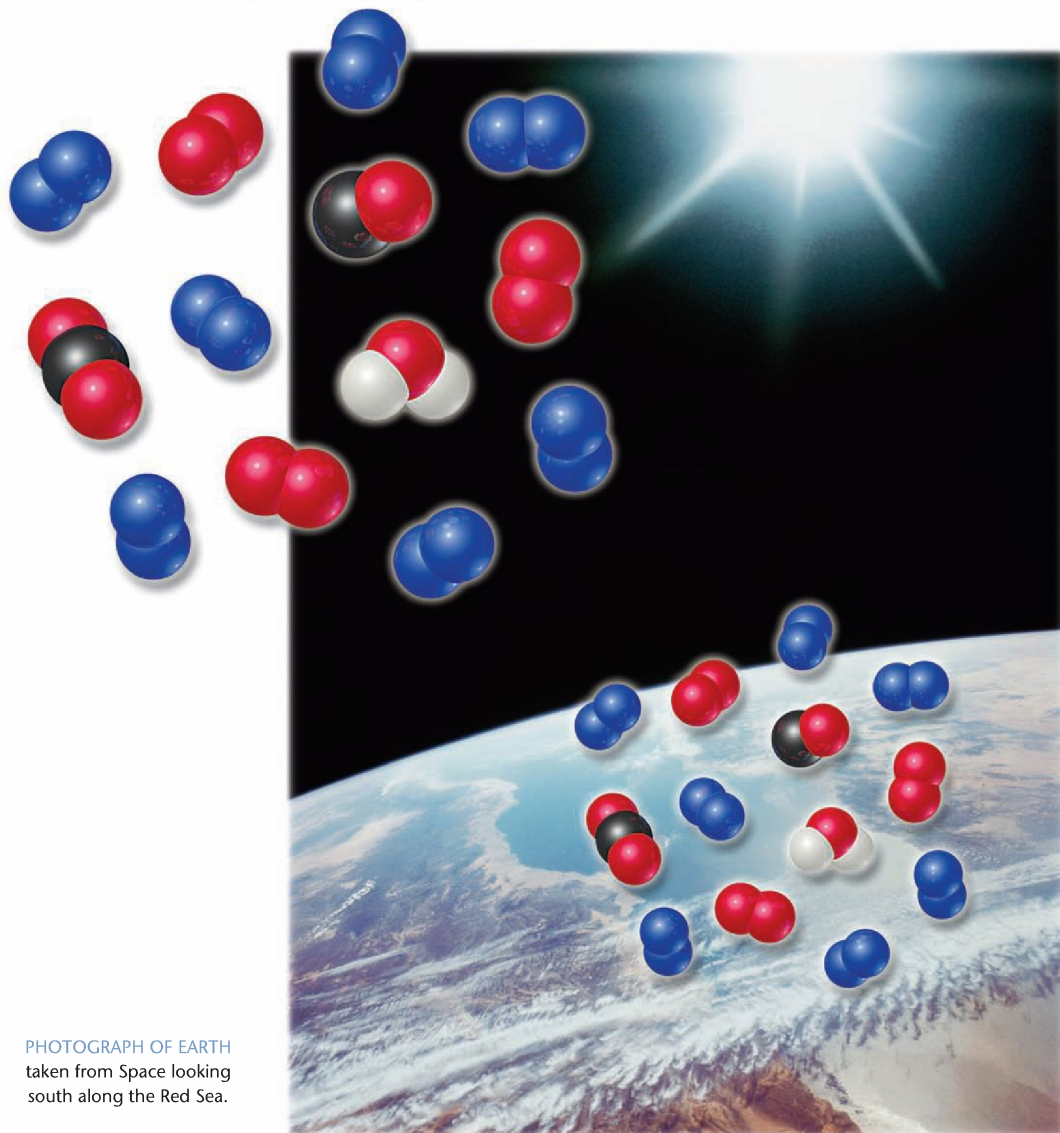


CHAPTER  
18

CHEMISTRY OF THE  
ENVIRONMENT



PHOTOGRAPH OF EARTH  
taken from Space looking  
south along the Red Sea.

### 18.1 Earth's Atmosphere

We begin this chapter with a general look at Earth's atmosphere. We will consider the temperature profile of the atmosphere, its pressure profile, and its chemical composition.

### 18.2 Outer Regions of the Atmosphere

We next examine the outer (or upper) regions of the atmosphere, where the pressure is very low. These regions absorb a great deal of high-energy radiation from the Sun through *photoionization* and *photodissociation* reactions. By filtering out high-energy radiation, these processes make it possible for life as we know it to exist on Earth.

