspapers and polyethylene bags. Both consist of polymer-type molecules, long chains of repeating chemical units bound together. What happens when we throw them away? A newspaper placed in sunlight turns yellow. If one were to bury it in the ground, within a few months it would decompose beyond recognition. The polyethylene bag, however, resists the usual processes of decay. Putting it in the sunlight, burying it in the ground, throwing it into the ocean, treating it with strong $acid$ —anything short of burning it causes almost no apparent damage or physical change to the polyethylene.

 β Newspaper is made from wood pulp, which is mostly cellulose. OH because there are enzymes available with just the right structure to What is the difference between newspaper and polyethylene? Cellulose consists of long chains of sugar molecules. Being a natural material, cellulose is easily broken down by natural processes lock onto the bonds between the sugar units and catalyze their breaking. On the other hand, polyethylene is an unfamiliar material in nature; so no enzymes have evolved to catalyze the breakdown of its structure. Polyethylene is just one of many synthetic materials that is nonbiodegradable. Others include polystyrene (used in Styrofoam products) and polyvinylchloride (used in vinyl products).

PROBLEM **[**

Much of what we throw away is in the form of nonbiodegradable plastic bottles and containers. Would you be willing to do without these items to reduce the amount of solid waste found in our environment?

 $\overline{P1}C$

Make a list of nonbiodegradable products that you use daily. Try to find other products, either natural or synthetic, that are biodegradable and could be substituted for products on your list. What are some of the advantages and disadvantages of using nonbiodegradable products? What steps can be taken to dispose of these products without harming the environment?

Crop-damaging insects pose the greatest threat to crop production. Insecticides are dispensed in various forms and in a variety of ways-by plane, by truck, and by hand.

E-23 Pesticides-Where Did the Birds Go?

During and after World War II, chemists developed synthetic chemical pesticides. Among these pesticides are the chlorinated hydrocarbon insecticides, of which DDT is the most familiar. These pesticides have been used to wipe out vast populations of insects that carry diseases and attack food crops. As a result, many countries have been able to increase their much needed food supplies.

After having used DDT and similar insecticides for about thrity years, however, we are now discovering that there is an environmental price to pay for their benefits: these compounds remain in the environment for many years after being used. For this reason they are often called persistent pesticides.

When an animal eats plants or insects that have been sprayed with DDT, most of the DDT remains in the animal's body tissues, since little is flushed out of the animal's body with the liquid waste. This happens because DDT has a low solubility in water but a great affinity for fatty tissue. Therefore, DDT readily accumulates in fatty tissue. When another animal eats the animal contaminated with DDT, the pesticide is passed on.

Now we can understand how DDT becomes concentrated in the bodies of certain species of animals. As we discussed in section E-21, an animal must consume much more than its own mass from the lower levels of the food chain. For example, when there is DDT in the food of an animal at the third trophic level, the animal will soon acquire a much greater DDT concentration in its fatty tissue than was present in its food from the second trophic level. Therefore, pesticides become more concentrated at each higher step of the food chain. In a typical aquatic food web, the DDT concentration may be a fraction of a part per billion in the water, 0.01 ppm in

TIME MACHINE Pesticides

DDT CONCENTRATIONS

1 ppm

Thin shells of birds' eggs have been traced to environmental pollutants, specifically to the chlorinated hydrocarbons used in pesticides. Some shells are so thin that they are crushed by the weight of the incubating parent.

the phytoplankton, a few parts per million in the fish, and 100 ppm or more in birds that eat the fish. Thus, the DDT is concentrated tenfold or more with each step up the food chain.

Since predatory birds (condors, eagles, pelicans, falcons, ospreys) are at the tops of long chains, it is not surprising that the effects of DDT have shown up most dramatically in them. DDT and similar pesticides have caused the populations of these birds to decline markedly in recent years, in fact to such a degree that some species face possible extinction. Two major effects of DDT seem responsible for these declines, and both are related to the fact that high concentrations of this pesticide alter the level of sex hormones in the bodies of the female birds. First, the calcium stored in the bird's body is not transported effectively to the eggshells being formed. This causes the shells to be abnormally thin and too fragile to survive until hatching. Second, the time of egg hatching is thrown a few days off schedule, thereby lessening the young birds' chances of survival.

People, too, may face serious problems from DDT and other chlorinated hydrocarbon pesticides. Since most of our food comes from the first and second trophic levels, we do not accumulate as high a pesticide concentration as birds do. Nevertheless, on the average, North Americans have about 3 ppm of DDT and its breakdown products in their fatty tissues—nearly as high as the 5-ppm limit generally considered safe. Many chlorinated hydrocarbon pesticides have been found to be cancer causing, or carcinogenic. Compounds known to have serious adverse effects have been banned from all but the most critical uses in the United States, but many are still used in other countries.

Most pesticides enter the environment as a result of legitimate efforts to control weeds or insects, and some enter the environment as wastes from industrial processes. Probably the most tragic environmental incident to date in the United States involved the release of Kepone, a chlorinated hydrocarbon. Kepone is an effective roach and banana-pest killer and was made in the United States for export to South America and Europe. It is highly toxic to people and animals, causing tremors, lack of coordination, muscle spasms, sterility, and cancer.

From 1973 to 1975 Kepone was produced by a small chemical plant in Hopewell, Virginia. As a result of inadequate controls, Kepone was deposited throughout the plant, in the workers' clothes and bodies, and in the air of Hopewell. Many of the workers suffered severe illnesses. Kepone was dumped into the sewer system in such quantities that it killed the beneficial bacteria in the town's sewage-treatment plant. It also found its way into the James River, whose sediments became highly contaminated with Kepone. Fish in the river still have such high concentrations of Kepone that they are unfit for human consumption, and fishing has been banned since December 1975.

The plant was closed after these problems were discovered, but solutions to the problems remain to be found. The James River now has thousands of kilograms of Kepone lying in its sediments, and no one knows how to remove it. Scientists speculate that the Kepone could move to the Chesapeake Bay and Atlantic coast in amounts sufficient to destroy the seafood industries in those areas. As the tide moves up the James River, some Kepone dissolves in the saltier water and becomes mobile. Its presence has been reported as far north as the New Jersey shore.

The companies responsible for the Kepone tragedy were fined for environmental violations. But any fines are small compared with the final cost of repairing the damage such an incident can cause. There is a lesson to be learned here: in the long run it is much cheaper and more sensible to prevent the release of toxic substances than to try to clean up the environment after it has been polluted.

The combination of hot weather, pollution, and a decreased oxygen level in this body of water made survival impossible for thousands of fish.

Insects cause millions of dollars' worth of damage to the environment and to our food crops each year. Beetles feed on plant leaves (right). Below, rice weevils attack rice crops.

 $AC = 48$

E-24 Shall the Bugs Take Over?

In view of the problems caused by modern insecticides, should we just stop using them? Simple as it seems, this is probably not the solution, since it could result in food shortages from insect damage to crops as well as the spread of diseases such as malaria. Many people would surely die of starvation and from the insect-borne diseases. Fortunately, there are many ways in which we may be able to control the damage caused by insects without the use of dangerous pesticides. A few of the possible alternatives are to

- inspect all plants and produce entering the country to prevent the introduction of new species of insects,
- breed new species of crops that have greater resistance to insect attack,
- \bullet introduce predators that feed on insect pests, and
- develop synthetic sex attractants to isolate insects for controlled destruction.

The introduction of insect predators has been quite successful in the control of several types of insects. The insect predators include not only larger species that eat the crop-destroying bugs, but also small parasites, fungi, and even viruses.

57

The development of synthetic sex attractants has also been found to be a viable solution to the insect problem. These sex attractants lure insects into a trap containing a poison or an electric discharge that kills the insect. To develop these substances, scientists analyze an insect and isolate minute quantities of the natural sex attractant. Once the substance has been analyzed and its structure determined, chemists try to develop methods for synthesizing it in large quantities. One such synthetic compound is being used against the gypsy moth, which damages millions of acres of forests and

Male gypsy moth.

orchards each year. A more difficult project, because it involves combining four substances, has been to isolate the sex attractant of the boll weevil, an insect that destroys cotton crops. When the boll CH_3CH_2O weevil sex attractant is perfected, it will help to replace toxic pesticides that are currently being used to save the cotton crops from $CH_3CH_2\dot{O}$ destruction.

Many farmers now use nonpersistent pesticides to control insects. These compounds, such as malathion and parathion, are termed nonpersistent because they break down in the environment within a few days or weeks after their application. Unfortunately, these pesticides are not without their problems. They are so toxic to the human nervous system that they may he dangerous to people working in the fields where the pesticides have been applied.

MALATHION CHCOCH, CH, Ċн,сосн,сн,

Scientists have found that traps containing sex attractants of insects are an effective means of controlling insect pests. When the trap is baited with the appropriate sex attractant, it is possible to attract and control the specific pest in a given area without causing damage to the rest of the environment and its inhabitants.

As this model indicates, DNA consists of two parallel chains that form a double helix. The DNA molecule in a living cell is very important because of the genetic information it contains. Chemical toxins can cause changes in the arrangement of this genetic information, resulting in mutations within the cell.

E-25 Carcinogens in the Environment

There is much concern that some synthetic chemicals introduced into the environment, or used in food, clothing, and other consumer products, may increase our chances of getting cancer. Scientists who study patterns of disease rates among various population groups find that the occurrence rates of cancers of certain areas of the body vary greatly from one country to another around the world. Although the incidence of many types of cancer has been increasing over the past thirty years, rates of some types have been decreasing—for example, stomach cancer in the United States. The latter reduction may be a result of improved refrigeration, preparation, and handling of food.

Studies of cancer rates must be done very carefully to account for several factors. For example, the total cancer rate increases simply because of an increase in population. The chance that any person will get cancer has increased also because people now live longer and cancer occurs more frequently among older people. Even considering these factors, however, we cannot completely explain the increase in cancer rates. Some of this increase may be the result of the introduction of vast quantities of synthetic chemicals into daily use, particularly since World War II. There is often a twenty- to thirty-year time lag between exposure to a cancer-causing chemical and the appearance of the disease. Therefore, the effects of having introduced synthetic chemicals into our society may just now be appearing.

A comparison of data on the occurrence of cancer in different countries reveals great variations in the rates of cancer for a particular part of the human body. For example, the rate of cancer of the esophagus is two hundred times greater among men of certain areas of Africa than among men in the United States. Stomach cancer is thirty times more prevalent among men of Japan, Russia, and Iceland than among men in the United States. Similar variations in cancer rates have been found for specific types of cancer that affect women.

In evaluating such data, researchers determine the lowest rate around the world for a given type of cancer. This is considered to be the natural rate. It is assumed that higher rates are caused by factors within the local environment. Viewing the incidence of cancer in this way, researchers have estimated that only 10 to 20 percent of all cancer is the result of natural causes. This leaves the remaining 80 to 90 percent related to local environmental factors. These factors vary from one area to another and include such things as personal habits (smoking, consumption of alcohol, types of food eaten, methods of preparing food, and so on), chemicals naturally present in or absent from the soil and water of the area, and radioactivity,

which is present either naturally or from technological sources. It is important that these local environmental factors be identified and, if possible, eliminated from our surroundings.

As noted previously, there is concern that cancer rates have increased because of human exposure to carcinogenic chemicals. These chemicals can cause disruptions of the genetic material (DNA) within cells. Substances causing these disruptions, or mutations, of genetic material are called mutagens. Some mutations cause cells to multiply wildly, creating the condition called cancer. If a chemical is mutagenic, there is a good possibility that it is also carcinogenic. An intense effort is under way to identify carcinogenic substances and to eliminate those substances from our environment. This is difficult to do; obviously, a researcher can't expose test groups of people to various chemicals and see which ones cause cancer.

Fortunately, indirect methods for identifying carcinogenic substances are available. Examination of the medical records of workers in various manufacturing plants reveals a connection between some of the workers' health problems and the chemicals to which they may have been exposed. Industrial workers are exposed to specific substances in concentrations that are thousands of times higher than the concentrations to which the general population is exposed. Diseases thought to be caused by these substances often appear with much greater frequency among workers exposed to these higher concentrations. As an example, in 1961 sixteen cases of a rare form of liver cancer were found among workers who manufactured vinyl chloride. Sixteen cases of a more common type of cancer wouldn't have caused so much concern, considering the thousands of workers in the industry. But because this type of liver cancer is so rare, it is unlikely that those sixteen workers just happened to develop it. Therefore, it seems probable that vinyl chloride is a carcinogen.

As a result of this finding, the levels allowed for human exposure to vinyl chloride have been sharply reduced. In addition, questions have been posed concerning the safety of consumer products made from vinyl chloride, such as the plastic polyvinyl chloride (PVC). Thousands of vinyl chloride gas molecules are linked together to form the polymer PVC.

 $n =$ repeating units

PVC is widely used in household products such as bottles, food containers, and thin plastic wraps. As far as is known today, however, PVC products are safe to use.

TIME MACHINE

1912 Norwegians A. Hoist and T. Froelich discover vitamin C.

The most widely used method of checking for carcinogenic chemicals is through animal tests. A control group is fed a normal diet while a test group is fed a normal diet plus heavy doses of the substance being investigated. After a few months the animals are checked for tumor growth. If the test group is found to have significantly more tumors than the control group, then the chemical is probably carcinogenic. Further investigation and research would then be conducted to confirm the results.

Chemicals under study are tested on at least two different types of animals, since animals react in various ways to certain chemicals. Whereas some animals may develop tumors, others may be unaffected. The major difference is in the way that the chemicals are metabolized—that is, how they are chemically changed in the body. A particular animal may metabolize some carcinogens in a way that renders them harmless. In other cases, although the chemical itself is not normally carcinogenic, it becomes carcinogenic when the animal metabolizes it. Also, even if a substance causes cancer in several varieties of test animals, it is not necessarily carcinogenic to humans. On the other hand, although arsenic (As) appears to be carcinogenic to humans, it is not carcinogenic to any type of animal in which it has been tested.

The testing of a chemical compound with laboratory animals requires a very large expenditure of time and money. It is impossible to use this method to test the thousands of new chemicals produced each year, much less to investigate the effects of the hundreds of thousands of chemicals already in use. Several less costly and faster tests are being developed, although none has yet proved reliable enough to completely replace animal testing.

In one simpler procedure-the Ames test-chemicals are tested to determine if they cause mutations in the common salmonella bacteria. (These bacteria cause food poisoning when food is not properly prepared.) The test identifies mutagens, but about 90 percent of the known carcinogens tested also give a positive result. Although not 100 percent accurate, the test is being used to screen thousands of compounds. A positive result doesn't prove that a compound is carcinogenic, but it does indicate that the compound should be further tested with animals.

We continue to read or hear about chemicals in wide use that are found to have carcinogenic effects. Here are just a few examples of such compounds.

- Many chlorinated hydrocarbon pesticides, such as DDT, aldrin, dieldrin, heptachlor, and chlordane, have been found to be carcinogenic. They have been banned from all but the most critical uses in the United States.
- 4-methoxy-m-phenylenediamine sulfate (4-MMPD) and some other compounds used in hair dyes have been found to cause

 \overline{O} CH₃

cancer in test animals. Because of a law passed by Congress in 1938, the Food and Drug Administration (FDA) cannot ban these "coal-tar" dyes from cosmetics, but they can require manufacturers to place a warning label on the products.

- Chloroform (CHCl₃) is widely used as a solvent in chemical laboratories and in the chemical industry. Before it was found to be carcinogenic, it was also an ingredient in some over-the-counter cough syrups.
- Benzene (C_6H_6) , used widely in chemistry laboratories and industrial plants as a solvent, increases the incidence of leukemia (cancer of the blood). Its use has been highly restricted.
- Polychlorinated biphenyls (PCBs) are compounds that have been found to be carcinogenic (section $E-6$). In 1979 their manufacture was banned.
- 2,2-dibromopropyl phosphate (IRIS) is a flame retardant that was applied to children's sleepwear until it was found to be carcinogenic. It is now no longer used.
- Saccharin, a commonly used artificial sweetener, has been a subject of much controversy. Extensive testing shows it to be weakly carcinogenic. It has been argued that its benefits (to diabetics and people with weight problems) outweigh the hazards.

This is just a sampling of the compounds investigated during the 1970s that were found to be carcinogenic. Some of these findings caused enormous disruptions in the chemical industry and other places where the compounds have been used. Because of the almost monthly announcements of additional chemicals being taken out of use, some people have the impression that all chemicals in general are carcinogenic or otherwise unsafe. Of course, this is a false impression. Probably only 10 percent or fewer of the known compounds are carcinogenic. But now that better methods of testing are available, some compounds that had been widely used for years and were thought to be safe are now being listed as carcinogenic. Therefore, every chemical that will come in contact with people should be fully tested to determine that it is safe.

Another group of chemicals that has come under close inspection includes the food additives. These chemicals prolong the "shelf life" of a food product, help it retain its appearance, or improve its taste. When a food additive is declared unsafe, we often read or hear statements such as "You'd have to drink three hundred bottles of it a day for the rest of your life to have any problems; so it's silly to ban it." This figure was obtained by adjusting the dose of additive per unit weight of the test animal to the average weight of a person. However, the argument ignores several important concepts. First, in order to get a meaningful result from an experiment that takes only a few months, test animals are fed massive doses of the tested compound. The effects on the test animals might be similar at much

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A POLYCHLORINATED BIPHENYL(PCB)

H

TRIS
2,3 – dibromopropyl phosphate

SOLUBLE SACCHARIN

TIME MACHINE

An antibiotic-producing culture is grown on a nutrient surface within a test tube.

lower doses over many years of exposure, but such an experiment is not possible because of the short natural lives of small test animals. Second, people are usually not affected in the same way that test animals are affected. Although people might be less sensitive to chemical substances than animals, to be on the safe side we must assume that people are at least as strongly affected as the test animals. Third, although typically only half of the animals in a test may develop tumors, we must be concerned about anything that would affect even a fraction of 1 percent of the human population. Keep in mind that 1 percent of the United States' population is about 2.2 million people!

Some people tend to believe that all natural things are good and harmless. But there are thousands of poisonous compounds within the natural environment, many of which are used by plants or animals as a protection against predators. Some natural compounds are also carcinogenic. For example, aflatoxins, which are produced by certain molds that form on food such as peanuts, corn, rice, and oats, are extremely carcinogenic. Just 1 ppb of aflatoxin can cause liver cancer in test animals. Although aflatoxins are occasionally found on foodstuffs in the United States, our methods of harvesting, drying, and storing grains and other foods usually preserve them in such a way that molds do not form. Aflatoxins cause more serious problems in countries located in the tropics, where the hot and wet climate promotes the growth of mold.

In our thinking about carcinogenic and otherwise toxic chemicals or, for that matter, any of the dangers associated with technological societies, it is essential that we maintain our sense of perspective. Any change to our environment risks upsetting its balance, but we must be careful to weigh the possible dangers of change against the benefits we hope to achieve.

PROBLEMS

- 1. To get a feeling for the efficiency of the transfer of nutrients from one trophic level to another, calculate the number of days it takes you to consume an amount of food equal to your own mass. You can assume that you consume about 1 kg of food per day, or determine your own specific quantity.
- 2. Suppose that the concentration of a pollutant is 10 ppb in phytoplankton at the first trophic level. Assume that all of the pollutant is retained in the body of the consumer at each higher trophic level. If the transfer of energy and nutrients from one level to the next is 10 percent, calculate the

concentration of the pollutant that would be expected in the consumer at the fifth trophic level.

- 3. Explain the logic by which cancer experts have concluded that 80 percent or more of cancer cases are caused by local environmental factors.
- 4. Briefly describe the three main methods by which we determine if chemicals are carcinogenic or mutagenic.
- 5. When a food additive is banned from use because it is found to be carcinogenic, we may read or hear statements such as "You'd have to eat a hundred pounds of it a day to cause a problem." Explain the fallacy of this kind of statement.

The Air Environment

Have you ever approached a city from the surrounding countryside and observed a dark haze hanging over the expressways and skyscrapers? This foglike veil over the skyline is caused by a form of pollution—air pollution. In heavily populated areas, air pollution is a serious environmental problem. Is it a problem in less populated areas? Is air pollution a problem in your area? Everyone agrees that we should clean up the air, but is it possible to do so while also providing for our energy needs?