### 18.3 Ozone in the Upper Atmosphere

We will see that ozone in the *stratosphere* acts as a filter of high-energy ultraviolet light. Human activities have contributed to the depletion of the ozone layer by introducing into the stratosphere chemicals that perturb the natural cycle of ozone formation and decomposition. Notable among these chemicals are *chlorofluorocarbons*.

### 18.4 Chemistry of the Troposphere

We complete our discussion of the atmosphere by examining its innermost region, the *troposphere*, which is the region in which we live. Many minor constituents of the troposphere affect air quality and the acidity of rainwater. The concentrations of

many of these minor constituents, including those that cause *acid rain* and *photochemical smog*, have been increased by human activities. Carbon dioxide is an important minor constituent of the atmosphere because it acts as a "*greenhouse*" gas that warms Earth's atmosphere.

### 18.5 The World Ocean

We next turn our attention to our water environment. Almost all the water on Earth is in the world ocean. Seawater contains many salts that participate in the global cycling of the elements and nutrients.

### 18.6 Freshwater

Our discussion of water concludes with a look at freshwater. Processing seawater to obtain freshwater is energy intensive. We count on freshwater sources to supply most of our needs, but these sources often require treatment to render them usable.

### 18.7 Green Chemistry

We conclude our discussion of the environment by examining *green chemistry*, which seeks to eliminate pollution at its source. Green chemistry is an international initiative to make industrial products, processes, and chemical reactions compatible with a sustainable society and environment.

**IN 1997, REPRESENTATIVES OF 130 NATIONS MET IN KYOTO, JAPAN,**  
to discuss the impact of human activities on global warming.  
Out of that meeting came an initiative to work toward a global  
treaty that would, among other things, spell out actions  
to be taken to reduce emissions of gases that cause

global warming. In 2001 in Bonn, Germany, 178 nations signed a treaty based on the so-called Kyoto Protocols. In 2007, the United Nations Intergovernmental Panel on Climate Change issued a report declaring that human activity has "very likely" been the driving force for the warming trend observed worldwide over the past 50 years. These efforts to address environmental concerns at the international level indicate that many of the most urgent environmental problems are global in nature.

As technology has advanced and the world human population has increased, we have put new and greater stresses on our environment. Paradoxically, the very technology that can cause pollution also provides the tools to help us understand and manage our environment in a beneficial way.

Chemistry is often at the heart of these issues. The economic growth of both developed and developing nations depends critically on chemical processes that range from treatment of water supplies to industrial processes. Some of these processes produce products or by-products that are harmful to the environment.

We are now in a position to apply the principles we have learned in earlier chapters to an understanding of how our environment operates and how human activities affect it. In this chapter we consider some aspects of the chemistry of our environment, focusing on Earth's atmosphere and water. Both the air and water of our planet make life as we know it possible. To understand and maintain the environment in which we live, we must understand how human-made and natural chemical compounds interact on land and in the sea and sky. Our daily decisions as consumers mirror those of the leaders meeting in Bonn and similar international meetings: We must weigh the costs versus the benefits of our actions. Unfortunately, the environmental impacts of our decisions are often very subtle and not immediately evident.

## 18.1 EARTH'S ATMOSPHERE

Because most of us have never been very far from Earth's surface, we often take for granted the many ways in which the atmosphere determines the environment in which we live. In this section we will examine some of the important characteristics of our planet's atmosphere.

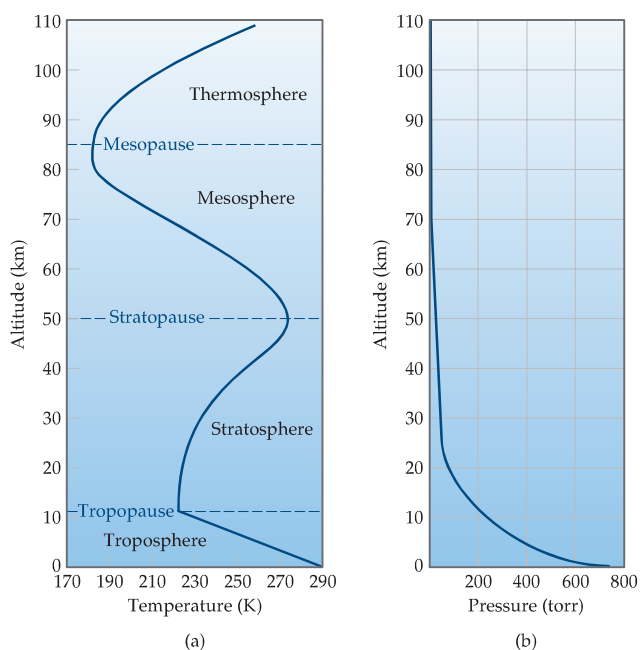
The temperature of the atmosphere varies in a complex manner as a function of altitude, as shown in Figure 18.1(a). The atmosphere is divided into four regions based on this temperature profile. Just above the surface, in the **troposphere**, the temperature normally decreases with increasing altitude, reaching a minimum of about 215 K at about 12 km. Nearly all of us live our entire lives in the troposphere. Howling winds and soft breezes, rain, and sunny skies—all that we normally think of as “weather”—occur in this region. Commercial jet aircraft typically fly about 10 km (33,000 ft) above Earth, an altitude that approaches the upper limit of the troposphere, which we call the *tropopause*.

Above the tropopause the temperature increases with altitude, reaching a maximum of about 275 K at about 50 km. The region from 10 km to 50 km is called the **stratosphere**. Beyond the stratosphere are the *mesosphere* and the *thermosphere*. Notice in Figure 18.1(a) that the temperature extremes that form the boundaries between adjacent regions are denoted by the suffix *-pause*. The boundaries are important because gases mix across them relatively slowly. For example, pollutant gases generated in the troposphere pass through the tropopause and find their way into the stratosphere only very slowly.

Unlike temperature, which varies in a complex way with increased altitude, the pressure of the atmosphere decreases in a regular way with increasing elevation, as shown in Figure 18.1(b). Atmospheric pressure declines much more rapidly at lower elevations than at higher ones because of the atmosphere's compressibility. Thus, the pressure decreases from an average value of 760 torr (101 kPa) at sea level to  $2.3 \times 10^{-3}$  torr ( $3.1 \times 10^{-4}$  kPa) at 100 km, to only  $1.0 \times 10^{-6}$  torr ( $1.3 \times 10^{-7}$  kPa) at 200 km. The troposphere and stratosphere

▼ **Figure 18.1 Temperature and pressure in the atmosphere.**

(a) Temperature variations in the atmosphere at altitudes below 110 km.  
(b) Variations in atmospheric pressure with altitude. At 80 km the pressure is approximately 0.01 torr.



together account for 99.9% of the mass of the atmosphere, 75% of which is the mass in the troposphere. Consequently, most of the chemistry that follows focuses on the troposphere and stratosphere.

### Composition of the Atmosphere

Earth's atmosphere is an extremely complex system. Its temperature and pressure change over a wide range with altitude, as we have just seen. The atmosphere is constantly bombarded by radiation and energetic particles from the Sun. This barrage of energy has profound chemical effects, especially on the outer reaches of the atmosphere (Figure 18.2▶). In addition, because of Earth's gravitational field, lighter atoms and molecules tend to rise to the top of the atmosphere, especially in the stratosphere and upper layers that are not as turbulent as the troposphere. Because of all these factors, the composition of the atmosphere is not uniform.

Table 18.1▼ shows the composition by mole fraction of dry air near sea level. Although traces of many substances are present,  $N_2$  and  $O_2$  make up about 99% of the atmosphere. The noble gases and  $CO_2$  make up most of the remainder.

When speaking of trace constituents, we commonly use *parts per million* (ppm) as the unit of concentration. When applied to substances in aqueous solution, parts per million refers to grams of substance per million grams of solution. ∞ (Section 13.4) When dealing with gases, however, one part per million refers to one part by *volume* in 1 million volume units of the whole. Because volume ( $V$ ) is proportional to the number of moles  $n$  of gas via the ideal-gas equation ( $PV = nRT$ ), volume fraction and mole fraction are the same. Thus, 1 ppm of a trace constituent of the atmosphere amounts to one mole of that constituent in 1 million moles of total gas; that is, the concentration in ppm is equal to the mole fraction times  $10^6$ . Table 18.1 lists the mole fraction of  $CO_2$  in the atmosphere as 0.000375. Its concentration in ppm is therefore  $0.000375 \times 10^6 = 375$  ppm.

Before we consider the chemical processes that occur in the atmosphere, let's review some of the important chemical properties of the two major components,  $N_2$  and  $O_2$ . Recall that the  $N_2$  molecule possesses a triple bond between the nitrogen atoms. ∞ (Section 8.3) This very strong bond is largely responsible for the very low reactivity of  $N_2$ , which undergoes reaction only under extreme conditions. The bond energy in  $O_2$ , 495 kJ/mol, is much lower than that in  $N_2$ , which is 941 kJ/mol. ∞ (Table 8.4) Therefore,  $O_2$  is much more reactive than  $N_2$ . For example, oxygen reacts with many substances to form oxides. The oxides of nonmetals, for example  $SO_2$ , usually form acidic solutions when dissolved in water. The oxides of active metals, for example  $CaO$ , form basic solutions when dissolved in water. ∞ (Section 7.7)



▲ **Figure 18.2 The aurora borealis.** This luminous display in the northern sky, also called the northern lights, is produced by collisions of high-speed electrons and protons from the Sun with air molecules. The charged particles are channeled toward the polar regions by Earth's magnetic field.