A ground inversion, caused by fog and industrial smoke, along with a lack of wind formed a smog layer that hung over St. Louis, Missouri.

Industrial pollution, such as particle emissions from burning fuels, is now controlled by antipollution regulations.

Composition of the Atmosphere by Volume (%)

E-26 Airing the Problem

We live at the bottom of a "sea" of air that is held to our planet by Earth's gravitational field. The pressure of the atmosphere is produced by the weight of air at higher altitudes pushing downward. At sea level the pressure caused by the overlying air is about 1 atm (atmosphere). This is the same as 1.01×10^5 Pa (pascals), or 101 kPa (kilopascals), in SI units. If we fill a glass tube with mercury (Hg), invert it, and place the open end in a vat of mercury, the pressure of air on the surface of the mercury at 1 atm is enough to support a column of mercury 76 cm high. Gas pressure is commonly measured in terms of centimeters of mercury.

As we move to higher altitudes, the air becomes "thinner"-that is, the air pressure drops because there is not as much overlying air pushing down. At about 5.5 km, the air pressure is half the sealevel value. The drop in air pressure with increasing altitude is the opposite of exponential growth. The pressure drops by about half for every 5.5-km increase in altitude, so that at 11 km it is down to about one-fourth of sea-level pressure. Small amounts of gas exist above 100 km, but about 95 percent of the mass of the atmosphere lies below 20 km.

The mass of our planet's atmosphere is about three hundred times less than the mass of the hydrosphere (the water of the Earth). But the atmosphere is just as important in sustaining life on Earth: it provides both the oxygen (O_2) for people and animals to breathe and the carbon dioxide $(CO₂)$ for photosynthesis in plants, and it distributes water from oceans and lakes back to land in the form of rain. Along with the hydrosphere, the atmosphere also distributes heat over the Earth so that temperatures are tolerable in winter, at night, and at midday. By comparison, temperatures on the dry, airless moon range from 115° C in daylight to -184° C in darkness.

Clean air consists mainly of nitrogen (N_2) , oxygen, argon (Ar) , carbon dioxide, and variable amounts of water vapor, along with hundreds of other substances in trace amounts. In polluted air, however, one or more of the substances that are usually present in only trace amounts are found to exist in much higher concentrations. These pollutants can cause serious environmental and health problems.

What substances cause the problem of air pollution in our environment? There are six classes of pollutants of major importance near ground level:

- \bullet sulfur dioxide (SO₂),
- carbon monoxide (CO),
- nitrogen oxides (NO and NO₂, referred to collectively as NO_x),
- hydrocarbons (HC, a wide variety of compounds containing carbon and hydrogen),

- particulate material (materials made of particles larger than molecular size, but small enough to remain suspended in the air for hours or days), and
- photochemical oxidants (a group of strong oxidizing agents). By far, the main member of this group of pollutants is ozone (O_3) .

Five of the six classes of pollutants are emitted directly from $\begin{pmatrix} 1 & \text{dist} & \text{HEARD} \\ \text{FARI} & \text{Coulz} & \text{Coulz} \end{pmatrix}$ sources such as fuel combustion (especially in power plants), motor vehicles, industrial plants, and the incineration of solid wastes. These five classes are known as *primary* pollutants. Air pollutants in the sixth major class (photochemical oxidants) are formed by chemical reactions that involve the primary pollutants; therefore, the members of this class are called secondary pollutants.

'Mostly hydrocarbons, but excludes methane (CH,) and some other weakly reactive substances.

Transportation and industry have been major causes of air pollution in heavily populated areas. What is the air quality near the highways and industrial sites in your area?

FUMIFUGIUM:

0 A, The Inconvenience of the A E R, A N D SMOAKE of LONDON D I S S I P A T E D. TOGETHER With fome REMEDIES humbly propofed By J. E. Efq; To His Sacred MA JES TIE, A N D To the PARLIAMENT now Affembled. Publifbed by His Majefties Command. Lucret, I. c. Carbonumque gravis vis, aque odor infinustur Quam facile in cerebrum?-

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Perhaps the first scientific look at the problems of air pollution, this book was presented in London to King Charles II and Parliament in 1661.

TIME MACHINE

1775 Sir Percival Potts in England recommends that chimney sweeps bathe more often to reduce the incidence of cancer from contact with soot.

In 1971 the Environmental Protection Agency (EPA) established air-quality standards for six classes of air pollutants. These standards were designed to protect human health and to aid in cleaning up the atmosphere. They state the maximum amounts of air pollutants permitted over specific periods of time. In 1978 the EPA added a seventh standard for atmospheric lead (Pb). This substance typically makes up 1 to 2 percent of the particulate matter in urban air.

'Averaging time is the period of time during which air samples are taken in order to calculate the average concentration of each pollutant.

tNot to be exceeded more than once per year. f Not applicable.

The existence and enforcement of air-quality standards may not result in an air environment that is acceptable to everyone. (For example, environmentalists and industrialists have disagreed about how much impact these standards will have on our health and on the "cost" of cleaning our air.) But there is agreement that when the standards are not exceeded, the atmosphere is cleaner and more healthful.

"Hello," Sulfur Dioxide

One air pollutant has been blamed for more sickness, death, and destruction than any other. This pollutant is sulfur dioxide (SO_2) , including the secondary products formed by reactions of $SO₂$ with the air. For centuries many of the world's cities have been plagued

п.

with air that has a high concentration of SO_2 . This problem is especially serious in places where large amounts of coal (which contains sulfur) are burned; one by-product of this burning is SO_2 .

 $S(s)$ + $O_2(g)$ \longrightarrow $SO_2(g)$

There are three major sources of $SO₂$ in our air. More than half of the $SO₂$ is produced by electric power plants that use fuels such as coal and oil, which contain 0.5 to 5 percent sulfur as an impurity. The second-largest source of SO₂ production is fuel combustion by $\frac{1}{\sqrt{700\text{AV}}}\frac{1}{11447}$ YOU COUDN. industry.

Sulfur dioxide is also formed by industrial processes that extract metals from the sulfide ores of iron (FeS or FeS₂), zinc (ZnS), copper (CuS), and lead (PbS). During this extraction process the sulfur is "burned" away in the presence of air, releasing $SO₂$. An example of this process is the extraction of copper from copper sulfide.

 $CuS(s)$ + $O_2(g)$ ------> $Cu(s)$ + $SO_2(g)$

Sulfur dioxide released into the atmosphere does not remain there indefinitely. Some of it is eventually deposited at ground level, especially when it rains, and some is slowly converted to

Atmospheric pollution in Chicago is being monitored from the top of the John Hancock Center. A solar-radiation detector is used to determine the amount of haze in the atmosphere. Continued development of similar instruments will lead to more accurate measurement and better control of airborne pollutants and their sources.

TIME MACHINE Air Pollution

laws restricting smoking in public buildings and on public transportation.

sulfuric acid $(H₂SO₄)$ droplets and sulfate particles. An intense research effort is now in progress to find out how $SO₂$ is transformed into these products; if we knew the process, we might be able to control it. Although we're not sure of the oxidizing agent, some SO_2 may be oxidized to sulfur trioxide (SO₃) gas.

Sulfur trioxide is the anhydride of sulfuric acid. In other words, if $SO₃$ is added to water—such as fog droplets in the air—it forms $H₂SO₄$.

 $SO₃(g)$ + H₂O(*l*) \longrightarrow H₂SO₄(aq)

Other processes that form sulfuric acid may be equally important or more so under some atmospheric conditions. For example, SO_2 may deposit on particles that contain catalysts such as carbon soot, or salts of iron (Fe), manganese (Mn), or vanadium (V), which speed up the reaction of $SO₂$ with oxygen.

in London. Visibility is reduced to 1 m December 1952 London was covered with a thick fog that lasted for London was once one of the world's most heavily polluted cities. Since most of its buildings were heated with coal, the city's chimneys released enormous amounts of $SO₂$ and particles into the air. These pollutants mixed with the heavy fogs that blanketed the city and gave it an appearance that Londoners termed "pea soup." Some of these atmospheric mixes have proved to be lethal. In several days. After it cleared, health records revealed that more than four thousand deaths could be linked to this one incident.

> Cities in the United States have had similar incidents. In 1948 an industrial plant located in a valley in Donora, Pennsylvania, emitted $SO₂$ and particles that became trapped in stagnant air. What occurred was an atmospheric inversion. A warm upper layer of air trapped the cooler layers of air below, thereby keeping the pollutants in the valley. Six thousand residents became ill and twenty deaths were attributed to air pollution. During November 1966 an atmospheric inversion of stagnant, polluted air was responsible for many deaths over much of the east coast, including over one hundred deaths in New York City.

> Many of those who die as a result of such air-pollution épisodes are people who have had severe respiratory problems. Other people with conditions such as chronic bronchitis or related respiratory ailments find that their conditions are seriously aggravated when these episodes occur.

> Recall that in order to reduce the severity of air pollution effects, the EPA set standards for various air pollutants, including $SO₂$ (section E-26). The yearly standard for the concentration of SO_2 was set at 80 μ g/m³ (micrograms per cubic meter) of air. This amount could be stated as about 30 ppb of $SO₂$ in air, that is, 30

molecules of $SO₂$ for every billion air molecules. According to governmental standards, the $SO₂$ concentration averaged over an entire year should be less than 80 μ g/m³, and during any 24-hour period the average should not exceed 365 μ g/m³ more than once per year.

Of course, when Congress passes a law or the EPA sets a regulation stating that the concentration of a pollutant should not exceed a certain value, the law or regulation by itself does nothing to make it happen. In the case of air pollutants, the country is divided into many air-quality control regions where pollutants are measured. If some pollutant concentrations are found to exceed the standards, states must develop "implementation plans" for reducing pollutant levels. Some of these measures are discussed in the following section.

Pollution Scale for Measuring Air Quality

A value for air quality known as the Pollution Standard Index (PSI), or the Air Quality Index (AQI), is often reported along with the daily weather reports. The EPA standard for each pollutant is assigned a PSI value of 100. The PSI value reported in the news media each day usually refers to the air pollutant with the highest concentration compared with its EPA standard.

70

The release of SO₂ affects nonliving materials (above) as well as living plants and animals. Over a half-century ago, SO₂ from a copper-smelting plant destroyed the vegetation on this land in Tennessee (below), causing lasting effects.

E-28 Controlling SO_2 —Then What?

Several measures were taken during the late 1960s and early 1970s to lower $SO₂$ concentrations in heavily populated areas. Local regulations prohibited the burning of high-sulfur fuels in cities. Power companies were forced to build any new plants well outside city limits. Newly constructed power plants and other sources of $SO₂$ pollution (such as smelters) were required to build emission stacks 200 to 300 m in height. Released at these higher altitudes, SO_2 remains airborne for longer periods of time and becomes diluted before it settles back to ground level. These measures have proved successful: $SO₂$ concentrations in the air of cities in the United States have decreased over the past several years.

Unfortunately, as $SO₂$ concentrations were being reduced, the results of new studies suggested that SO_2 , by itself, may not be the main air-pollution culprit endangering our health. An EPA study compared the health records of people in communities exposed to high levels of a variety of air pollutants with records of people living in areas with clean air. The results of this study indicate that H_2SO_4 and sulfates such as ammonium sulfate, $(NH_4)_2SO_4$, are much more damaging to health than $SO₂$ by itself. (Although the design of the EPA study has been criticized, studies with animals appear to confirm the conclusion.) These findings are not surprising, especially in the case of H_2SO_4 , since it is a strong acid. Sulfuric acid and sulfate salts can cause inflammation and swelling of the respiratory tract and narrowing of the respiratory passages, which impairs breathing. Besides being very irritating to humans,

 $H₂SO₄$ is also damaging to almost anything with which it comes into contact-from vegetation to buildings. Much of the extensive discoloration and decay of building facades over the past century are the results of $SO₂$ and its by-products in the atmosphere reacting with limestone $(CaCO₃)$, a commonly used building material. This reaction leads to a powdering or blistering of the surface of the stones and to eventual deterioration of the building. Outdoor art treasures in cities such as Rome have suffered more damage from air pollution in the twentieth century than in all the past centuries of their existence. Wind and weather also contribute to the erosion of buildings and statues, but the major culprit is the toxic chemical process that destroys the limestone.

CALCIUM CARBONATE
(limestone) SULFURIC ACID

(limestone) SULFURIC ACID CALCIUM SULFATE WATER CARBON DIOXIDE
CaCO₃(s) + H₂SO₄(aq) -----> CaSO₄(s) + H₂O(l) + CO₂(q) (Iimestone) SULFURIC ACID CALCIUM SULFATE WATER CARBON DIOXIDE
CaCO₃(s) + H₂SO₄(aq) ------> CaSO₄(s) + H₂O(l) + CO₂(g)

E-29 Sulfuric Acid in Action

You can determine the effects of sulfuric acid on various materials by testing samples found in your environment. Collect as many types of samples as possible. These can include pieces of concrete, marble, limestone or other rocks, glass, different types of metals, colored fabrics, paper, cardboard, and a leaf from a plant.

Place each material in a watch glass. With a medicine dropper place a single drop of dilute H_2SO_4 solution on each material. Let the solution remain on the materials for a while. Which materials are most affected by the acid? Which are least affected? Discuss your results and relate these to the problem of H_2SO_4 in your environment.

miniexperiment

Since sulfates and H_2SO_4 result from SO_2 reactions, one would suppose that the lowering of $SO₂$ levels would also reduce conis not the case: although $SO₂$ levels have been dropping, sulfate levels have remained approximately the same.

centrations of these other substances in the air. Unfortunately, this
is not the case: although SO₂ levels have been dropping, sulfate
levels have remained approximately the same.
How can this be explained? The pollutio How can this be explained? The pollution-control measures taken thus far have resulted in the release of $SO₂$ outside densely populated areas or else at higher altitudes. Therefore, the concentration of $SO₂$ in the air over cities has decreased, but the total amount of $SO₂$ emitted hasn't been significantly reduced. The total quantity of SO_2 released in 1977 was 24.7 million metric tons, only slightly less than the 29.8 million metric tons released in 1970.

The problem with sulfates and sulfuric acid is that they are formed slowly over a period of several days and over great distances as the sulfur dioxide is carried along by winds. The sulfuric

acid you breathe in Cleveland may come from Chicago; so the power plants located outside Cleveland may have little effect on the sulfuric acid concentration in the Cleveland air. Since the air that generates sulfuric acid and sulfates passes over rural areas between cities, the "clean" areas also suffer high concentrations of these pollutants.

In this way sulfates have become a regional problem. A particular city or state cannot reduce sulfate levels just by controlling its own sulfur dioxide emissions. Only a combined effort by all areas within a radius of about 1000 km will solve the problem. An area of special concern is the northeastern United States-east of the Mississippi River and north of Tennessee. Heavy industry and electric-power generation, especially through the Ohio Valley, in this region create very high emissions of sulfur dioxide. Prevailing winds cause the area from Illinois to the eastern seaboard to have some of the nation's highest sulfate levels. As late as 1979 there was no air-quality standard for sulfates, but one was anticipated by late 1981.

When sulfates are carried as very fine particles in the air, they cause much of the "haze" associated with air pollution (section E-33). Therefore, we frequently find huge rural areas of the eastern United States covered by a haze of sulfate particles, especially in summer when sulfur dioxide converts to sulfate most rapidly.

E-30 It Isn't Raining Rain

Another problem related to air pollution is acid rain. Very pure water has a pH of 7. Rainwater that falls in areas with unpolluted air has a pH of about 5.6. It is more acidic than pure water because the absorption of carbon dioxide $(CO₂)$ from the atmosphere forms carbonic acid (H_2CO_3) . But rain falling in areas that have polluted air frequently has a pH of 4 or less. When this acidic water runs into lakes, it can change the pH of the receiving water enough to make it uninhabitable for the fish and vegetation normally found there.

Despite our efforts to control air pollution, the problem of acid rain seems to be getting worse instead of better. For example, in the eastern United States and southeastern Canada, surveys comparing the pH of rainwater in recent years with that of about twenty years ago indicate as much as a tenfold increase in acidity. The situation seems to be similar in other industrialized nations where oxides of sulfur and nitrogen pollute the atmosphere.

The acid-rain problem has been under extensive investigation since 1976 through the use of large networks of rain collectors, especially in the eastern United States. These are operated by the Environmental Protection Agency and many state Agriculture Experiment Stations. Agriculturists are involved in this research because of their concern about the effects of acid rain on crops.

AVERAGE pH OF ANNUAL PRECIPITATION 1955-1956

AVERAGE pH OF ANNUAL PRECIPITATION 1972-1973

Note that the contour for pH 4.52 covers a much larger area in this graph than in the graph for 1955-1956.

In a controlled-environment center a scientist studies the effects of acid rain on a wide variety of plants. High levels of acid rain can kill certain types of plants and probably reduces crop yield in others. Acid rain prevents some plants from forming viable seeds or fruits.

clean containers to collect your samples. If possible, collect rainwater from different areas. Immediately after a rainfall, test your samples for pH either right in the field or back in the laboratory. In the field you can measure the pH of the water with pH paper; if you are in the laboratory you can use either pH paper or a pH meter. Record your values and compare the results with those found by other members of the class.

Questions: What is the range of pH values of rain in your area? Are there any locations with low pHs? If so, are they close to a source of pollution that releases large amounts of $SO₂$? Discuss your observations.

A temperature inversion holds smoke from $E-32$ industrial areas over Chicago.

Can Anything Be Done?

Although measures taken so far have reduced the exposure of urban populations to SO_2 , these measures have not lowered the levels of the actual problem makers— H_2SO_4 and sulfates. What can we do about the problem of sulfates, especially those produced by the combustion of coal, the largest source of $SO₂$? We could burn low-sulfur (<1 percent) coal, of which we have substantial reserves in the western part of the country. But then we face the problem of transporting this coal to the east coast, where there is a greater need for it.

Some sulfur can be removed from coal before the coal is burned. About half of the sulfur in coal is in inorganic forms (mostly pyrite, FeS₂) and can be removed fairly easily. But the remaining sulfur is bound to carbon compounds, and the present process of removing it is very costly. Several other processes are under development, but all of them would ultimately increase the cost of coal. As discussed in section E-63, scientists are working on processes to convert coal into a clean-burning gas or liquid, but at this time these fuels are more expensive than petroleum and natural gas.

Perhaps the most controversial process for limiting power-plant emissions of sulfur oxides $(SO₂$ and $SO₃)$ involves the use of scrubbers to remove the SO_2 and SO_3 from exhaust gases before they leave the emissions stacks. Scrubbers are devices that spray water—or an aqueous solution such as limewater, $Ca(OH)₂$ —as a fine mist into the exhaust gases in the stacks to remove watersoluble substances. The most common approach is the wet lime-limestone process. Powdered limestone (mostly calcium carbonate, $CaCO₃$) is mixed with the pulverized coal and injected into the combustion zone. At the high temperatures that exist there, the limestone decomposes.

The SO_2 and SO_3 released from the coal then react with the CaO to produce calcium sulfite (CaSO₃) and calcium sulfate (CaSO₄). The stack is then "scrubbed" with a solution of $Ca(OH)_2$, which collects the CaSO₃ and CaSO₄ and reacts with any remaining SO_2 or SO_3 . Although technically feasible, this operation adds about 10 percent or more to the cost of electricity. In addition to buying the lime or limestone, the power companies must dispose of vast amounts of $CaSO₃$ and $CaSO₄$. There is much debate about the need for this process in coal-fired plants. However, if we must burn additional coal to cope with our energy needs, something will have to be done to prevent further deterioration of our air quality.

In some situations SO_2 can be considered a "resource-out-ofplace." In places where strong sources of $SO₂$ exist (mainly sulfide ore smelters), methods are being used to convert the $SO₂$ into $H₂SO₄$, a useful product. At present it is not economical to convert SO_2 from power plants into H_2SO_4 ; however, if it does become feasible, this source could supply nearly all of the H_2SO_4 used by the chemical industry.

E-33 On a Clear Day

Our major cities rarely have days with truly clear skies. Even when the sun is shining brightly we seldom can see the skyline several kilometers away. The smog or haze that blankets the city of Los Angeles is often so thick that it is difficult to see the mountains that surround the city.

Polluted air contains gases and suspended particles. Most of the gases are colorless except for nitrogen dioxide $(NO₂)$, which is reddish brown. It is the particulate matter that causes the haze in the air. Light hits the particles and either bounces off (light scattering) or is absorbed. When these events occur, less light gets through the atmosphere to reach your eyes, and the sky appears darker. The suspended particles cause objects only a kilometer away to look fuzzy, whereas in clean air objects remain distinct even at a distance of 100 km.

Atmospheric particles can be traced to many sources. Erosion of rocks and soil by wind, the bursting of water bubbles at the surface of the sea, and the explosions of volcanoes are a few of the natural sources of particles in the air. Fuel combustion in power plants and industrial processes are large sources of particles produced by human activities. In addition, all vehicles that use leaded gasolines emit large quantities of particles that contain lead, and diesel engines release fine particles of carbon soot.

Skyscrapers in New York City are barely visible through the air pollution that hangs over the city.

Some Sources of Atmospheric Particles

An emissions particle from a coal-fired power plant-magnified 2000 times. Photograph courtesy of Roger J. Cheng.

EXPERIMENT

Some particles released into the atmosphere are so large that they fall to the ground almost immediately. But most particles with radii of less than 1 μ m (micrometer; 1 μ m = 10⁻⁶ m = 10⁻³ mm) are so small that they remain suspended in the atmosphere for a few days. These suspended particles affect health, visibility, global weather, and climate. It is these fine particles that cause most of the light scattering because they are about the same size as the wavelength range of visible light—from violet (400 nm = 0.40μ m) to red $(750 \text{ nm} = 0.75 \text{ }\mu\text{m}).$

In the following experiment you will demonstrate the light scattering of growing particles by setting up a reaction that forms colloidal sulfur in a water solution. This light-scattering phenomenon is known as the Tyndall effect.

E-34 Light Scattering

You will need a large, rectangular glass tank-such as an aquarium-a slide projector, and a screen (or a light-colored wall). Place the tank between the projector and the screen and fill it about three-fourths full of water.

A suspension of colloidal sulfur in water can be produced by the following chemical reaction.

Turn on the projector and add 100 cm³ of 0.1 M sodium thiosulfate $(Na₂S₂O₃)$ and 100 cm³ of 0.1 M hydrochloric acid (HCI) to the water. Stir; then observe the beam of light as it passes through the solution in the tank. As the particles form, they grow in size. The particles will continue to grow and more particles will form until almost no light is transmited through the suspension.

Remember, the colloidal-sized sulfur particles are suspended in the water, not dissolved in it. Several hours after the experiment, you may find that the sulfur particles have grown large enough to have settled to the bottom of the tank.

QUESTIONS:

- 1. What was the color of the light as it was first scattered by the particles in the solution?
- 2. What was the color of the light you first saw on the screen? Can you explain this observation?
- 3. As the particles grew, how did the colors of the scattered and transmitted light change? Can you explain these changes?
- 4. What was the color of the light that was last transmitted through the solution?
- 5. From this information can you explain why the sky is blue when the sun is overhead and why the sun often appears to be reddish orange as it is setting?

E-35 Particles We Breathe

Most airborne particles fall within two size ranges. The group with larger radii—between 2 and 20 μ m—is relatively harmless. These particles are formed by mechanical or abrasional processes such as grinding and erosion of rocks and soil by wind, and they include the rocklike fragments released when coal is burned. This group of particles consists mostly of common, nontoxic elements such as aluminum (Al), silicon (Si), oxygen (0), calcium (Ca), and potassium (K) —elements that comprise most of the Earth's crust. The major exception to the harmless nature of these larger particles occurs in the case of those that come from the mineral asbestos. But in general, the more harmful forms of pollution, as well as light scattering or haze, are the results of smaller particles that have radii of less than $1 \mu m$.

When coal, oil, or gasoline is burned, high temperatures cause the volatile elements in these fuels to vaporize and become gases. As these exhaust gases cool, certain substances condense to form fine particles. Many toxic elements such as arsenic (As), selenium $\frac{\text{minmin} \, \text{min} \, \text{$ (Se), and cadmium (Cd) are volatile, and as they condense they are usually deposited on the fine particles in the atmosphere. Many of the chemicals that are released into the atmosphere as gases also settle on fine particles—the sulfates and sulfuric acid formed from SO_2 , the ammonium ion (NH₄⁺) formed from ammonia gas (NH₃), and the nitrates formed from NO and $NO₂$.

The total mass of particles emitted into the atmosphere is monitored by government agencies that have set up regulations for their control. These laws state that particulate matter in the atmosphere must be kept to less than 75 μ g/m³ (section E-26.) Most of the steps taken in various communities to achieve this level have eliminated the large particles from the air, but not the smaller ones. Unfortunately, a specific standard has not yet been set for the finer particles that cause the more serious problems.

The worldwide concern over air pollution and its effects on living organisms is illustrated in this stamp from Hungary.

SURFACE OF NORMAL LUNGS

DAMAGED LUNGS

Fibers in the mineral asbestos (above) and a microscopic view of the cancer-causing fibers (below).

When we breathe in particles from the air; those with radii greater than about $5 \mu m$ are large enough that most are captured by the hairs of the nostrils and the moist membranes of the passages leading to the lungs. These stop some of the small particles also, but about half of them do reach the lungs. When this happens, the lungs have a defense mechanism that removes the particles. The insides of the lungs are coated with sticky mucus, which traps the particles. Tiny, hairlike structures called cilia wave back and forth and gradually clean the lungs.

After many years of exposure to urban air pollution, the lungs may slowly deteriorate, just as they may be damaged by the personal "air pollution" of smoking cigarettes. Damaged lungs lose much of the cleansing action that the cilia and mucus provide, and particles then remain lodged in the lungs, causing serious health problems. Many of the particles in polluted air are carcinogenic. These particles are produced whenever a person drives a car, burns wood in a fireplace, charcoal-broils a steak, burns coal or oil in a furnace, or smokes a cigarette.

Some kinds of particles can be retained even in healthy lungs. An example of this type of troublesome particle is asbestos, a naturally occurring mineral that contains long double chains of tetrahedrons consisting of atoms of silicon, aluminum, and oxygen. Because of its chainlike structure, asbestos is separated into fibers and woven into a heavy cloth. This heavy cloth, as well as other forms of asbestos, has many important uses. Because of their mineral qualities, materials produced from asbestos are fireproof and make good electrical insulators. Asbestos is used extensively in brake linings, electric insulation, fireproofing for buildings, and insulation around furnace pipes.

Unfortunately, it has been found that workers in the asbestos industry have rates of lung cancer far greater than the rate of lung cancer in the overall population. Upon close investigation, it was found that tiny, needlelike fibers of asbetos become embedded in lung tissue. Since they are mineral particles, they are not dissolved or removed by body fluids. These particles may remain in the lungs for years, causing constant irritation and leading to the formation of lung cancers. Asbestos also poses a threat to the general population because so much of it is present in our surroundings. Many school buildings have had to be remodeled to remove large amounts of asbestos that had been used as building materials.

Asbestos can also be a water pollutant. Some mining companies recover iron from an ore known as taconite. The ore contains much rock material that must be removed, and this material contains asbestos. For a period of over ten years, one mining company dumped 60 000 metric tons of this material per day into Lake Superior. Such activities may be the reason that asbestos fibers

have appeared in the drinking water of Duluth, Minnesota. Environmental and governmental groups have therefore been fighting to stop disposal of the mine tailings in the lake.

PROBLEM **Letter and the contract of the contra**

Choose one of the problems covered in this section and discuss how it affects you and the area where you live. What would you suggest as a means of controlling the problem or of stopping the problem altogether?

E-36 Automobile Exhaustion

Automobiles are a major source of several types of air pollutants hydrocarbons (HC), nitrogen oxides (NO_x), and carbon monoxide (CO). The incomplete burning of gasoline in automobile engines causes the emission of HC and CO. If a car's engine were completely efficient (resulting in complete combustion), the chemical reaction would be similar to that for the complete combustion of octane (one of the many HC compounds in gasoline).

 $2 C_8H_{18}(l) + 25 O_2(g) \longrightarrow 16 CO_2(g) + 18 H_2O(g)$

However, there is usually not enough oxygen in the engine cylinder to react completely with all of the HC. This means that there is incomplete combustion and that some of the carbon emitted in the exhaust is in the form of CO instead of $CO₂$.

 $2 C_8 H_{18}(l) + 17 O_2(g) \longrightarrow 16 CO(g) + 18 H_2O(g)$

Carbon monoxide is a colorless, odorless gas that is poisonous. When inhaled, it replaces oxygen in the bloodstream, and if it replaces 60 percent or more of the oxygen in the blood, the brain

does not receive enough oxygen to function properly. So if a person is subjected to high concentrations of CO (several thousand parts per million)—such as when running an engine in a closed garage or riding in a car with a faulty exhaust system—death can occur. At lower CO concentrations, less serious problems such as headaches and nausea result.

The average concentration of CO in most cities is below 10 ppm. Although levels of 10 ppm or less do not cause serious problems, levels as high as 100 ppm frequently occur in traffic tunnels, parking garages, and busy intersections. Workers in those areas or drivers caught in traffic tie-ups often become uncomfortable and less mentally alert. Average smokers have a CO concentration of about 5 percent in their hemoglobin all day. Tests have shown that students do not do as well on math problems even at CO hemoglobin concentrations as low as 2 percent! At present it is not known if there are any chronic effects of long-term exposure to low levels of CO.

E-37 Photochemical Smog

There are many sources of hydrocarbons and other organic compounds in the atmosphere. When there is incomplete combustion, some unburned hydrocarbons are emitted in automobile exhaust. In addition, volatile hydrocarbons evaporate from fuel tanks or are lost to the air as the tank is being filled. Other organic compounds evaporate into the air from industrial and dry-cleaning plants and as solvents from freshly painted surfaces. Large amounts of hydrocarbons and other organic substances are released naturally from vegetation—evaporated from trees and plants and emitted from decaying material in swamps.

The major gases that compose air are nitrogen (N_2) and oxygen $(O₂)$. When air is drawn through a hot engine, the high temperatures cause the molecules of these gases to react to form nitrogen oxides—principally nitric oxide (NO).

$$
N_2(g) + O_2(g) \longrightarrow 2 NO(g) \qquad (1)
$$

In the atmosphere NO is further oxidized to form nitrogen dioxide $(NO₂)$ by reactants such as ozone $(O₃)$.

$$
NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \qquad (2)
$$

Nitrogen oxides and hydrocarbons are the principal substances that form photochemical smog when they react with the energy of sunlight. Photochemical smog is the air-pollution problem that has historically plagued the cities of southern California, but it has become a serious problem for other cities as well, especially during hot weather.

When ultraviolet (UV) light from the sun strikes molecules of NO₂, free oxygen atoms are sometimes released.

$$
NO_2(g) + UV light \longrightarrow NO(g) + O(g) \qquad (3)
$$

These free, highly reactive, oxygen atoms react with atmospheric O_2 molecules to form O_3 .

$$
O(g) + O_2(g) \longrightarrow O_3(g) \qquad (4)
$$

As shown in reaction (2), O_3 reacts with NO, producing more NO₂. Reactions (2) through (4) wouldn't cause much of a problem if they were the only reactions that occurred. Note that they form a cycle: the O_3 used up in (2) is regenerated in (4). The same kind of cycle occurs for the other reactants. As long as sunlight is available (to provide energy for the reactions), there is an equilibrium among the three compounds, NO, NO₂, and O₃.

Unfortunately, another complex set of reactions occurs on warm, sunny days. These reactions—which involve CO, HC, and NO_x are so complicated that scientists don't yet fully understand them, although some of the results are known. Nitric oxide is converted into $NO₂$, among other things; then, because of reactions (2) through (4), more O_3 is produced. This sequence of events is shown by the typical concentration pattern of NO, $NO₂$, and $O₃$ throughout the day in Los Angeles.

The concentrations of NO and O_3 in the air of Los Angeles are usually low early in the morning. But later in the morning, when automobile traffic is heavy, NO from automobile exhaust builds up. Photochemical reactions gradually convert NO into $NO₂$, which causes O_3 to build up. As the day progresses, NO_2 and O_3 are gradually reduced because of decreasing sunlight, reactions with other chemicals in the air, and dispersal by the wind. Other types of photochemical reactions that also occur under warm, sunny conditions produce a variety of organic chemicals known as aldehydes and ketones. In addition, some organic compounds react with NO_x to form a family of compounds called peroxyacyl nitrates (PANs).

TYPICAL URBAN CONCENTRATIONS OF NO, NO₂, AND O₃

Most smog-related problems are caused by ozone, aldehydes, ketones, and PANs. These substances are known as photochemical oxidants—photochemical because they are formed in reactions initiated by light, and oxidants because most are strong oxidizing agents (section E-26). Photochemical products, especially ozone, attack rubber and destroy its strength and elasticity. They irritate human membranes and eyes and damage flowers, vegetables, and trees. Although ozone is present in much greater concentrations than the other photochemical oxidants, most of the human irritation is thought to be caused by aldehydes, ketones, and PANs. Studies have shown that high smog levels decrease the performance of athletes, but the long-term effects of smog on our health are not yet known.

At one time smog was considered a phenomenon restricted to Los Angeles. But we now find that on hot, sunny days in both urban and rural areas of the eastern United States the levels of ozone are frequently above the EPA standard of 120 ppb. In Washington, D.C., for example, all of the air pollution alerts between 1974 and 1976 were the result of high oxidant levels in the air.

Reactions that form photochemical oxidants occur slowly. Winds often carry polluted air from one city to the next. Depending on the direction of the wind, auto exhausts released in New York City in the morning may form ozone in Boston by late afternoon. We can't solve oxidant problems on a local basis; only measures taken regionally or nationally will help alleviate these conditions.

EXPERIMENT E-38 NO₂ Ways About It

Sample-collecting device: A small 50-cm³ Erlenmeyer flask or a large 50-cm3 test tube can serve as a container for a sample-collecting device (sampler). When using your sampler be sure that the tip of the medicine dropper is positioned close enough to the bottom of the container to be covered by the absorbing reagent, but not so close that the air flow is stopped. A bicycle pump, or a similar device, must also be calibrated for air sampling. Work with your teacher to set up this device.

Now you are equipped to collect your air sample. Note: It is important that you do not place reagents in the sampler until you are in the field and ready to collect a sample.

Sample collection: Place 25 cm³ of the $NO₂$ absorbing reagent in the flask and connect the sampler to the pump.

To collect a sample, pass about 10 000 cm^3 of air through the absorbing reagent in the sampler. To calculate the number of pump strokes to use, divide 10 000 cm3 by the volume of your pump per stroke. Be sure to count the number of pump strokes you use. Once you have passed 10 000 cm³ of air through the reagent, the sampling is complete. Disconnect the sample container from the sampler and stopper it. Now you are ready to test the sample in the laboratory.

Standard preparation: Place a range of standard sodium nitrite solutions $(0, 0.5, 1.0, 1.5,$ and (2.0 cm^3) in five separate 50 -cm³ graduated cylinders. Then with NO₂ absorbing reagent, dilute each graduated cylinder to 25 cm³. Next, add 1 cm³ of hydrogen peroxide, 10 cm³ of sulfanilamide, and 2 cm³ of N-NED reagent to the solution in the cylinder. Allow 10 minutes for color development. Pour each standard into a large labeled test tube and place the tubes in order in a test-tube rack. They will be used later for sample comparison. The standards you have just made contain 0, 0.006, 0.012, 0.018, and 0.024 mg of $NO₂$, respectively.

Sample analysis: Pour the sample you collected in the field (absorbing reagent) into a 25-cm³ graduated cylinder, and if necessary add additional absorbing reagent to bring the volume to 25 cm^3 . Place 20 cm^3 of this sample in a 150 -cm³ beaker. Then add 1.0 cm^3 of hydrogen peroxide solution, 10 cm^3 of sulfanilamide solution, and 2.0 cm^3 of N-NED reagent to the sample in the beaker. Allow 10 minutes for color development.

When you have completed these steps compare the color of the unknown air-sample solution with the colors of the standards. After you have matched your sample to the NO₂ standard with the closest color, you will have an estimate of how much $NO₂$ (in milligrams) is present in your air sample.

Calculations: To calculate the $NO₂$ concentration in the air, use the following equations.

 $NO_2(\mu g/m^3)$ = $\frac{mg NO_2 \times 1000 \ \mu g/mg}{\text{volume of air (cm}^3) \times 0.000 001 \ m^3/cm^3}$ $\frac{mg\,NO_2}{\text{volume of air (cm}^3)} \times 1000\,000\,000$

In your report be sure to record the location where you found your air sample, along with the sample's concentration of $NO₂$.

Questions: The EPA standard for $NO₂$ is 100 μ g/m³. Did anyone in the class find concentrations higher than the standard? Where were the highest values found? Where were the lowest values found? What explanations can you suggest for the results found for the different areas tested?

CH, CH, $CH₃$ -CH₂-Pb-CH₂-CH, $\dot{C}H_2$ Ċн,

The tendency of young children to put objects in their mouths can be especially dangerous when the objects contain lead.

 $21C$

E-39 Lead as an Air Pollutant

The fourth major air pollutant from automobiles—after hydrocarbons, carbon monoxide, and nitrogen oxides-is lead. Petroleum companies add tetraethyl lead (TEL) to gasolines to boost the octane ratings for high-performance engines. Leaded gasolines contain up to 1.5 g of lead per gallon.* For reasons that are not understood, the TEL prevents the knocking of engines. (Knocking occurs when combustion does not proceed smoothly in the cylinder.) The lead is emitted in the automobile exhaust in the form of very fine particles of lead halides such as $PbCl_2$, $PbBr_2$, and PbBrCl.

In areas where there is heavy traffic, the atmospheric concentration of lead particles is very high, typically one to several micrograms per cubic meter. This can be a serious health hazard because lead is poisonous when taken into the body. High concentrations of lead particles are deposited in the dust along highways and on city streets and sidewalks. Lead particles are also deposited on food plants and may be ingested if the food is not carefully washed. We breathe many of these particles into our lungs, where they may become trapped.

Most cases of lead poisoning occur in children and are more prevalent in older, rundown sections of cities. Many of the homes in these areas contain surfaces covered with old lead-based paint and have lead-based putty around the windows. Sometimes children eat lead-bearing chips of paint or dried putty from windows. Before this was found to be a cause of lead poisoning, hundreds of children died and many thousands of illnesses now traceable to lead went undiagnosed. Since then, lead-based paints used for painting the interiors of houses, apartments, and schools have been removed from the market. However, there are many buildings today that still contain surfaces with lead-based paint. Although lead paint is certainly a major cause of lead poisoning, an EPA study conducted in California showed that paint is not the only cause. Lead from auto exhaust also strongly increases lead concentrations in the bodies of people living near heavily traveled highways.

When lead enters the body, it circulates through the system until it is deposited in the bones. While it is circulating, the lead can harm the kidneys and interfere with the formation of red blood cells. Lead poisoning causes disruption of the body's metabolic processes and can upset the nervous system to such a degree that permanent brain damage or even death results.

[&]quot;SI and English System units are usually not combined. However, mixed units have been used here and will also be used in later sections of this module in order to be consistent with the information in current EPA regulations.

E-40 Lead Astray

A large amount of the lead in gasoline comes out of the exhaust system of automobiles and pollutes the atmosphere with large particles, which then fall to the ground. If this is true for your area, you should be able to measure the concentration of lead in a sample of soil.

Sample collection: Select a highway that is heavily traveled. Collect samples of soil, starting at the edge of the highway and continuing to 30 m away. In order to obtain control values for soil in the area, collect another soil sample at least 100 m from the heavily traveled area. Label your samples and make a map to show the location where you took each sample in relation to the highway.

In taking each sample, scoop up several grams of soil, place the soil in an envelope, and label it with a sample number. Take soil only from the top few millimeters of ground cover, and do not include any large stones, blades of grass, or pieces of debris. If you live in a city, you can obtain samples by sweeping dust from sidewalks and streets. If possible, have your class divide into groups and take samples from various sites.

Analysis: Carry out the following procedure for each soil sample. Measure 1 g of the sample and record its mass to the nearest 0.01 g. Place it in a 150-cm³ beaker and add 20 cm³ of 0.1 M HNO₃. Mix thoroughly for a few minutes. The lead will react with the nitric acid and dissolve as Pb²⁺.

Decant the acid solution into a 250-cm³ Erlenmeyer flask, leaving the undissolved soil behind. Wash the acid solution in the flask with a second 20-cm³ portion of 0.1 M HNO₃; decant as before into the 250-cm³ flask.

Add 4 to 5 drops of methyl orange indicator to the flask. Then slowly add just enough dilute sodium hydroxide (NaOH) to turn the solution yellow. This step reduces the acidity of the solution. Add 0.1 g of tartaric acid and mix well. Add ammoniacal buffer solution until a pH of 10 is observed using pH test paper. Add about 2 cm³ of Eriochrome Black T indicator so that a deep amber color forms. Titrate the sample with 0.001 M EDTA until the last trace of amber color disappears. The color at the end point is olive green.

 Pb^{2+} + H₂ (EDTA) \longrightarrow Pb (EDTA) + 2 H⁺

Calculation: You can determine the mass of Pb in each soil sample as follows.

mass of Pb (g) = no. of moles EDTA × molar mass of Pb
\n= vol. EDTA (cm³) ×
$$
\frac{0.001 \text{ liter}}{\text{cm}^3}
$$

\n× molarity EDTA $\left(\frac{\text{moles}}{\text{liter}}\right)$ × 207 $\left(\frac{\text{grams}}{\text{mole}}\right)$
\n= vol. EDTA (cm³) × 0.001 × 0.001 × 207
\n= vol. EDTA (cm³) × 2.07 × 10⁻⁴

EXPERIMENT

To find the concentration of lead in each soil sample in parts per million (or micrograms of Pb per gram of soil), use the equation

concentration Pb (ppm) =
$$
\frac{\mu g Pb}{g soil}
$$
 = $\frac{g Pb}{g soil}$ × 10⁶

Record your results and enter them on a map of your area.

Questions:

- 1. What were the highest values of lead concentration in the soil samples? What were the lowest values?
- 2. Do your results vary according to the distance from the edge of the highway? Why or why not?
- 3. Was lead detected in the control samples taken farther from traffic? If so, average the lead concentrations in the control samples. Consider this amount as the natural lead concentration in the soil, and subtract this value from the other sample values. Plot a graph of the resulting concentrations as a function of distance from the road. What do you conclude about the concentrations of lead in your area?

Has lead-based paint been used in your home (or a friend's home)? The following is a simple experiment to detect the presence of lead in paint. Collect samples of paint from places where the surfaces are chipped or peeling, or obtain bits of loose putty from around windows. Place the samples in an envelope, label them, and bring them to the laboratory for examination.

EXPERIMENT **E.3. E-41 Lead in Your Home?**

Place about 0.10 g of paint chips in a test tube. Be sure that the sample is free of wood and other foreign particles. Add three drops of concentrated nitric acid $(HNO₃)$. The nitric acid dissolves the lead.

Place the test tube in a boiling-water bath for 15 minutes. Caution: Be sure to heat the test tube and its contents in a fume hood to avoid breathing the nitrogen oxide fumes. Also make sure the room is well ventilated during this process. Remove the test tube from the water bath and add 2 cm³ of distilled water. (Note: If the paint was collected from a "gifted" radiator, it may contain interfering elements such as silver (Ag), thallium (TI), or mercury (Hg). In this case, use a 1-percent sodium sulfite (Na₂SO₃) solution instead of distilled water.

Allow the test tube to stand undisturbed for 10 minutes or until any undissolved material settles. Transfer the clear liquid to a clean test tube.

Place the test tube containing the clear liquid in a water bath (about 65°C) for 5 minutes. With a medicine dropper, allow 10 drops of 20-percent potassium iodide (KI) solution to fall directly onto the liquid in the tube. Do not shake the test tube.

If there is more than 1 percent of lead in the original paint sample, a yellow precipitate of lead iodide (PbI₂) is immediately formed.

It has been found that many people, especially children, are exposed to too much lead. An important measure of exposure to lead is the concentration of lead in the blood. These concentrations range between 5 and 20 μ g Pb/100 cm³ of blood for people in technologically advanced nations. If the level is above 60 μ g Pb/100 cm³ of blood, a person can show symptoms of lead poisoning. At levels between 40 and 60 μ g Pb/100 cm³, even if there are no obvious physiological symptoms, there is evidence that children do not perform as well in school.

Fortunately, steps are being taken to reduce our exposure to lead. Many cities have conducted campaigns to detect and remove lead-based paints from houses and apartments. Most cars manufactured since 1975 have been equipped with catalytic converters (section E-42). Because lead damages the converters, autos that have them must use lead-free gasoline. By 1979 about 40 percent of the gasoline consumed was unleaded. Furthermore, petroleum manufacturers have been required to reduce the concentrations of lead in leaded gasoline. During the early 1970s the average concentration was 2 to 3 g of lead per gallon of gasoline, and it has currently dropped to 0.5 g per gallon. Concentrations of lead in the atmosphere have also been dropping since the standard for maximum levels of lead in the atmosphere $(1.5 \mu g/m^3)$ was established. With the continuing decrease in the use of leaded gasoline, most areas should have little difficulty in meeting the standard.

E-42 Unclean at Any Speed?

What can be done to reduce undesirable emissions from automobiles? Several steps were taken during the 1970s. For example, emissions from the crankcase (which contains the oil that lubricates the pistons) are now circulated back into the engine to prevent their release into the environment. Improved gas-tank caps prevent the escape of gasoline fumes by evaporation. Both measures have decreased the emission of hydrocarbons into the atmosphere.

The major environment-related improvement to automobiles came on the 1975 models. In order to meet strict limits on carbon monoxide and hydrocarbon emissions, the auto manufacturers placed catalytic converters in the exhaust systems of most autos. These devices contain catalysts, such as platinum (Pt) and palladium (Pd), which speed up the complete oxidation of carbon monoxide and hydrocarbons to form carbon dioxide and water vapor. These then enter the atmosphere.

Catalytic converters have proved to be successful. When they are used properly, it is possible to tune an engine for optimum efficiency (which was not possible using the control methods of the 1972-74 models). The result is usually higher gasoline "mileage."

This lightweight catalytic converter is typical of those found in many newermodel automobiles.

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'In all states except California.

Another problem caused by automobile emissions is that of NO_x . The amount of NO_x emissions permitted for new automobiles is being reduced to 1.0 g per mile. To decrease the NO_x emissions, a new type of catalyst will be needed in the catalytic converter, one that uses CO as the reducing agent.

$$
2\,\mathsf{NO}(g) + 2\,\mathsf{CO}(g) \xrightarrow{\text{catalyst}} \mathsf{N}_2(g) + 2\,\mathsf{CO}_2(g)
$$

This may require two different catalysts—one to reduce NO to N_2 and another to oxidize CO and HC. But scientists are working on the development of single, "three-way" catalysts that would simultaneously oxidize CO and HC and reduce NO. Three-way catalysts made of platinum and rhodium have been developed, but they require that the engine be carefully controlled to ensure that the exhaust contains the correct proportions of CO , NO_x , and HC.

E-43 Cleaner Power for Autos

The discussion of automobile emissions in the preceding section has assumed the continued use of the spark-ignition internalcombustion engine (ICE). In a conventional ICE, gasoline is mixed with air in the carburetor and the air/fuel mixture is pulled into a cylinder by the downstroke of the piston. The mixture is then compressed by the upstroke of the piston and ignited by the spark plug. The hot, expanding gases produce enormous pressure on the piston and force it down (the power stroke), causing the crankshaft to rotate. The burned gases are released through the exhaust valve on the next upstroke of the piston.

Most automobiles manufactured in the United States have internal-combustion engines that contain four, six, or eight cylinders. Most of the pollution associated with these engines is created inside the cylinders. But pollution there is difficult to control; so most pollution control on conventional internal-combustion engines must be done on the exhaust *after* it leaves the engine.

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COMBUSTION IN A SPARK-IGNITION ICE

Obviously we need to develop cleaner sources of power for automobiles and, because of the energy shortage, sources that are at the same time efficient in the use of fuel. One possibility involves the greater use of diesel engines. They have long been used in most large trucks, and small diesel engines are now gaining popularity for use in automobiles as well. Unlike conventional ICEs, diesel engines have no spark plugs. The compression of air in the cylinder heats the air to a high temperature. When sprayed into the cylinder, the fuel is ignited by the high-temperature air. Diesel engines are about 20 percent more fuel-efficient than conventional ICEs. They also use a lower-quality fuel that is normally less expensive than gasoline. Diesel engines emit only small amounts of carbon monoxide and hydrocarbons, so they should have little difficulty meeting the standards for those emissions. But nitrogen oxide emissions are so high for diesel engines that they will probably need exhaust controls to meet emission standards.

The major emissions problem in diesel engines is particle emission. Diesel engines emit about fifty times as much particulate matter per mile as gasoline engines with catalytic converters do and ten times as much as those that use leaded gasoline. You've undoubtedly seen the clouds of smoke that diesel trucks belch out as they go up a big hill! This exhaust is made up mostly of small particles of carbon soot that absorb and scatter light quite effectively. These particles are also suspected of containing carcinogenic organic compounds. Depending on the size of the engine, diesel-powered autos emit from 0.2 to 1 g of particles per mile. The EPA has proposed regulations that would limit this emission to 0.6 g per mile in 1981 and 0.2 g per mile in 1983. If these rules go into effect, some particulate control device will be needed on larger diesel auto engines.

A very different kind of power source is the electric motor, which operates on batteries. Electric motors have been used for years in golf carts and in fork-lift trucks used for short-distance operations inside buildings. A few electric-powered vehicles are in operation on highways. They have many advantages: the motors require very little maintenance; they are highly efficient and inexpensive to run,

The electric automobile is not a new invention (top left). But with technological improvements, such as more efficient batteries and the use of computerized electronic controls, electric automobiles will soon be competitive with fuel-burning automobiles.

costing about 1 cent per kilometer (about 2 cents per mile) or less for electricity; and they produce virtually no pollution. (Keep in mind, however, that the power plant that makes the electricity for recharging the batteries does produce pollution.) The major problems with electric cars are the huge weight of batteries they must carry and their limited range, typically 150 km (about 90 miles) between battery recharges. Also, there is a limit to the number of times batteries can be recharged. After a few years of operation, the batteries have to be replaced, which at the present time is very expensive to do.

Research is currently being done to develop batteries that would store a much greater charge per unit weight than the familiar leadacid storage battery. Even with these disadvantages, however, present-day electric cars could help solve many of our problems with urban air pollution and gasoline shortages. Most of our travel by automobile involves less than 150 km (90 miles) of driving per day, the range for which electric vehicles become economical.

Another type of solution to the problems of air pollution and energy waste by automobiles is the greater use of public transportation. Trains use far less energy and release less air pollution per passenger per unit of distance than automobiles do. Although greater use of trains over long distances would help solve these problems, it is even more important to make greater use of mass transportation in large cities.

E-44 The Greenhouse Effect

We generally think of the effects of human activities as being small compared with those of nature. Can we pollute the atmosphere on a global scale? Surprisingly, the answer is "yes!"

The climate of the Earth is strongly affected by the atmospheric concentration of carbon dioxide, which plays a vital role in a phenomenon known as the greenhouse effect. This term refers to the fact that our planet absorbs light from the Sun and converts this energy into heat, which accounts for most of the warmth at the Earth's surface. Some of the sunlight that strikes the Earth, however, is reflected back into space by clouds, by particles in the atmosphere, and by the Earth's surface. If the Earth absorbed energy from the Sun without returning an equal amount to space, it would become hotter and hotter. But, like any warm object, the Earth radiates energy to its surroundings. The wavelength of radiated energy depends on the temperature of the radiating object. The higher the temperature of an object, the shorter the wavelengths of emitted light. The surface of the Sun has a temperature of about 6000 K (kelvins). About 9 percent of the Sun's radiation is high-energy ultraviolet light, 46 percent is visible light, and 45 percent is lowenergy infrared (IR) light. The Earth's surface, which has a temperature of about 280 K, radiates only low-energy IR light. Infrared light of certain wavelengths is strongly absorbed by three gases in the atmosphere, carbon dioxide (CO₂), water (H₂O) vapor, and ozone (O_3) .

The greenhouse effect takes its name from an analogy between the Earth's atmosphere and a greenhouse. In a greenhouse the visible portion of sunlight passes through the glass panes, warming the inside. The warm interior then emits IR light, which cannot penetrate the glass and is trapped inside. This causes the air inside to become much warmer than the outside air. (Also, the glass enclosure shields the interior from winds that would cool it.)

The absorption of Earth's IR radiation by H_2O vapor, CO_2 , and O_3 is much like the trapping of IR radiation in a greenhouse: the Earth's atmosphere is warmer than it would be without these gases. The amounts of these gases are regulated mostly by natural processes. The problem arises because human activities have significantly increased the concentration of $CO₂$ in the atmosphere.

One would not normally consider $CO₂$ to be an air pollutant. It is produced naturally when people and animals breathe and when plants respire or decompose. During the past century, however, we have dug up and burned vast quantities of fossil fuels. These fuels contain large amounts of carbon, which is released mainly as $CO₂$ during combustion. The quantities of $CO₂$ released into the atmosphere during the past century have been so large that the

THE GREENHOUSE EFFECT

A greenhouse provides warmth for the growth of plants when the temperature outside is too low. The greenhouse traps infrared light and keeps the air inside warmer than the air outside.

How would an increase in temperature affect areas such as this one? What would happen to the surrounding areas?

Seal by ERIC

concentration of $CO₂$ in the air has risen about 13 percent! Several attempts have been made to calculate the outcome of increased $CO₂$ in the atmosphere. The best estimate regarding its effect on temperature is that the mean global temperature would increase about 1°C if the current concentration of $CO₂$ were doubled, which may happen as early as 2025.

Why should we be concerned about a slight increase in the world's temperature? Some people living in the Temperate Zone would prefer warmer winters. But even a small temperature change could have serious effects. The productive farming lands of the Temperate Zone might turn into barren deserts. If the warming trend continued for many years, the Earth's polar ice caps would melt, causing sea levels to rise about 60 m —a disaster for low-lying coastal areas! <

What has happened to temperatures around the world? Because of year-to-year fluctuations of temperature, long-term records must be examined for any possible trends. Careful analysis of old weather records suggests that from about 1860 to 1940, worldwide temperatures increased by about 0.8°C. Starting in 1940, however, there seems to have been a cooling trend—a drop of $0.3^{\circ}C$ up to 1970.

Why haven't worldwide temperatures steadily continued to rise as more $CO₂$ is added to the atmosphere? For one thing, not all of the $CO₂$ released into the atmosphere stays there. As you will learn in experiment E -55, the greater the pressure of $CO₂$ above water, the greater the concentration of dissolved $CO₂$ in water. About half of the $CO₂$ released into the atmosphere through human activities in the past century has dissolved in the oceans. The oceans contain much greater amounts of $CO₂$ (mostly in the form of the bicarbonate ion, $HCO₃⁻$) than the atmosphere has—about fifty times as

much. If we were to give the process sufficient time, we would find that nearly all of the excess CO_2 now in the atmosphere would OF CARB dissolve in the oceans. This would take centuries, however, because the deep waters of the ocean mix very slowly with the surface waters.

But there may also be many other factors that affect worldwide
mperatures. For example, there may be slow changes in the $\frac{5}{6}$ = 320 temperatures. For example, there may be slow changes in the amount of light emitted by the Sun: perhaps the Sun has radiation $8\frac{8}{3}$ $_{315}$ cycles lasting hundreds of years. Concerning this point, we are $\frac{1}{1965}$ fairly certain that for 90 percent of the time during the past 600 million years, the Earth's surface was so warm that there were no permanent polar ice caps. But the past million or so years in the life of our planet seem to have been an unusually cold interval of time, typified by polar ice caps and many periods of advancing and retreating glaciers in the Northern Hemisphere. We are not sure of the reason for this cold period. Some scientists think that it is associated with the drift of Antarctica to its present position at the South Pole. As we shall see in the following section, human activities release certain materials that may cause a decrease in air temperatures.

E-45 Global Effects of Particles

Small particles in the atmosphere also have an influence on global temperatures. Depending on their nature and size, the particles can either raise or lower the Earth's temperature. If, for example, they are of such a size that their major effect is to reflect incoming sunlight back into space, they tend to cool the Earth. On the other hand, if they absorb sunlight or IR light emitted by the Earth, they tend to warm the Earth.

The greatest fluctuating natural source of particles is volcanoes. Large volcanic eruptions release enormous amounts of particulate matter, some of which rises into the upper atmosphere and can often be detected throughout the world. In 1883 the spectacular eruption of Krakatoa in Southeast Asia ejected billions of particles into the stratosphere (altitude above 12 km). Sunlight reflected the widely scattered dust, resulting in a brilliant display of dramatic red sunsets that were seen throughout the world for several years. An unusually large amount of volcanic activity has occurred on Earth over the past thirty years. Perhaps the particles released during these eruptions have caused or contributed to the cooling trend that is now being observed.

Human activities also contribute to the release of particles into the atmosphere (section E-33). The continued release of additional particles may more than offset the greenhouse effect and contribute

ATMOSPHERIC CONCENTRATION OF CARBON DIOXIDE

Volcanic activity, such as the eruption of Paricutin in Michoacan, Mexico, in 1943, pours tons of particles into the atmosphere.

Weather balloons are among several devices used to study the movement of air masses containing particles.

TIME MACHINE CFMs (Fluorocarbons) vs. Ozone

- 1931 In Norway, Erik Rotheim patents the spray can. 1940s Spray-can product with fluorocarbons is introduced on the market. 1974 Roland and Molina present ozonedepletion theory: fluorocarbon
- molecules that escape into the stratosphere can convert ozone into oxygen.
- 1977 Government regulations phase out the use of nonessential fluorocarbon compounds (propellants in aerosol spray cans).
- 1979 Over 98 percent of spray cans in use contain hydrocarbons, nitrous oxide, or carbon dioxide as the propellant.

to the cooling of the Earth's surface. Scientists don't know what fraction of the particles in global circulation arises from human activities and what fraction arises from natural sources. Also, we don't know for sure whether the overall effect of the particles is a cooling trend or a warming trend.

J impact on the world's air-pollution problem in time to prevent In order to help answer these questions, the United States National Oceanographic and Atmospheric Agency (NOAA) has set up experiment stations at various locations around the world. These stations, located in Hawaii; the South Pole, Samoa, and Alaska, collect information about changes in global temperatures, particles, cloudiness, and other climatic conditions. Data from these network stations, along with information from weather satellites, should help us to determine the seriousness of the human disastrous effects on the planet.

E-46 Ozone-Spray It Away?

As we discussed in section E-4, the stratosphere contains an ozone layer. (Actually it's not a layer, since the maximum concentration, at 25 to 30 km, is only a few parts per million.) Ozone (O_3) is made naturally when very high-energy UV light strikes oxygen molecules (O_2) high in the stratosphere, breaking them into oxygen atoms.

 $O_2(g)$ + UV light \longrightarrow 2 $O(g)$

The highly reactive oxygen atoms quickly react with oxygen molecules to form O_3 .

$$
\mathsf{O}_2(g) + \mathsf{O}(g) \longrightarrow \mathsf{O}_3(g)
$$

Although the concentration of O_3 in the atmosphere is small, it is very important. Ironically, whereas O_3 is a harmful air pollutant at ground level, it is highly beneficial in the stratosphere because it prevents much of the UV light emitted by the Sun from reaching ground level. The UV light would be harmful to us if it were not absorbed by this O_3 "shield." We couldn't go outdoors without covering our eyes and skin, since the UV rays would damage the eyes and greatly increase the incidence of skin cancer.

In 1974 it was thought that much of the O_3 in the stratosphere might be destroyed by a seemingly harmless product of modern society-the chlorof luorom ethane (CFM) compounds (commonly referred to as fluorocarbons) that were being used as the propellant in about half of the aerosol spray cans on the market. The use of aerosol sprays had almost become a way of life; many products, such as bug spray, deodorants, paint, and hair spray, were being dispensed through the action of these compounds.

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As the product is released from the dispenser in the form of a fine mist, the propellants inside are so volatile that they evaporate into the air. Being gases at normal pressures and temperatures, they tend to remain airborne indefinitely. CFMs are so chemically inert that there are no known reactions in the lower layers of the atmosphere that destroy them. Gradually they make their way to the stratosphere. Stong UV light from the Sun (not yet absorbed by the ozone layer) strikes these compounds and causes reactions that ultimately result in the conversion of O_3 into ordinary O_2 gas.

Because the CFM propellants pose a potential threat to the ozone layer, federal and state agencies took action in 1977 to remove these compounds from further use in aerosol spray cans. The ban has not caused any serious problems for consumers, since manufacturers of aerosol products have replaced CFM propellants with other types of propellants that do not affect the ozone layer.

Interpreting atmospheric data.

PROBLEMS **FOR A RESIDENCE**

1. For each of the pollutants listed in column I select the major source of that pollutant from among those in column II. (Note: There may be more than one major source for some pollutants.)

I.

- sulfur dioxide (SO2)
- carbon monoxide (CO)
- $\frac{1}{2}$ nitrogen oxides (NO and NO₂)
- lead particles (Pb)
- hydrocarbons
- atmospheric particles

 \mathbf{H} .

- a. automobiles
- b. coal-fired power plants
- c. oil-fired power plants
- d. lead and copper smelters
- e. dry-cleaning plants
- f. oil refineries
- 2. a. What measures have been taken to reduce urban concentrations of $SO₂$ on a national scale? in your area?
	- b. Have these measures been successful on a national scale? in your area?
- 3. a. Why are we now more concerned about the production of sulfates and sulfuric acid as pollutants than about SO₂ itself?
	- b. Have urban concentrations of these pollutants been reduced along with those of sulfur dioxide? If not, why not?
- 4. a. List all of the essential "ingredients" of photochemical smog.
	- b. Write the formula for the compound that is the major product of the reactions in photochemical smog.
	- c. What method is used to reduce carbon monoxide and hydrocarbon emissions from most post-1974 automobiles? Has this measure proved effective?
- 5. Discuss, from a chemical viewpoint, some of the difficulties involved in reducing pollution caused by both carbon monoxide and oxides of nitrogen from automobiles.
- 6. a. Explain how increased concentrations of carbon dioxide in the atmosphere are expected to cause an increase in atmospheric temperatures.
	- b. What would be the effect on worldwide temperatures of increasing the amounts of fine particles emitted into the atmosphere?
- 7. In 1977 an estimated 1.1 \times 10⁶ metric tons of particulate matter were released annually by "transportation." Assume that half of that amount comes from automobiles, which are nearly all gasoline-powered. What would be the total amount of particulate matter released by vehicles if half of the cars switched to uncontrolled diesel engines, which release about ten times more particulate matter than was released by the leadgasoline-powered engines that were used in 1977?

Energy: Use and Crisis

In 1973 great shortages of petroleum products, especially gasoline, developed in the United States. People waited for hours in long lines to get gasoline; the era of inexpensive, seemingly unlimited supplies of fuel was over. Most of us lost our concern, however, once the gasoline lines disappeared. But in 1979, the shortage recurred. The lines were often longer and the prices were higher. More people paid attention the second time, but will such a crisis occur again? Which of our energy sources will be affected next?

E-47 Feast to Famine

The energy crisis that arose in 1973 continues to plague us. Many people feel that this situation is the result of financial manipulation to increase oil-company profits. What has really happened is that the United States has passed its peak of domestic oil production. By 1979 our nation had become dependent on imports to satisfy about 45 percent of its oil-consumption needs. In addition, imported oil is becoming less reliable.

steadily becoming more expensive, and our sources of supply are
becoming less reliable.
Fossil fuels such as oil, coal, and natural gas provide nearly all of
the energy to satisfy the world's current energy needs. These fo Fossil fuels such as oil, coal, and natural gas provide nearly all of the energy to satisfy the world's current energy needs. These fossil fuels are nonrenewable; they were formed over millions of years from the remains of plants and animals that were covered by soil and rocks. Yet by the end of a brief three-hundred-year span of history that began in 1750 with the Industrial Revolution, the world
will have concurred much of its facell fuel uses were asset in the subwill have consumed much of its fossil-fuel reserves, except possibly coal.

Fossil fuels have provided us with an abundance of inexpensive energy that has made ever-increasing convenience a part of our way of life. The impending exhaustion of these fossil fuels lies at the heart of our present energy crisis because it threatens to curtail the use or increase the cost of many conveniences we now take for granted.

Oil, coal, and this fossilized "giant horsetail" fern leaf result from physical and chemical changes that began in swamps (left) over 250 million years ago.

TOTAL USE OF OIL IN THE U.S.

 $Barnel$ -standard unit used in measuring oil quantities. One barrel = approximately 159 liters (42 gallons).

TIME MACHINE

The offshore gas-drilling rig (above) and the "horse-head" pump (below), bring oil to the surface.

 \overline{C}

1846 War begins between the United States the work done to transfer energy from your body to an object when How did we get into this situation? How can we get out of it? We must understand the energy crisis, not only because it is an important issue itself, but also because our handling of this crisis has enormous implications for the future of the environment. Before continuing our discussion of energy, we will review the meaning of some energy-related terms. The basic unit for measuring energy is the joule (J). To understand what a joule of energy is, think about you move the object. The amount of work done depends on two variables-the force you must exert, measured in newtons (N), and the distance that you move the object, measured in meters (m). The total work done is equivalent to the amount of energy transferred from your body to the object and is expressed in joules.

work (J) = force (N)
$$
\times
$$
 distance (m)

How much power can you apply when lifting an object? Power is the rate at which energy is converted from one form into another.

$$
power = \frac{\text{energy}}{\text{time}}
$$

If we express energy in joules and time in seconds, then power is expressed in watts (W). In other words, 1 W equals 1 J per second. For example, a 60-W lamp uses energy at the rate of 60 J per second. Two larger units of power are the kilowatt (kW), 1000 W, and the megawatt (MW), 1 000 000 W.

The electric company charges for electric energy in units called kilowatt-hours (kWh). Since 1 kW equals 1000 W and 1 hour equals 3600 seconds, 1 kWh equals 3 600 000 J.

Several other units are used to measure energy, especially in English-speaking countries. Most of these units are based on measurements of heat. For example, the calorie was originally defined as the amount of heat required to raise the temperature of 1 g of water by 1°C. Now the calorie is defined by its relationship to joules.

$$
1 \text{ calorie} = 4.184 \text{ J}
$$

The energy content of food is commonly measured in kilocalories, also written as Calories.

1 Calorie = 1 kilocalorie = 4184 J

The heat content of fuels is usually measured in British Thermal Units (BTUs).

 $1 B T U = 1052 J = 1.05 kJ$

Very large amounts of energy are often quoted in terms of quadrillions of BTUs, called *quads*.

1 quad = 10^{15} BTUs = 1.05×10^{15} kJ

In 1976 the total energy used by the United States was about 65 quads.

Of course, all forms of energy could be expressed in joules; then you wouldn't have to know about calories, BTUs, and quads. But we have reviewed these terms so that you can better understand articles written about energy problems and also relate food energy to other forms of energy.

In the United States the news media report amounts of fuel in terms of barrels of oil, cubic feet of gas, and tons of coal. Whereas the conversion factors between the various units of energy just discussed are precise numbers, the energy content of a unit of fuel such as a ton of coal is not a precise number. It depends on the amount of ash, moisture, and other impurities in the coal. The following are the approximate values of energy released in the combustion of various fuels.

1 ton of coal (2000 pounds) = 910 kg coal = 2.5×10^{10} J 1 barrel of crude oil (42 gallons) = 6.1×10^9 J 1 cubic foot of natural gas = 1.1×10^6 J 1 gallon of gasoline = 1.3×10^8 J

E-48 Energy Sources and Uses

Those of us living in the United States have an enormous appetite for energy. During this century our annual use of energy has multiplied about seven times, while our population has multiplied only about three times—from 75 million people in 1900 to 220 million people in 1975. In other words, the energy we use per person (per capita energy) has more than doubled during this century, making our per capita energy use the highest in the world.

A JOULE

This "Christmas-tree" pipe formation is part of a large network that controls the flow of natural gas from a well.

Energy Use per Capita (1971)

The processing and shipping of coal is an immense operation. This traveling stacker at a terminal on Lake Superior can handle 3600 metric tons of coal per hour.

FLOW OF ENERGY IN THE UNITED STATES-1975

TIME MACHINE Electrical Energy

- 1882 Thomas Edison builds first electric power station to power his newly developed commercial electric lamp. 1882 First hydroelectric power plant is built in the United States. 1895 First large-scale American development for producing electricity by water power is opened in Niagara Falls, New York. 1933 Congress creates the Tennessee
- Valley Authority (TVA) to provide electric power, flood control, water recreation, and navigable waterways in Tennessee and surrounding states.
- 1936 Completion of Boulder Dam-one of the largest dams in the world supplies hydroelectric power to Arizona, Nevada, and California.
- 1954 United States amends the Atomic Energy Act to permit use of nuclear energy for production of electricity.
- 1957 First full-scale nuclear electric power plant begins commercial operation in Shippingport, Pennsylvania.
- 1979 Three Mile Island nuclear power plant incident refocuses attention on hazards of nuclear reactors as a source of electric power.

Let's examine the flow of energy in the United States in 1975. (Energy is given in units of 10'5 kJ, or 0.95 quads, per year.) Despite talk of new energy sources, such as nuclear, geothermal, and solar energy, 95 percent of our energy (65 out of the total 68 units) still comes from the fossil fuels-coal, oil, and gas. The remaining 5 percent comes mainly from hydroelectric and nuclear energy.

You may have noticed that our "books don't balance": we produce 68 units of energy, but we consume only 56 units. The energy loss occurs principally in the generation of electricity from the heat of fossil or nuclear fuels in steam-electric plants. In such plants heat generates high-pressure steam that drives turbines connected to electric generators. For every unit of energy available as heat, we obtain only about one-third of a unit of electrical energy. The rest is lost either as thermal pollution or in the transmission of this energy. The 18.6 units of input heat energy yield only 6.8 units of electric energy for consumers-an overall efficiency of about 36 percent.

How is all this energy used? Residential use accounts for only about 10 units of the 56 units consumed, or 18 percent. Transportation consumes about 34 percent of the energy, of which personal use in automobiles accounts for about half, or 17 percent of the total United States energy use. Thus, our direct use of energy as consumers is about 35 (18 + 17) percent of the total. The remaining two-thirds we use indirectly-in industry to produce our goods (35 percent), in public and commercial transportation (17 percent), and in institutions such as schools, stores, offices, and government buildings (13 percent). 101

How do we use energy in our homes? The major uses are for heating and cooling, which make up about 90 percent. Only about 10 percent is used for lighting and other appliances. Since 57 percent of the energy is used for heating homes, we could save great amounts of energy by insulating homes more efficiently. Also, as will be discussed in section E-57, much of the energy needed for heating purposes could be obtained from the Sun.

Most people are amazed to find out what a large part of our energy (about 35 percent) is used to mine ores, purify metals and other materials, and manufacture automobiles, television sets, dishwashers, tennis racquets, and other consumer products. Additional energy is used to transport the raw materials to the manufacturers and the products to the consumers.

In questions about recycling materials, we usually think in terms of conserving our deposits of ores. Recycling also saves large amounts of the energy that would otherwise be used to dig up the ores, transport them, separate the metals from tons of rock, and purify the metals. The energy savings potentially available through recycling the three primary metals—iron, aluminum, and copper are substantial. Aluminum (Al) production requires especially large quantities of energy, since aluminum is purified by electrolysis of a molten fluoride solution. If electricity from a coal-fired plant were used to produce aluminum, about 8 metric tons of coal would

The energy produced by water flowing through dams is used to turn massive electric generators (below right) at hydroelectric plants such as this one at the Shasta Dam in California.

Recycling aluminum is one of the best methods we have for conserving this nonrenewable resource. Every time the metal from an aluminum can is recycled there is a savings of 95 percent of the energy needed to make a can from "new" metal. Discarded aluminum cans are brought to a recycling center (above) where they are pressed into bales, melted (bottom left), and remade into cans.

be needed for each metric ton of aluminum produced! Much less energy is required to recycle aluminum; the same is true for both iron (Fe) and copper (Cu). Recycling these three metals could save about 3 \times 10¹⁵ kJ (2.8 quads) of the 68 \times 10¹⁵ kJ (65 quads) the United States uses annually—a saving of over 4 percent. That may not seem like very much, but our solution to the energy crisis over the next few years will probably depend on many small conservation steps like this one, along with the contributions of small new energy sources.

E-49 The Oil Squeeze

Now let's take a careful look at oil-the fuel that brought the energy crisis to a head. The United States possessed very large deposits of crude oil—not as large as the deposits elsewhere in the world, but enough to support the country's great industrial needs and technological developments. For many years the United States was the world's leading oil-producing nation. We are still a major oil producer, but unfortunately we are an even greater consumer. One of our problems is that we became a major consumer before most other nations did. As a result, our vast oil fields in Texas, Oklahoma, and Louisiana are beginning to run dry. Despite the fact that we are developing new wells—mostly in offshore areas and Alaska—domestic oil production, which peaked at about 11 mb/d (million barrels per day) in the early 1970s, has declined to about 10 mb/d. While oil production has remained relatively constant, United States consumption has risen from 10 mb/d in 1960 to about 18 mb/d in 1979. We've had to make up the difference with imports, which have risen from 1 mb/d in 1950 to about 8 mb/d in 1979, or about 45 percent of our oil supply! Unless we develop large new domestic sources (which seems unlikely) or reduce our needs for oil, we will become even more dependent on foreign supplies.

How do we use all this oil? In 1975, 10 percent of the oil (and some natural gas) was used as a raw material in the petrochemical industry for the manufacture of plastics, fertilizers, pesticides, and other consumer products. Petroleum is so valuable as a chemical that some experts have argued that burning it is wasteful and that we should, instead, conserve it for future use by the chemical industry.

By far the greatest use of petroleum is for transportation. Petroleum products generate so much energy per unit volume that a small amount can transport a vehicle hundreds of kilometers. In addition, refined petroleum products are a very convenient, mobile energy source: they are in liquid form and are therefore easy to distribute by pipeline. For these reasons, petroleum supplies over 96 percent of the energy used for transportation, with only minor

This stamp (above) illustrates the production of petroleum. When this photograph of Signal Hill, California (below), was taken in 1945, there were nearly 20 000 wells in one producing oil field.

This is a section of the 1290-km Trans-Alaska Pipeline, which carries 1.2 million barrels of oil a day from the well to the consumer.

Petroleum Uses in the United States-1975

Uses of Energy for Transportation-1975

amounts coming from gas, coal, and electricity. Automobiles consume over half of the petroleum energy used for transportation, followed by trucks, aircraft, and railroads. It is clear that if we are to reduce our demand for oil, much of the reduction must come from a decrease in the use of petroleum energy by automobiles and trucks.

In the wake of the 1973-74 petroleum shortage, several measures were taken to reduce oil consumption.

- Many electric power plants switched from gas or oil to coal.
- Many industries found that by modifying their procedures they could reduce energy consumption.
- Government offices, schools, and businesses saved energy by lowering thermostats in winter and raising them in summer, by shutting off unneeded lights, and by lowering the temperature of hot water.
- Homeowners and apartment dwellers took steps to conserve energy. The federal government encouraged conservation by giving income-tax credits for the cost of installing energy-saving measures such as better insulation, solar water heaters, and more efficient furnaces.
- The national speed limit of 88 km per hour (55 miles per hour) saved gasoline—and about ten thousand lives per year—in the United States.
- Catalytic converters on new automobiles allowed engines to be better tuned and also meet new emission standards.
- The federal government passed laws that require auto manufacturers to increase the efficiency of the cars they produce. By 1985 the average "mileage" of all the types of autos sold must be increased to 11.7 km per liter (27.5 miles per gallon).

 $\frac{1}{55\%}$ least 4 mb/d less than we would have if the rate of use before 1973 11% had continued. But why did the rate rise again after 1975? There are In part because of these measures, petroleum use in the United States stopped its upward climb and dropped until 1975, when it started to climb again. Nevertheless, in 1978 we probably used at several reasons.

- \bullet The economy of the United States improved. As a result, more energy was needed to make and haul goods. In addition, more people were traveling.
	- The United States suffered some unusually severe winters, which created a need for more oil for heat, particularly in the Northeast.
	- Several years with rainy harvests in the Midwest caused farmers to expend extra energy in drying grains to prevent spoilage.
- 3.5% Perhaps the biggest reason is that there was a huge increase in drivers and motor vehicles between 1973 and 1979.

Limiting the use of energy on the road (bottom right), as well as in our homes, is a must if we are to conserve the nonrenewable resource oil. Adjusting thermostats (top left) and adding insulation (top right) help to lower energy consumption in homes and commercial buildings. A new, heat-pump water heater (bottom left) promises to save one-half to two-thirds of the energy used by conventional electric water heaters.

 $\sim 10^{-10}$

 ϵ

The cylindrical block and the bricks shown here were produced from combinations of recycled bottles, telephone-book paper, and plastics and can be used as construction materials.

What can we do to reduce the nation's need for energy? Continued use of some of the methods previously discussed will help, especially the required improvement of engine efficiency. But these measures probably won't be sufficient. We could effect major savings by using more efficient modes of transportation for both people and goods. Automobiles are not very efficient because most of the energy is used to move the car itself. The more people who ride in a vehicle, the greater is its efficiency in terms of passengers moved per unit of fuel. Transportation on rails is more efficient than transportation on roads, and transportation on water is even more efficient—at least for cargo. We should therefore increase our use of car pools, buses, and trains for people, and trains and barges for cargo.

There are many ways by which we can conserve energy, especially petroleum. In a later section we will discuss the idea of converting coal into oil to reduce the demand for petroleum. We could replace oil with coal by drawing electric power from the combustion of coal and using electric automobiles. If necessary, we could ration supplies of fossil fuels. But another approach is to replace our present energy sources with new ones. These will be discussed in later sections.

miniexperiment

E-50 The Energy Watch Wrap-up

In miniexperiment E-5 you were asked to keep a record of the energy used in your unit (household, apartment building, or school). Now it is time to finish that exercise. Using your final readings, calculate the average amount of energy your unit uses per day. Divide this amount by the number of people who occupy the unit to get the per capita daily amount of energy used. Compare the values with the following figures, which are based on data in section E-48 and the current population of the United States (approximately 220 million).

Household

Average daily per capita direct use of energy (including transportation)

Apartment

Average daily per ca residential use of ene

School

Apartment		
Aparentment		
Average daily per capita	=	$\frac{10.3 + 19.4/2 \times 10^{15} \text{ J/yr}}{2.2 \times 10^8 \text{ people}} \times 365 \text{ days/yr}} = 2.5 \times 10^5 \text{ J/day}$
Average daily per capita	=	$\frac{10.3 \times 10^{15} \text{ J/yr}}{2.2 \times 10^8 \times 365} = \frac{10.3 \times 10^{15} \text{ J/yr}}{2.2 \times 10^8 \times 365} = 1.3 \times 10^5 \text{ J/day}$
School		
Average daily per capita	=	$\frac{\text{commercial}}{2.2 \times 10^8 \times 365} = \frac{6.6 \times 10^{15} \text{ J/yr}}{2.2 \times 10^8 \times 365} = 8.2 \times 10^4 \text{ J/day}$

residential $+$ $\frac{1}{2}$ transportation 220 million people \times 365 days/yr

Questions: How do the data you found for your unit compare with the national average for that type of unit? Is the amount you found above the average? If you live in an area that is much colder than the national average temperature, more space heating is needed in your area and your figures may be somewhat higher. But if your area is not much colder than the average and your unit uses a significantly above average amount of energy you should be concerned. What do you think can be done to reduce the amount of energy used in your unit?

PROBLEM [

Regardless of how your unit compared with national averages, make a list of ways in which your household, apartment, or school could save energy. Consider such options as turning off unneeded lights, changing thermostat settings, installing storm windows or insulation, cutting out unnecessary automobile trips, and using other modes of transportation. Be specific in listing these measures, such as replacing 100-W incandescent light bulbs with 25-W fluorescent units. Then try to calculate the amount of energy your suggested changes would save. If your survey included the use of automobiles, how did their gasoline consumption compare (a) with the national average of 6.1 km per liter (14.35 miles per gallon) for 1979, and (b) with the "mileage" for some of the most efficient automobiles now available? (Note: If you have an automobile that runs well, we wouldn't encourage you to trade it, even if it is not very efficient. Remember that much energy is required to manufacture products and that we can therefore help reduce energy consumption by keeping the products in service for as long as possible.)

A specialized photographic process using heat-sensitive film produces photographs called thermograms. This process is now being used to monitor heat loss (and therefore energy waste) in buildings. In the initial thermogram (top right) in a study of a typical home , the white areas indicate heat escaping from doors, windows, and the chimney. After these areas have been insulated, a second thermogram (bottom right) shows reduced heat loss. Through the use of this process, problem areas in buildings can be detected and properly insulated to conserve energy.

Oil spilled in accidents, such as the sinking of this oil tanker, causes coastlines to become polluted and destroys both animal and plant life.

E-51 Energy and the Environment

The future quality of our environment depends a great deal on the solutions we find to the energy crisis because nearly every form of energy production or use causes environmental problems. Take oil as an example. In addition to the air pollution that results from burning it, oil occasionally leaks from offshore oil wells or spills from tankers in accidents at sea. Oil from these sources pollutes nearby beaches and harms waterfowl by coating their feathers with tarry residues. Coal causes even more serious environmental problems. Besides contributing to the problem of air pollution, our use of coal involves the scarring of the landscape through strip mining, the danger of mine accidents, and the increased incidence of black lung disease among miners.

Nuclear fission, our most recently developed source of energy, has its own peculiar environmental problem. Because nuclear fission is a less familiar source of energy than fossil fuels, we will preface our discussion of the environmental problems it causes with a general description of its use as an energy source.

E-52 Energy from Nuclei: Fission

The fuel for nuclear fission reactions is an isotope of uranium. Recall that isotopes are atoms of the same element that have different masses. When the nucleus of the isotope $^{235}_{92}U$ is struck by a neutron $\binom{1}{0}$, it fissions (splits) into two nuclei of roughly equal mass. These smaller nuclei are known as *fission products*. In addition, two or three neutrons are released. The fission products and neutrons have considerable kinetic energy, and when they collide with other particles this kinetic energy is shared, thus increasing the overall temperature. In this way nuclear fission produces. heat. One of the possible ways in which 235U can fission is

 $^{235}_{92}U + ^1_{0}n \longrightarrow ^{143}_{54}Xe + ^{90}_{38}Sr + ^{31}_{0}n$

If on the average at least one of the neutrons given off in each fission strikes another 235U, causing a new fission event, a chain reaction occurs. Once started, this reaction continues to produce $\Big($ Sr more fission until much of the 235U is "burned up." Uncontrolled nuclear chain reactions provide the enormous destructive force of an atomic bomb. But in nuclear reactors, where the concentration of 235U is too small to cause a nuclear explosion, fission is a large source of useful energy. Fission of 1 kg of 235 U releases about the same amount of energy as burning 3000 metric tons of coal.

Most nuclear reactors contain 235U fuel in the form of pellets assembled into fuel rods. These rods are covered with a light, noncorrosive metal, such as a zirconium alloy. The fuel rods confine the uranium and radioactive fission products so that they don't contaminate other parts of the reactor. Water circulates through the reactor to cool its interior and transfer the heat to a heat exchanger. The heat exchanger generates steam, which powers a turbine for the production of electricity.

URANIUM FISSION

Precise measurements of nuclear-fuel pellets are made inside a laboratory glovebox. The pellets are then assembled into fuel rods for use in nuclear reactors.

Fuel rods, each holding about two hundred fuel pellets, are inspected (top left) before being assembled into latticelike frames (top right). These fuel bundles (bottom left) are then inserted into the core of the nuclear reactor (bottom right). During each refueling, one-third of the fuel elements are replaced.

The environmental problem peculiar to nuclear fission is that most of its products are radioactive. When they decay, most of these products emit high-energy electrons called beta (β) particles and gamma (y) rays. Although similar to visible light waves, gamma rays have over a million times more energy than visible light. Beta and gamma emissions are collectively called radiation. (Refer to The Heart of Matter: A Nuclear Chemistry Module for a more detailed discussion of nuclear fission.)

Before considering the effects of radioactive isotopes on the environment, two facts should be emphasized.

- 1. A radioactive isotope of an element behaves in the same way chemically as ordinary stable isotopes. For example, $^{90}_{38}Sr$ (strontium), a radioactive product of fission, behaves in the same way as ordinary stable strontium.
- 2. Beta particles can travel as far as several meters through the air, but they can penetrate only thin layers of human skin. Therefore they are not very dangerous so long as their sources are outside the body. Gamma rays, however, can pass directly through the body, similarly to X rays used to photograph the inside of the human body. These gamma rays are hazardous whether they originate from materials inside or outside the body.

When beta particles or gamma rays pass through human tissue, molecules in the path of the radiation are disrupted. The disruption of these molecules can have serious consequences: skin burns, loss of hair, nausea, diarrhea, coma, or death may occur from exposure to high levels of radiation over short periods of time.

The effects of large radiation exposures (measured in terms of a unit called a rem) are well known; however, it is quite difficult to determine the effects of long-term exposure to radiation in amounts below 25 rem per year. Our best information comes from studies of irradiated animals and from studies of survivors of atomic bomb blasts, X-ray technicians, and workers in nuclear research and industry who have had large exposures. Radiation occasionally causes disruption of molecules such as deoxyribonucleic acid (DNA), which provides the genetic code for all cells. condition called cancer.

Cells may then start reproducing themselves wildly—producing a
condition called cancer.
The incidence of cancer resulting from large lifetime doses of
radiation is known, but we do not know how to predict the cancer
rate The incidence of cancer resulting from large lifetime doses of radiation is known, but we do not know how to predict the cancer rate at the low doses that people of the general population receive. Some scientists say we should assume that the cancer rate is proportional to the total dose. This is the linear hypothesis. Others think that cells repair themselves between irradiations, so that no cancers are caused until the dose is greater than some threshold value.

Pollen is collected from irradiated jute plants in order to study chromosome changes caused by radiation. Scientists are constantly studying the effects of radiation on living organisms in the environment.

Effects of Radiation Exposure

WHAT ABOUT LOW DOSES?

radiation dose

The policy of the Nuclear Regulatory Commission has been to design all nuclear activities so that the exposure to the general population is far less than the 0.08 to 0.2 rem that we receive annually from natural sources (natural background radiation): cosmic rays from outer space and naturally radioactive elements in rocks and building materials. Today the radiation dose received by the general public from nuclear energy activities is only about 0.001 rem per year, far less than the 0.025-rem dose received from a chest X ray.

Although present radiation exposures from nuclear energy are quite small, we must continue to minimize human exposure to all forms of gamma and X radiation. Each exposure, however small, slightly increases the risk of cancer. It is estimated that each additional 1-rem exposure to 1 million people will cause an additional two hundred deaths from cancer. By far the largest source of radiation due to human activities is the medical use of radioactive isotopes and X rays for diagnosis and the various kinds of radiation for the treatment of cancer. Although these uses have benefits that probably far outweigh the associated risks, doctors and dentists should not overuse these tools and should be sure that their equipment and methods are designed to minimize exposure.

E-53 Hazards of Fission Reactors

When an electric company proposes to build a nuclear power plant, there is great concern among citizens' groups and environmentalists. In part the concern stems from people's unfamiliarity with nuclear reactors and the processes involved. Burning a piece of coal is something most people can understand—but they often ask, "What is a gamma ray?" Also, there is the connection in people's minds between nuclear energy and nuclear weapons. Although it is true that there are hazards connected with nuclear power plants, these risks must be weighed against the pollution and hazards connected with other forms of electric-power generation.

Under normal operating conditions, nuclear reactors release small amounts of radioactive materials into the surrounding air and water. As discussed in section E-52, however, the exposure to the population by normal activities of the nuclear energy industry is quite small compared with natural background radiation and medical uses of radiation.

As already noted, nuclear reactors cannot explode like a nuclear bomb. However, a primary concern is that an accident might cause a reactor to leak radioactive isotopes such as radioactive iodine barium, and strontium into the environment. Such an accident might be an earthquake, a chemical explosion, or a loss of control of the reactor itself. The dangers would be similar to those of radioactive fallout from the explosion of a nuclear weapon. Evacuation

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of the area would be necessary, because the air and water in the area would be contaminated and many people's bodies would absorb radioactive isotopes. For example, radioactive iodine would concentrate in the thyroid gland and radioactive barium and strontium (chemically similar to calcium) would concentrate in bones and teeth.

A major problem with reactors is that the operators of the plants can't just throw a switch to shut them down immediately. It's easy to stop the chain reaction of nuclear fission by inserting control rods into the reactor. Control rods contain elements such as cadmium (Cd) or boron (B), which absorb neutrons so strongly that the chain reaction can't continue. But even after the chain reaction stops, the reactor continues to release heat as a result of the radioactive decay of the fission products. Soon after the chain reaction stops, the reactor produces heat at about one-tenth of the rate during normal operation. At first heat production drops rapidly, since many of the fission products decay with half-lives of seconds and minutes. (The half-life of a radioactive element is the time it takes for its radioactivity to drop to half its initial value.) Then the heat production drops off more slowly, because of the decay of radioactive products with half-lives of days to years. But as long as a reactor is producing heat, it must be cooled. Otherwise, it would get so hot that it would eventually melt the core and perhaps release considerable amounts of radioactive products into the environment.

Many lines of defense are taken to prevent nuclear accidents.

- Before a reactor is built, its design and location must be approved at many levels of government, from local communities and the state to the Nuclear Regulatory Commission.
- There are many sensors of temperature, coolant flow rate, power level, neutron flow, and radiation in the reactor itself, in the building, and in the surrounding area. If any unusual condition develops, an alarm alerts reactor operators or, for very serious conditions, control rods are automatically inserted into the reactor to shut it down.

The control room is the "nerve center" of a nuclear power plant.

- Huge concrete shielding blocks surround the reactor to keep radiation levels to a minimum.
- Large tanks contain emergency core-cooling water to make sure that the core can be cooled down if for any reason it loses its normal cooling water.
- The entire reactor is surrounded by a containment shell that can withstand considerable shocks or explosions without releasing contaminants into the environment.
- Reactor operating personnel must be trained and licensed, and inspectors frequently check reactors to make sure they are operating properly.

Since we have so little experience in the operation of reactors (the first were run during the early 1940s), we don't really know how accident-prone they are. Because of this lack of information, a group of nuclear scientists did a step-by-step analysis of safety factors involved in the operation of a reactor. They estimated such factors as how frequently pipes would break and valves would fail and combined these estimates to obtain an overall estimate of the probability of serious reactor accidents. They predict that the frequency of nuclear accidents with fatalities should be quite low less than one accident per one hundred years in which ten or more people are killed, assuming one hundred reactors are operating. (Compare this result with the rate of fatalities due to airplane crashes: there are about five such accidents per year that kill ten or more people and about one accident every two years in which one hundred or more people are killed.) These calculations regarding the safety of nuclear reactors have been hotly debated since they were made in 1974.

On March 28, 1979, the United States suffered its most serious nuclear-reactor accident. One unit of the Three Mile Island nuclear power plant near Harrisburg, Pennsylvania, underwent a series of mishaps that caused part of the reactor core to lose coolant for a period of time. The exact causes of the problem are not known, because the containment shell was so filled with radioactive products that investigators could not go in to find out exactly what happened. It is known, however, that some coolant water pumps weren't working before the accident, a valve failed to close, some gauges in the control room gave wrong readings, and some improper corrective measures were taken.

In addition, there was a totally unexpected event during the crisis: a bubble of hydrogen gas under high pressure formed within the containment shell. The bubble formed from the reaction of zirconium with reactor coolant water at high temperature. The hydrogen gas presented a serious problem, as it filled spaces normally occupied by coolant water and posed the threat of a chemical explosion that would spread radioactivity throughout the area. The

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situation was so severe that plans were made to evacuate about three hundred thousand people. Some people voluntarily left their homes. Fortunately, the hydrogen bubble slowly dissolved in the water and the reactor cooled down.

The accident at Three Mile Island clearly demonstrates that there is a need to reexamine the procedures and regulations involving nuclear-power reactors and, indeed, the future of nuclear fission as a source of energy.

Another serious problem for the nuclear industry is the disposal of radioactive fission products. Some of the fission products have very long half-lives- 28 years for $\frac{90}{85}$ (strontium) and 30 years for $^{137}_{55}Cs$ (cesium). Since radioactivity is a nuclear property, it cannot be destroyed by heat, chemical reaction, or any other known treatment.

We cannot just throw these radioactive wastes away. If ⁹⁰Sr were released into water, it would be incorporated into the shells of aquatic animals and the bones and teeth of other animals, including humans. Beta particles from its decay in the bones would bombard the bone marrow where blood is manufactured and could lead to leukemia (cancer of the blood).

To date, most radioactive wastes have been concentrated in aqueous solutions that are placed in underground storage tanks. If an explosion or earthquake were to rupture such a tank, releasing the radioactive solution into the groundwater system in the surrounding area, the effects could be disastrous. Plans to form the wastes into chemically inert solids for storage are currently under investigation.

DECAY OF ⁹⁰Sr

Depending on their level of radioactivity, nuclear wastes can be stored in groundlevel tanks (left) or buried in underground shafts (right), which are then sealed.

As we enter the 1980s there is much debate about the various proposed solutions to the energy crisis. Conservation could help a great deal, but additional energy sources will be needed. In the later sections of this module, we will discuss several new energy sources that may become quite important in the future. Over the shorter range, coal and nuclear energy are probably the only sources that can be increased enough to meet our major needs, despite the problems they entail.

The nuclear power plant (above) and the coal-powered generator (below) illustrate two alternative sources of electric power. The use of these could be expanded to supply a greater part of our total energy needs in the future.

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E-54 Lost Heat-Where Does It Go?

Most fuel-burning plants that produce electricity are steam-electric plants. Heat from nuclear reactions or from the combustion of coal, oil, or gas produces high-temperature, high-pressure steam. The steam expands in a turbine, causing the blades to rotate rapidly. The shaft of the turbine is connected to a generator that produces the electricity. After the steam has expanded as much as possible and has done its work in the turbine, it must be cooled, condensed to liquid, and routed back to the boiler to be made into steam again. In this cooling and condensation process, the steam releases heat energy into the environment—energy that has not been converted into electricity. Consequently, a steam-electric plant, or any other heat engine, cannot convert heat energy entirely into the mechanical energy (the power that rotates the turbine shaft) that ultimately produces electrical energy. This inefficiency is fundamental to the nature of heat and mechanical energy and is not merely the result of friction or mechanical design.

Suppose we have steam at a temperature of 500°C. We could convert all of this heat energy into mechanical energy only if, after doing its "work" in the turbine, the steam has given up all of its heat energy. In other words, the steam must cool to the lowest temperature that can exist, -273 °C or 0 K. The result would be a theoretical efficiency of 100 percent. But this is a completely hypothetical situation, because no area on Earth is cold enough to cool steam to such a low temperature. The steam is usually cooled with water from rivers, lakes, and oceans at temperatures from about 5°C to 30°C. The theoretical efficiency of the plant (the ratio of electrical energy produced to the amount of heat energy released to heat the steam) is expressed by

efficiency
$$
=\frac{T_1 - T_2}{T_1}
$$

In this equation T_1 is the temperature of the steam and T_2 is the temperature of the cooling water, both expressed in kelvins.

$$
TK = t^{\circ}C + 273
$$

Plants typically operate with steam at about 773 K (500°C) and cooling water at about 293 K (20°C). Substituting these temperatures in the formula, we see that the theoretical efficiency is

efficiency =
$$
\frac{773 - 293}{773} = \frac{480}{773} = 0.62 \text{ or } 62\%
$$

At most, only about one-half of the heat is converted into electricity. We see that to obtain the highest efficiency possible one should use steam of the highest possible temperature and cooling water of the lowest possible temperature.

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This stamp commemorates Great Britain's commitment to the production of electric power by nuclear reactors.

Today's nuclear plants generally operate with steam at slightly lower temperatures than do fossil-fuel plants. As a result, the overall efficiency of fossil-fuel plants is slightly higher than that of nuclear plants, about 42 percent versus 33 percent, after transmission losses and friction have further reduced the efficiency of the conversion of heat energy in the plant into electrical energy in your home. Consumers receive only 6.8 \times 10¹⁵ kJ (6.5 quads) of electrical energy out of the 18.6 \times 10¹⁵ kJ (17.7 quads) of energy supplied for electric-power generation, for an overall efficiency of 37 percent.

The inefficiency in the generation of electricity is an important factor to consider in any discussion about how wisely we use energy. It is a waste of energy to heat homes or cook food by electrical-resistance heating (the heat produced when electricity passes through a wire). To obtain 1 kJ of this heat in your home, the power plant had to burn about 3 kJ worth of coal or oil. It would be more efficient for you to burn the fuel at your home and use only about 1 kJ.

The inefficiency of steam-electric plants entails not only the fact that heat energy is wasted but also that the waste heat itself can become a pollutant. All steam-electric plants, whether they use coal, oil, gas, or nuclear fuel, must deposit waste heat somewhere—either in water or in the atmosphere. Most of the waste heat is dumped into cool water, which then becomes warmer. What are the effects of thermal pollution-the dumping of waste heat into streams? One effect is that the solubility of gases dissolved in the stream changes with temperature. You can observe this effect in the following experiment.

EXPERIMENT

SAMPLE WORKSHEET

E-55 The Fizz Is Familiar

Temperature **COLOGONITY** Temperature C₂ hydroxide (NaOH), a base. The reaction for this experiment is The gas used in this experiment is carbon dioxide $(CO₂)$, since it is readily available in the form of soda water. You can measure the amount of CO₂ solution easily because the $CO₂-H₂O$ solution is acidic, as shown by testing it with litmus paper. This solution can be titrated with sodium

 $CO₂$ + NaOH \longrightarrow NaHCO₃

From the equation you can see that the amount of $CO₂$ in solution is directly proportional to the amount of NaOH used in the titration. Before you open the bottle of soda water, the solution is supersaturated. (How do you know?) Therefore, before each titration, the solution should be stirred with a stirring rod just until the fizzing stops.

Temperature °C that beads of water form on the inside surface of the buret, wash the Rinse a 50-cm³ buret three times with 5 cm³ of tap water. If you notice buret thoroughly with soap and water. Rinse the buret until the water drains smoothly off the inside surface.

Now rinse the buret three times with 5 cm³ of standard sodium hydroxide (NaOH) solution. Allow some of the sodium hydroxide to drain through the tip of the buret.

Fill the buret with the standard sodium hydroxide solution to about 1 cm above the 0-cm3 mark. Then drain the solution drop by drop until the bottom of the meniscus is at the 0-cm³ mark. Be sure the tip of the buret is completely filled with solution.

Add exactly 25 cm³ of cold soda water to a beaker. Stir, and as soon as the fizzing has stopped, record the temperature. Then add 2 or 3 drops of the indicator, phenolphthalein. Titrate the soda water rapidly with sodium hydroxide solution. At the end point the solution should be a very pale pink. Record the volume of NaOH used.

Prepare another 25-cm³ sample. This time use soda water that is at room temperature (20°C). When the fizzing has stopped, record the temperature and add phenolphthalein. Titrate the sample rapidly. Record the volume of NaOH used. Then heat a 25-cm³ sample of soda water to 65°C. Record the temperature and add phenolphthalein. Titrate the hot soda water rapidly. Record the volume of NaOH used.

Plot a graph of the observed volumes of NaOH as a function of temperature.

QUESTIONS:

- 1. How does the solubility of $CO₂$ in water change with increasing temperature?
- 2. Why does a carbonated drink "go flat" when it is left uncovered?
- 3. Why does a bottle of warm cola fizz when the top is removed?
- 4. Relate your observations to the problem of thermal pollution.

As you observed, the solubility of carbon dioxide in water decreases with increasing temperature. This is true for most gases. In particular, the concentration of dissolved oxygen in water is lower in warm water than in cold water. When a body of water is warmed several degrees by thermal pollution, desirable fish may die or leave to find a more suitable habitat. Often they are replaced by hardier "trash" fish, which may be edible but are generally not in high demand by consumers.

Although water that is warmed in this way can be harmful to the environment, in some ways it can be beneficial. In fact, thermal pollution is another example of a resource-out-of-place. The warm water could, for example, be used for irrigation, since heat increases the growth rate of irrigated crops. The warm water could also be used to heat buildings or swimming pools. We need to develop ways to take better advantage of this resource-out-ofplace, both to help relieve the energy crisis and to prevent thermal damage to natural waters.

Fish-farming operations, such as the growing of oysters in holding racks make use of heated water emitted from power plants. Under ordinary conditions this waste heat is a source of thermal pollution.

PROBLEMS

- 1. a. If a coal-fired power plant operates with steam at 350°C and uses cooling water at 15°C, what is its theoretical efficiency?
	- b. Suppose the power plant produces 500 MW of electrical power. (One megawatt is equal to one million watts.) How much coal must it burn per hour?
	- c. If the cooling water for the plant in part (a) is warmed 10°C as it passes through the plant, calculate the number of liters per minute needed to carry away the excess heat.
- 2. In 1976 about 7 mb/d of gasoline were consumed in the nation's approximately 100 million automobiles.
	- a. If each automobile was driven an average of 24 000 km (15 000 miles) per year, what was the average "mileage" for the "fleet"?
	- b. How many millions of barrels per day of gasoline would have been used by automobiles in 1976 if the average "mileage" had been 11.7 km per liter (27.5 miles per gallon), which will be required of new cars sold in 1985 and beyond?
	- c. Suppose that the average automobile in 1976 did get 11.7 km per liter. Assuming that other uses of petroleum and domestic oil production stayed the same, how much petroleum would the United States have had to import in 1976? (Refer to the graph in section $E-47$.) How much did the United States actually import in 1976?
- 3. Suppose that in 1976 the nation had adopted a gasoline-rationing plan that would have restricted average consumption to 7.6 liters (2 gallons) per day per automobile.
	- a. How much gasoline (in millions of barrels per day) would have been consumed by the 100 million automobiles referred to in problem 2?
	- b. By what amount (in millions of barrels per day) would the nation have been able to reduce its petroleum imports if the measure in part (a) had been adopted?
	- c. If your energy survey in miniexperiment E-5 included the use of automobiles, what was their average consumption in liters (or in gallons) per day? Is that rate below or above the rationing figure suggested in part (a)?
- 4. As previously discussed, the total annual use of energy in the United States in 1975 was about 68×10^{15} kJ (64.6 quads).
	- a. If the population of the United States was about 210 million at that time, what was the per capita use of energy per day (in kilojoules)?
	- b. The average adult in the United States requires about 2400 Calories of food energy per day. Calculate the ratio of the total use of energy per day, from part (a), to the food energy required per day.

Future Sources of Energy

As we approach the final decade of this century, our attention will continue to focus on the issues of energy and the environment. How can we meet our changing energy needs in the future without damaging the environment? It should be possible to clean up the emissions from some of our present sources, but can we find new sources of energy that are cleaner and more economical than the ones we have been using?

Inside a fusion-reaction chamber, eight laser beams are simultaneously focused on a small fuel pellet containing "heavy" hydrogen. This process is part of an attempt to produce usable energy from a reaction similar to one that takes place in the Sun.

E-56 Heat from the Earth

At the Geysers field in California (above right), which covers an area of more than 40 square kilometers, geothermal steam with a temperature of about 255°C is emitted from more than one hundred wells. Scientists believe that the water is heated by rocks located 5-8 km below ground level (below).

GEOTHERMAL STEAM

At many points below the Earth's surface, particularly in areas of recent or active volcanoes, there are pockets of molten rock called magma chambers. When water from the surface trickles down to these chambers, contact with the molten rock transforms the water into steam of high temperature and pressure. The high pressure forces the steam through cracks and channels in the rocks and toward the Earth's surface, where often it comes out in a violent blast. Energy of this type is known as geothermal energy. Examples of geothermal activity are the geysers (steam and hot-water vents) such as Old Faithful and Lone Star, in Yellowstone National Park, and the Geysers field in northern California. By drilling holes in the ground, we can tap areas of steam or hot water in a geothermal field and harness the energy. This energy can be used either directly to heat homes and buildings or indirectly to turn the blades of turbines to generate electricity.

Geothermal energy is being used in only a few areas of the world today. In Iceland, for example, many homes are heated by hot water or steam from geothermal fields. Certain sections of New Zealand and Italy also use geothermal energy. This energy source could be used in many areas throughout the world where magma chambers exist.

By 1979 the only full-scale geothermal power plant in operation in the United States was the Geysers Power Plant in northern California. At that time it was producing about 700 MW of electric power and was expected to increase to 1000 MW by 1980—enough power to supply a city of about a half-million people. This output

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is comparable to that of modern fossil-fuel (coal and petroleum) power plants, which typically produce from 500 to 2000 MW of power. The cost of building the Geysers Power Plant was about \$150 per kW, compared with \$1400 per kW for nuclear plants, \$900 per kW for oil-fired plants, and \$700 per kW for coal-fired plants.

Several other geothermal projects are now under way, including a 12-MW generating plant at Raft River, Idaho, and a 50-MW plant in the Imperial Valley of southern California. Other geothermal plants could be built in the United States, particularly in the Southwest. The United States Geological Survey estimates that 12 000 MW of geothermal electric power could be developed at competitive prices using wells no deeper than 3 km. Other surveys estimate that by the year 2000 geothermal plants could supply as much as 21 percent of our electric power.

Unfortunately, the use of geothermal power plants is not completely free of environmental problems. Sulfurous gases, mercury vapor, and water droplets containing salts may be released from underground along with the steam that is used. Control measures will have to be taken to prevent these harmful effluents from being released into the surroundings.

E-57 Harnessing the Sun

The Sun is the source of all energy at the Earth's surface, with the exception of nuclear energy. Even the energy of fossil fuels can be traced to the Sun. Green plants obtain energy from the Sun by photosynthesis, and animals eat the plants. The remains of plants and animals that lived millions of years ago were buried under sediment; slowly these remains were converted into fossil fuels.

The warming of the Earth's surface by sunlight gives rise to the energy of winds and rains, hurricanes, thunderstorms, and blizzards. Although the energy of sunlight reaching the Earth's surface is enormous, we make little direct use of it. In the southwestern United States, the rate at which the Sun's energy reaches the Earth during daylight hours is approximately equal to 1 kW per square meter. The amount of sunlight that falls upon only 0.5 percent of the land area of the United States could meet all of the nation's energy needs.

Unlike fossil fuels and uranium, the energy of sunlight is a renewable energy source—a source that is replenished as fast as we use it. Since solar energy is renewable, free, and clean, there is great interest in developing it as an alternative to fossil and nuclear fuels.

Solar energy has two major problems, however. First, it is a very diffuse source of energy. Whereas a 1000-MW coal-fired plant could fit into the space of a large city block, the light-collection

TIME MACHINE

Tornadoes, like all other destructive weather disturbances, are powered by the energy of the Sun (sunlight).

Sunlight is a pollution-free, limitless source of energy. The energy-collection panels on the roof of this office building (top) are part of a solar heating and cooling system being evaluated by the Department of Energy. The "power tower" is a large-scale use of sunlight to produce steam for the generation of electric power.

surfaces alone for a 1000-MW solar-electric plant would require 8 km2 of area, the size of about two thousand football fields! Second, solar energy is an intermittent energy source: it "shuts off" at night and on cloudy days. In winter, when heat is needed most, we receive the least amount of sunlight. Thus, to obtain a continuous supply of energy from the Sun, we must find ways to store that energy.

There are many forms of the direct use of solar energy. You use solar energy in a modest way in your home as the light and heat of sunlight come through your windows. Glass allows the visible portion of sunlight to pass through it and prevents the infrared radiation from escaping, just as in the greenhouse effect (section E-44). With careful use of this principle in building designs, substantial amounts of heating costs could be saved.

Other solar-energy systems for buildings are being tested. Most of these systems involve the use of a solar-heat collector-a series of dull black panels that absorb the Sun's energy. These are covered with glass or plastic to prevent the heat from escaping. Attached to the panels are coils through which a fluid, usually water, is circulated. As the water is heated, it is carried to a reservoir, where it can be withdrawn for use.

It would cost between \$6000 and \$20 000 to install a solar heating and cooling system in a single-family dwelling. (The exact cost depends on the type of system and the average temperature in the area.) This seems like a large investment, but it would eliminate most fuel costs for the life of the system. Also, the relative cost of solar energy decreases as the cost of other fuels increases.

As the world's oil supply dwindles, you won't read a news report stating that the last drop of oil was just pumped from the ground. Instead, oil will price itself out of the market, as eventually will other nonrenewable energy sources. As the richest deposits of oil run out, the oil must be obtained from less profitable wells. This is already happening. It was much cheaper to obtain oil from the rich deposits in Texas and Oklahoma than it is to to drill for and transport oil from offshore wells in the North Sea of Europe and from Alaska. At the same time, new developments in an emerging technology, such as in the area of solar energy, will bring down the price of this energy source. In some areas of the country, it is already less expensive to use solar heating if electric heating is the only alternative. Heating by gas or oil, however, is still less expensive than heating by solar energy in most places; but with sharply rising costs for nonrenewable sources of energy, solar energy is a promising alternative.

It will probably take years for large solar-electric plants to become economically feasible. Two basic designs are under consideration. In the first, solar panels collect the Sun's energy and transfer the heat to a fluid such as molten metal. The fluid from all the collectors

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is pumped through a central heat exchanger that heats water to make steam. The steam is then run through a turbine that is connected to an electric generator, just as in coal-fired plants. Because the flat sunlight collectors do not get very hot, the steam produced would have a temperature of 350°C or less. Since the efficiency of converting heat into electricity is reduced at low steam temperatures, this system would not be very efficient.

In the second design, greater efficiency is achieved by using lenses or curved mirrors to focus sunlight more intensely on the solar collectors, which would produce steam of higher temperatures. Consequently, for a given amount of electrical output, the lens system would require a much smaller collection area than in the first design. The lens system is expensive, however, because the lenses must be continuously rotated to keep the sunlight focused on the collectors (to compensate for the movement of the Earth).

The Department of Energy is investigating this second approach by supporting the construction of "power towers" near Albuquerque, New Mexico, and Barstow, California. At the 10-MW Barstow plant, a large group of mirrors is arranged in a 0.4-km² area on the ground with movable mountings to track the Sun. The mirrors reflect sunlight to a boiler at the top of a 180-m tower, where steam is produced. The steam is then used to drive a turbine that generates electricity. The cost of this system is very high--probably a minimum of \$2500 per kilowatt of power output. Therefore, extensive use of solar heating in homes will probably occur long before centralized solar-electric plants arc widely used.

A fresnel lens (above) is used to concentrate the Sun's rays on a solar cell for the direct conversion of sunlight into electricity. A solar furnace in the Pyrenees Mountains in France (bottom left) generates temperatures above 3300°C.

miniexperiment **1752 E-58 Sun Power**

You can find out how lenses may be used to focus the Sun's energy. Use a magnifying glass to focus sunlight on a small piece of newspaper. What happens to the newspaper? Caution: Focused rays of sunlight produce intense heat.

Now observe the effects of focused sunlight on a drop of water and on a sample of sodium sulfate decahydrate. What do you observe? You can also investigate the varying effects that magnifying glasses of different diameters have on these materials.

Besides converting the energy of sunlight into heat for the generation of electricity, we are also able to convert sunlight directly into electricity. Certain materials such as pure silicon (Si), cadmium sulfide (CdS), and gallium arsenide (GaAs) can be made into solar cells. When sunlight strikes them, these cells produce an electric current, and they can be hooked together to form solar batteries that yield substantial amounts of electric current. These batteries aré especially useful on space satellites because solar batteries do not run down the way storage batteries do.

Like solar steam-electric plants, however, solar batteries are quite expensive—about \$5 per watt of electric power. To illustrate this cost, if the average toaster draws about 1 kW, it would cost about \$5000 to provide enough solar batteries to run a toaster on a bright, sunny day! It is hoped that developments will occur soon to reduce the cost of these batteries to about 50 cents per kilowatt, thereby making solar batteries an economically competitive source of electricity.

A panel of solar cells.

miniexperiment **E-59** Electricity from the Sun

You can demonstrate the effects of a solar battery by connecting a voltmeter to a photovoltaic cell and exposing the cell to the Sun. Observe and record the reading on the voltmeter. Also, observe how this reading changes as the angle between the photovoltaic cell and the rays from the Sun changes. Determine the angle that obtains the highest reading on the voltmeter.

E-60 Growing Solar Energy

Green plants growing in a field are also solar-energy collectors. They absorb sunlight and use it to change carbon dioxide and water into oxygen and high-energy compounds such as simple sugars

 $(C_6H_{12}O_6)$. The simple sugars are often linked together to form carbohydrates. The photosynthetic energy stored in these compounds can be released by burning the material in air.

carbohydrates + oxygen \longrightarrow carbon dioxide + water + energy

Therefore, the heat given off when we burn wood comes originally from the Sun. During the late 1970s many people were solving their own energy problems by cutting wood and using wood-burning stoves for heating. Although this saves fossil fuels, it is not a very good energy solution in heavily populated areas: burning wood releases fine carbon particles that pollute the air. A variation of this idea, however, could provide a significant portion of the fuel used for automobiles in the near future. The sugar and starch of almost any plant can be converted into ethyl alcohol (C_2H_5OH) by fermenting the sugars in the presence of yeast.

> yeast ETHYL ALCOHOL CARBON DIOXIDE

> 2 C₂ H₃ OH + 2 CO₂ $C_6H_{12}O_6$ sugar

Fermentation stops when the alcohol concentration in a water solution reaches about 15 percent; so it is necessary to distill the alcohol to remove it from the water. Gasoline that contains up to 15 percent alcohol can be burned in an ordinary engine. This mixture of gasoline and alcohol is known as gasohol. Higher concentrations, up to 100 percent alcohol, can be used in engines that have been modified at a modest cost.

To reduce costly imports of oil, Brazil has developed a national network of distilleries that use local crops, such as cassava, as raw materials to produce alcohol for engine fuel. Other projects to use alcohol in auto fuels are under way in the United States. In 1979 about seven hundred gasoline stations were selling gasohol.

At present, most of the ethyl alcohol used for fuel is being produced from grain that could otherwise be used for food. While this \Box may be acceptable in times of a great surplus of grain, it seems questionable to convert food into fuel for automobiles when many people in the world are starving. Furthermore, with our present techniques for grain production in the United States, it "costs" more energy to produce alcohol than the energy we get back when the alcohol is burned! A more logical approach would be to use the grain for food and the remainder of the plant—the biomass (leaves and stalks)-to make alcohol. But in doing this, some of the biomass must be left on the soil to provide the humus (organic matter) that helps fertilize and recondition the soil.

Methyl alcohol ($CH₃OH$, also called "wood alcohol" or methanol) is another substance that can be used as a fuel. Its properties as a fuel are much like those of ethyl alcohol: both can replace gasoline, and both produce lower emissions of air pollutants. Methyl alcohol is now made almost entirely from methane (CH_4) , the

TIME MACHINE Solar Energy

The large, wind-turbine generator (top) is contrasted with the small farm windmill (foreground) used to pump water. An artist's model of OTEC (bottom) illustrates the use of the oceans' temperature variations for the production of electric power.

major constituent of natural gas. Since natural gas is in short supply, we would have to obtain methyl alcohol from more abundant sources. One possibility would be by coal gasification-the reaction of coal (mostly carbon) with water (section E-63), followed by the reaction of carbon monoxide with hydrogen to make methanol.

Unfortunately, coal gasification plants have not been built on a scale large enough to supply the amount of methanol needed to make the process economical.

E-61 Far-out Solar Schemes

The uses of solar energy may be categorized as *direct* or *indirect*. Direct uses are those in which heat or electricity is produced when sunlight strikes some type of solar-energy device. Indirect uses are those in which energy is produced by the burning of fossil fuels or alcohol. Energy from the Sun is the driving force for winds, rains, and currents in the oceans. The Sun and the moon produce the tides of oceans. The uses of these indirect forms of solar energy are now being developed and tested.

- Windmills: For centuries farmers have used windmills to grind grain, to pump water for animals, and recently to recharge the batteries of their equipment. Much larger windmills are being tested for use as small power plants. One windmill near Boone, North Carolina, produces electricity for five hundred homes; another one at Clayton, New Mexico, supplies electricity for sixty homes. Electricity can be produced by windmills for about 5 cents per kilowatt-hour. In some areas this is close to the cost of electricity produced by conventional plants.
	- Ocean Thermal Energy Conversion (OTEC): This process takes advantage of the solar energy that falls on bodies of water, particularly oceans, creating temperature differences within the water. There are places in tropical oceans where the surface temperatures are 20 to 25°C higher than the temperatures of water in the lower layers. The difference in temperature provides a source of heat energy that can run an electric power plant. Solar-heated surface water is used to vaporize a fluid such as ammonia $(NH₃)$. The ammonia vapor is piped into turbines to drive generators that produce electricity. Then the vapor is condensed back to liquid by the colder water and recycled. Experiments designed to test the OTEC operation are in progress, but practical use is probably years away.

• Tidal and current power: There are certain ocean inlets where the tide that rushes through fills a huge reservoir. An example of such an inlet is the Bay of Fundy in Canada. For years people have thought of constructing dams across such inlets. Theoretically, the dam's gates would open to let the tide in, then close. As the tide flows out, it would turn turbines to generate electricity in a hydroelectric plant. Experiments to generate electricity from tides are in progress in France and the Soviet Union.

Currents in the oceans, as well as the surf that pounds beaches, contain enormous amounts of energy. The Department of Energy is funding a project in which huge "watermills" will be suspended in the Gulf Stream off the coast of Florida to capture some of the energy of the current. Scientists around the world are exploring ways to use wave power, which is estimated to be about 40 MW per kilometer of an average ocean beach.

PROBLEM \square

In the tropics, oceans have surface temperatures of about 27°C, while their depths have temperatures of about 4°C. What is the theoretical efficiency of an OTEC plant in the tropics for generating electricity?

Tidal power generates electricity at the Rance Station on the northern coast of Brittany (France).

E-62 Energy from Nuclei: Fusion

The Sun and other stars produce their energy mostly by nuclear reactions (see The Heart of Matter: A Nuclear Chemistry Module). The Sun consists mainly of hydrogen atoms, which react near its center to produce helium, positrons (particles similar to electrons but with positive charge), and enormous amounts of energy.

 4 $H \longrightarrow$ 4 $He + 2$ 9 s^* + energy

This is an example of nuclear fusion-a reaction in which small nuclei come together to form larger ones, releasing energy in the process.

Because the positively charged nuclei repel each other, high energies are needed to bring the nuclei close enough together for a reaction to occur. The energies of atoms or molecules in gases are proportional to temperature. Therefore, fusion reactions occur easily in the center of stars because of the enormous temperatures that exist there-tens of millions of kelvins!

On Earth these conditions are produced in the explosion of a thermonuclear weapon, also known as a hydrogen bomb. In this device a nuclear fission bomb is detonated, which for a brief moment

'The symbol ${}^{6}_{1}$ β stands for a positron.

A Tokamak ("magnetic-bottle") Fusion Test Reactor is shown under construction at Princeton University.

Six of the twenty arms that conduct laser beams at the SHIVA laser-fusion system.

Bursts of laser light heat the surface of a fuel pellet.

Evaporating molecules exert enormous force on the pellet, causing it to implode (explode inward).

The high temperature and density of the imploded pellet result in a fusion reaction that yields helium, neutrons, and energy.

produces the high temperatures needed to trigger a fusion reaction. The fuel for the fusion reaction is a compound that contains lithium (Li) and a heavy isotope of hydrogen, either deuterium $(^{2}_{1}H)$ or tritium $(^{3}_{1}H)$. Many fusion reactions occur among the nuclei of lithium, deuterium, and tritium.

> ${}^{2}_{1}H$ + ${}^{3}_{2}H$ \longrightarrow ${}^{4}_{2}He$ + ${}^{1}_{0}n$ + energy ${}_{3}^{5}Li + {}_{6}^{1}n \longrightarrow {}_{2}^{4}He + {}_{3}^{3}H +$ energy

This type of reaction releases huge amounts of energy and is responsible for the destructive power of thermonuclear weapons.

 $\frac{40}{40}$ produce electric power. The fuel for these reactors would be Scientists are trying to develop nuclear fusion reactors in which energy could be extracted from fusion reactions and used to obtained from molecules of water that have heavy hydrogen atoms. In this way the Earth's oceans represent an almost unlimited supply of fuel. For example, the amount of energy obtained by "burning" the deuterium found in a liter of ocean water is equal to the energy of approximately 300 liters of gasoline! Unfortunately, the production of a controlled thermonuclear reaction is difficult to achieve. It is necessary to contain the reactants-a mixture of electrons and bare positive nuclei (known as a plasma)—which exist at temperatures of tens of millions of degrees! There is no known material container that has a melting point approaching millions of degrees.

> Scientists are trying to develop "containers" that make use of strong magnetic fields-"magnetic bottles"-to hold the plasma. The magnetic bottle would also squeeze the plasma, producing the high density and temperature of the material needed to make the thermonuclear reactions occur. Experiments done to date have been promising, but we are still years away from a practical fusion reactor.

> Scientists have also worked with lasers in their efforts to produce a controlled thermonuclear fusion reaction. A laser is a device that focuses concentrated bursts of light energy on exceedingly small targets. Scientists at Lawrence Livermore Laboratory in California are working with a device in which the light beams of twenty huge lasers converge on a tiny pellet (less than 0.1 mm in diameter) of frozen deuterium and tritium. This intense burst of energy produces the conditions needed for fusion to occur. If the process can be made practical, a power plant would "burn" ten to twenty pellets every second, each producing a mini thermonuclear explosion. In trial runs at Livermore, fusion has been produced in pellets, but the energy put into the lasers was about ten thousand times as much as was recovered from the fusion reactions. However, research improvements by 1985 are expected to result in a net gain of energy.. Even so, it will be many years before practical

power plants can be built to produce electricity at a reasonable cost. Since the energy available from fusion is virtually limitless, it is worth expending considerable effort to make a practical system.

There are environmental problems associated with fusion reactors, however, since the operation would produce large amounts of radioactive tritium. Although most of this tritium would be recovered and reinjected into the system as fuel, the problem of radioactivity would not be completely eliminated.

E-63 Synfuels to the Rescue?

At the height of the gasoline shortage in the summer of 1979, many people argued in favor of a vigorous development of synthetic fuels—synfuels—as a partial solution to the energy crisis. Synfuels include liquid fuels obtained from oil shale and tar sands, as well as liquid and gaseous fuels made from coal. North America has enormous reserves of these resources. For example, the United States has enough coal to last at least two more centuries. Canada has vast reserves of tar sands estimated to contain a total amount of fuel equivalent to more than 170 billion barrels of petroleum—enough to supply the world's petroleum consumption of about 20 billion barrels per year for 8.5 years.

Synfuels are not a new source of energy. Before World War II, Germany assured itself of a supply of a gasolinelike fuel by developing the Fischer-Tropsch process to liquefy coal. The first step of the process involves the reaction of coal with water.

$$
C(s)
$$
 + $H_2O(g)$ $\xrightarrow{\text{toperature}}$ $CO(g)$ + $H_2(g)$

The products, carbon monoxide and hydrogen, then react in the presence of catalysts to form hydrocarbons, such as those in gasoline.

$$
6 CO(g)
$$
 + 13 H₂(g) $\xrightarrow{\text{catalyst}}$ C₆H₁₄(l) + 6 H₂O(g)

The process is expensive and is normally used only by nations that have a low supply of petroleum. Germany used this method to produce 100 000 barrels of fuel per day. In 1979 South Africa had one liquefaction plant that produced 10 percent of that nation's needs for liquid fuel and two more plants under development. Several designs for liquefaction plants are under consideration in the United States, but none has become the clear choice. A small test plant being built in Catlettsburg, Kentucky, is expected to produce 1800 barrels of synthetic oil per day from 600 tons of coal.

Coal gasification, which yields a product very similar to natural gas (mostly methane, $CH₄$), is a more highly developed process

TIME MACHINE Energy Uses in Transportation

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1979 Gasoline crisis recurs.

A research scientist simulates underground coal gasification.

An underground view of the Anvil Points oil-shale mine near Rifle, Colorado.

than coal liquefaction. Coal consists of about 80 percent carbon, 3 to 6 percent hydrogen, 1 or 2 percent each of oxygen, nitrogen, and sulfur, and about 10 percent or more of mineral ash. In order to convert coal into methane, hydrogen (from water) must be added to form CH,.

The first step in coal gasification is to heat the coal to 600°C or more to drive off volatile chemical compounds that react to form methane and hydrogen. This heating leaves behind a carbon-rich char.

$$
\text{coal} \xrightarrow{600^{\circ}C} \xrightarrow{\text{METHANE}} \text{CH}_{4}(g) + H_{2}(g) + C(s) \qquad \text{residue} \qquad \text{char}
$$

The char then reacts with steam to cause several further reactions.

$$
C(s) + H_2O(l) \longrightarrow CO(g) + H_2(g)
$$

\n
$$
CO(g) + H_2O(l) \longrightarrow CO_2(g) + H_2(g)
$$

\n
$$
C(s) + 2H_2(g) \longrightarrow CH_4(g)
$$

The products of these reactions contain about 50 percent methane and excess hydrogen, but even more hydrogen is needed to convert the carbon monoxide that is formed into methane. This hydrogen is produced by further reactions of CO and $H₂O$. Finally, pipeline-quality gas is produced by purifying the methane of water vapor, carbon dioxide, and hydrogen sulfide $(H₂S)$, the latter being formed by sulfur in the coal. Studies for several coal gasification

1.3 3

plants based on the preceding reactions are in progress in the United States and Europe.

The production of synfuels from coal, oil shale, and tar sands represents a potential solution to the energy crisis. However, there are difficult environmental problems associated with the use of these resources. We have already discussed some of the problems related to the mining and use of coal (sections E-27 and E-51). The United States has enough oil shale to yield between 200 and 600 billion barrels of petroleum, but separating the oil from the mineral matter causes environmental problems. In order to break down the rocky material and remove the oil from it, the shale must be crushed and heated to about 400 to 500°C. About 20 percent of the energy contained in the shale must be used to provide heat for the recovery process. The major problems, however, are the enormous volumes of waste shale produced (about 2 tons per barrel of oil) and the need for about three barrels of water for every barrel of oil produced in this process. There is probably not enough water available near our oil-shale deposits to produce more than about 1 mb/d. Studies are under way to develop processes that would release oil from shale without removing the shale deposits from the ground.

Recovering oil from tar sands in Canada presents problems somewhat similar to those involved in the production of oil from oil shale. However, an operating plant already exists in Alberta that has an output capacity of 100 000 barrels per day and several other plants are under development.

Although in the long run synfuels may prove to be a very important source of gas and petroleum, we should not expect them to be an immediate solution to the energy crisis. It seems unlikely, even with a "crash" program, that the production of synfuels will exceed 1 mb/d by 1990. Critics argue that it would be unwise to try to build many synfuel plants now, since we know little about the practical problems involved in the processes of synfuel production. Another factor to be considered is the cost of oil produced by these plants. In 1979 most economists felt that this oil would cost anywhere from \$5 to \$25 per barrel more than the current world oil price.

Along with the environmental problems we have already mentioned, the synfuel processes produce carcinogenic hydrocarbons as impurities. These impurities will have to be monitored and destroyed to prevent their release into the environment.

E-64 What's the Energy in Our Future?

As you can see, the problems of energy and the environment are very complex. There are no obvious "best" solutions, except possibly the conservation of energy. Ideally we should investigate

This dish-shaped antenna is used to study the problems of beaming solar energy from a satellite in space back to the Earth for conversion into electricity.

Tar sands are extracted from an open pit at the Syncrude facility in Alberta, Canada.

these options on a small scale and adopt the ones that prove most successful. But if energy independence is to be achieved quickly, it may be necessary for us to risk using technology that has not been fully tested.

Although many of the new energy sources sound simple and attractive, the difficulties in making use of them on a large scale are enormous. The amounts of materials, the capital expenditures, and the number of skilled workers needed to build and install the equipment are staggering. For example, if it cost \$10 000 to install solar-energy systems in each of the 70 million houses and apartments in the United States, the total cost would be \$700 billion! Even if we spread the cost over twenty years, it would still be \$35 billion per year. Billions of dollars would also be required for each of the other contributing solutions to the energy crisis-to build synfuel plants, to retool the auto industry for different engines, to build more reactors and coal mines, and so on. But regardless of what we decide to do about energy, the road to abundant supplies will be long and difficult.

PROBLEMS[[]

- 1. a. Calculate the efficiency of a solar steam-electric plant operating with steam at 300°C and cooling water at 20°C.
	- b. If the power of sunlight that reaches the ground is 250 W per square meter, calculate the area of solar collectors needed for a 100-MW electric plant, ignoring losses due to friction and transmission.
	- c. The operation of a large air-conditioning unit in a three-bedroom, single-family home requires 6000 W. Using the information in part (b), how large a collector will be needed to cool this home continuously for 24 hours?
- 2. A test car uses ethanol fermented from sugarcane as fuel. The car is driven 20 000 km per year at 10 km per liter of ethanol. If each square meter of sugarcane yields 1.5 liters of ethanol, how much land must be planted with sugarcane to produce ethanol to fuel the car for one year?
- 3. Crops grown for their energy value have a typical yield of about 15 metric tons per acre. Each metric ton has an energy value of about 2 000 000 Calories. At this rate, how many acres per year are required to fuel a power plant that produces 1000 MW with an efficiency of 40 percent?
- 4. a. Using the energy information given in section E-48 and the population figure for the United

States-about 220 million people- calculate the total amount of energy used per day by an average family of four.

- b. If the amount of solar power falling on the Earth's surface is about 100 W per square meter, calculate the area of solar collection surface required to supply all of the energy needs for the family in part (a), assuming there are no energy losses.
- 5. Assume that gasoline engines in automobiles are about 25 percent efficient in converting the energy content of the gasoline into power needed to move an automobile. Also assume that an overall efficiency of 80 percent could be achieved by charging batteries and using electric motors to propel a car.
	- a. To supply electricity for the batteries in electric cars, would it be more efficient to burn gasoline in automobiles directly or to burn it in a power plant that has an overall efficiency of 33 percent?
	- b. Assume the average person drives 40 miles per day in an automobile whose "mileage" is 20 miles per gallon. Compare the cost of gasoline per day at \$1.20 per gallon with the cost per day of electricity at 5 cents per kilowatt-hour (assuming the efficiencies noted above).

 $\frac{1}{2}$

Where Do We Go from Here?

Environmental chemistry is a young science and the problems affecting our environment are very complex. Nevertheless, important strides have been made toward an understanding of how the products of our society affect natural environmental processes.

A research scientist in a toxicology laboratory conducts an analysis of a water sample to determine if it is contaminated with fibers of asbestos.

The controlling, collecting, and recycling of garbage (right) is one of the most effective ways that each one of us can help keep our environment clean.

Noise is often overlooked and underestimated as a form of pollution affecting our environment (as illustrated in the stamp). Research in this area has pointed out that continued exposure to high levels of noise can result in hearing loss. About 16 million Americans will suffer some form of hearing loss because of noise pollution. To help combat this problem, noise screens have been installed along superhighways (below). These help absorb traffic sounds, which affect people living in heavily traveled areas.

One of the most important developments in recent years has been our growing awareness of the environment and how the problems related to it affect us personally. Most of the environmental problems we encounter today have been evolving for many years-since long before we became aware of them. It wasn't until about twenty years ago that environmental issues really caught the public's attention. In 1962 Rachel Carson wrote Silent Spring, a book dealing with problems of pesticides in the environment. This book became the focal point of a rapidly growing concern for the protection of our environment.

Progress is being made through the efforts of scientists, politicians, students, public figures, and many other concerned citizens. The Council on Environmental Quality was established in 1970 as a "watchdog" for the government. The Environmental Protection Agency was established to monitor the effects of new materials that are being developed. The Food and Drug Administration and the Consumer Products Safety Commission have developed much better methods of determining the safety of foods and other consumer products. Both of these groups have become more vigilant in protecting us from products that are potentially hazardous. Many new laws have been passed that require a reduction in the release of pollutants into the environment and that, in general, weigh the environmental impact of technological progress against the benefits. The use of many products that have an adverse effect on our environment has been curtailed. Some of these products we will have to live without, but others have been replaced by alternatives that are environmentally safer.

Despite the gains that have been made, many serious problems remain to be solved. Although the rate of population growth is decreasing in technological nations, it remains high in the under-

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developed countries. Exponential growth in our requirements for many of the world's resources, especially food, is pushing the world ever closer to its carrying capacity. The Earth cannot support many more doublings of our demands on it!

In our search for solutions to the energy crisis, we find ourselves in the midst of a national dilemma. Abundant supplies of energy exist, especially from renewable sources, but considerable effort and time are necessary to make that energy available. We want to reduce our oil imports, or at least not increase them, yet we continue to use our gasoline-guzzling automobiles as much as we have in the past, if not more so. The use of solar power as an alternative to fossil-fuel home heating is strongly endorsed, but not on a fullscale basis. There is no quick solution to the problem. For now, however, we must conserve as much energy as possible. The major options for the next several years seem to be coal and nuclear energy, both of which have potentially serious environmental problems associated with them.

During the years after World War II, developments in medicine, travel, pesticides, plastics, and communications occurred so rapidly that people grew to believe there was a technological solution for everything. It was assumed that scientists and engineers would quickly come forward with answers to all of our problems. In more recent years, as problems with some of the products of our technological society have become apparent and shortages of many resources have occurred, people have begun to realize the limits and dangers of many modern developments. Some have even felt that we should reject scientific development entirely. The problem is not with science, however, but with the ways in which scientific knowledge is applied. The goal of science is to increase our understanding of how things work. The problems arise when these scientific discoveries are used to introduce new processes or materials without proper concern for their possible negative effects. But we have a great need for more scientific knowledge concerning such things as the effects of gases and particles on climate, the causes and prevention of diseases, the chemistry of energy source materials, and the behavior of materials in the environment.

When we are faced with the many problems of resources and the environment, it is easy to become discouraged. But despair is not the answer. What Rachel Carson started with Silent Spring has become a movement of millions of Americans who are concerned about the quality of life and the environment. Citizens along with scientists and engineers want to reverse the deterioration of their surroundings and are actively working on solutions to the problems. There is considerable reason for optimism about the preservation and enhancement of our environment and the quality of life. Although its balance is delicate, nature has great resilience and will serve us well if we give it a chance.

Rachel Carson, author of Silent Spring.

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 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?)
- Never smell a material by placing your nose directly at 11. 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 special precautions in addition to those discussed in this Appendix.

> $\frac{d}{2}$. $\hat{\mathcal{L}}$

Appendix II: Units and Conversion Factors

The Units of Energy

The basic SI unit of energy is the joule (J). The equation for the kinetic energy E of a moving object having mass m and velocity v is

 $E = \frac{1}{2}mv^2$

If mass is expressed in kilograms and velocity in meters per second (m/s), the energy is given in joules.

joules = $kg \times (m/s)^2$

When we work entirely with SI units, the joule is the only energy unit we need to know about. In regard to environ-

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mental problems, however, various other energy units are used. For example:

- Electrical energy is measured in kilowatt-hours (kWh), where the kilowatt is a unit of energy per unit time.
- The heat content of fuels is given in British Thermal Units (BTUs).(The cooling capacity of air conditioners is given in terms of BTUs of heat removed per hour.)
- \bullet The energy content of food—that is, the energy released when food is oxidized to $CO₂$ and $H₂O$ —is expressed in Calories.

Conversion of Energy Units to Joules:

- 1 Calorie = heat required to raise temperature of 1 g of water 1° C = 4.184 J
- 1 Calorie = heat required to raise temperature of 1 kg of water $1^{\circ}C = 4184$ J
1 BTU = heat re
- $=$ heat required to raise temperature of 1 pound of water 1°F

 $= 1052$ J 1 kwH = 3.6×10^6 J
1 quad = 10^{15} BTUs $= 10^{15}$ BTUs

 $= 1.05 \times 10^{15}$ kJ

the combustion of fuels (they may vary somewhat from one sample to another).

1 ton of coal = 910 kg coal = 2.5×10^{10} J

1 barrel of crude oil $(42$ gallons) = 6.1 \times 10⁹ J

1 cubic foot of natural gas = 1.1×10^6 J

1 gallon of gasoline = 1.3×10^8 J

UNITS OF POWER

Power is the amount of energy released or used per unit time. Power is expressed in units of joules per second or in other energy units divided by time. You are probably most familiar with the power unit watt (W), which is 1 J per second. Most light bulbs in your house use from 60 to 150 W of electrical power. Toasters and irons draw much more power, typically from 900 to 1200 W. The amount of power an appliance uses can also be determined from the voltage of the electricity and the current drawn.

A modern steam-electric plant produces about 500 000 kW or more of electric power.

power (watts) = voltage (volts) \times current (amperes)

Most line voltage in the United States is 110 or 115 V (volts). An appliance that draws 10 A (amperes) of current at 115 V, then, uses power at the rate of $10 \text{ A} \times 115 \text{ V} = 1150 \text{ W}$, or 1.15 kW. When the appliance is operated for 1 hour, the total energy used is 1.15 kWh.

Another familiar unit of power used especially with motors or automobile engines is horsepower (hp). One hp is equivalent to 746 W or 0.746 kW.

CONCENTRATION UNITS

The concentrations of trace elements or compounds are often given in parts per million (ppm). If the sample in question is a solid or a liquid, the value refers to parts per million by mass. This is the same as 1 g of substance in 1 metric ton (1000 kg) of material. It should also be noted that a concentration of 10 000 ppm is the same as 1 percent by mass.

In the gas phase, parts per million generally refers to numbers of molecules (or atoms). The concentration of $CO₂$ in the atmosphere is about 330 ppm, meaning that 330 out of every 1 million molecules of air are $CO₂$ molecules. This is equivalent to saying that 0.033 percent of the molecules in the air are $CO₂$.

The following are approximate values for energy released in the atmosphere are generally quoted in terms of mass per On the other hand, concentrations of particulate matter in unit volume, for example, micrograms per cubic meter $(\mu g/m^3)$. Often it is of interest to compute concentrations of gases in the same terms.

> Suppose we want to calculate the mass concentration of a gas having molar mass M . Let's assume that the air has a temperature of 25°C and a pressure of 1 atm (atmosphere). If air behaves as a perfect gas, 1 m^3 (10^3 liter³) contains 1000 liter/24.4 liter/mole = 41.0 moles of air. If the pollutant gas has a concentration of 1 ppm, then 1 m^3 of air contains 41×10^{-6} moles of pollutant having a mass of $\mathcal{M} \times 41 \times 10^{-6}$ g, or 41 $M \mu$ g. We can therefore relate the two concentration units by the equation

concentration (μ g/m³) = concentration (ppm) × 41 \mathcal{M}

For example, an SO₂ ($M = 64$) concentration of 1 ppm is converted to

concentration $SO_2 = 1 \times 41 \times 64 = 2620 \mu g/m^3$

Note that this conversion must be altered slightly (using the ideal gas law) if pressure and temperature are different from the values assumed above.

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TABLE OF INTERNATIONAL RELATIVE ATOMIC MASSES*

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

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

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 $\hat{\boldsymbol{\epsilon}}$

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147

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awrencium $\begin{array}{|l|c|c|}\n\hline\n\text{Fhuhum} & \text{Yterbum} & \text{Luetuum} \\
\hline\n69 & 70 & 71\n\end{array}$ $\frac{1}{2}$ 257) $\frac{3}{2}$ $\frac{1}{2}$ Nobelium
102 (254) Mendel'm
101 **PN** (256) Fm Fermium
| 100 Erbium
68 (254) Einsteinium Dysprosium Holmum
|66
|67 <u>ဖို</u> (254) 99 Californium $\ddot{\text{o}}$ (251) Berkellum
97 Bk | Praseody'n | Neodymium | Promethrum | Samarium | Europium | Gadolinium | Terbium
| 59
| 59 (245) $\overline{\overline{\epsilon}}$ Americium Curium
95 (245) $\overline{\mathbf{g}}$ (243) \mathbf{z} Pluton um (242) $\overline{9}$ $\begin{array}{c}\n\bullet \\
\bullet \\
\bullet\n\end{array}$ 237.0 Protactinium Uranium 238.0 \Box 8 \mathbf{a} $\frac{231.0}{2}$ $\overline{5}$ Cerium
58 f Thorium
90 $\overline{232.0}$ $\frac{1}{\ast}$

fThe 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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