**TABLE 18.1** ■ Composition of Dry Air Near Sea Level

Component*	Content (mole fraction)	Molar Mass
Nitrogen	0.78084	28.013
Oxygen	0.20948	31.998
Argon	0.00934	39.948
Carbon dioxide	0.000382	44.0099
Neon	0.00001818	20.183
Helium	0.00000524	4.003
Methane	0.000002	16.043
Krypton	0.00000114	83.80
Hydrogen	0.0000005	2.0159
Nitrous oxide	0.0000005	44.0128
Xenon	0.000000087	131.30

\*Ozone, sulfur dioxide, nitrogen dioxide, ammonia, and carbon monoxide are present as trace gases in variable amounts.

**SAMPLE EXERCISE 18.1** | Calculating the Concentration of Water in Air

What is the concentration, in parts per million, of water vapor in a sample of air if the partial pressure of the water is 0.80 torr and the total pressure of the air is 735 torr?

**SOLUTION**

**Analyze:** We are given the partial pressure of water vapor and the total pressure of an air sample and asked to determine the water vapor concentration.

**Plan:** Recall that the partial pressure of a component in a mixture of gases is given by the product of its mole fraction and the total pressure of the mixture  $\Leftrightarrow$  (Section 10.6):

$$P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}P_t$$

**Solve:** Solving for the mole fraction of water vapor in the mixture,  $X_{\text{H}_2\text{O}}$ , gives:

$$X_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P_t} = \frac{0.80 \text{ torr}}{735 \text{ torr}} = 0.0011$$

The concentration in ppm is the mole fraction times  $10^6$

$$0.0011 \times 10^6 = 1100 \text{ ppm}$$

**PRACTICE EXERCISE**

The concentration of CO in a sample of air is found to be 4.3 ppm. What is the partial pressure of the CO if the total air pressure is 695 torr?

**Answer:**  $3.0 \times 10^{-3}$  torr

**18.2 OUTER REGIONS OF THE ATMOSPHERE**

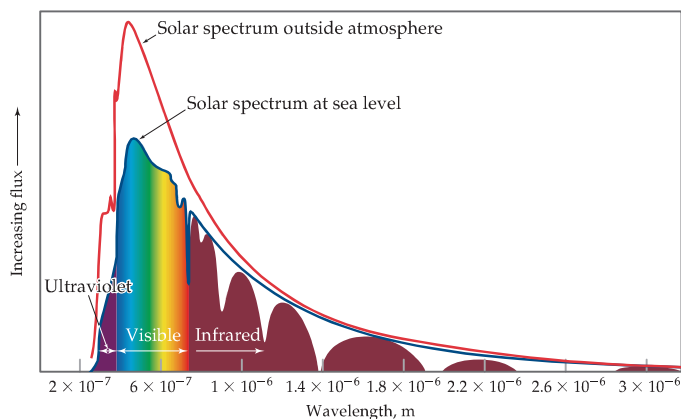
Although the outer portion of the atmosphere, beyond the stratosphere, contains only a small fraction of the atmospheric mass, it forms the outer defense against the hail of radiation and high-energy particles that continuously bombard Earth. As the bombarding radiation passes through the upper atmosphere, it causes two basic kinds of chemical changes: photodissociation and photoionization. These processes protect us from high-energy radiation by absorbing most of the radiation before it reaches the troposphere where we live. If it were not for these photochemical processes, plant and animal life as we know it could not exist on Earth.

**Photodissociation**

The Sun emits radiant energy over a wide range of wavelengths (Figure 18.3  $\blacktriangleleft$ ). To understand the connection between the wavelength of radiation and its effect on atoms and molecules, recall that electromagnetic radiation can be pictured as a stream of photons.  $\Leftrightarrow$  (Section 6.2) The energy of each photon is given by the relationship  $E = h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the radiation. For a chemical change to occur when radiation strikes atoms or molecules, two conditions must be met. First, there must be photons with energy sufficient to accomplish some chemical process such as breaking a chemical bond or removing an electron. Second, molecules must absorb these photons. When these requirements are met, the energy of the photons is used to do the work associated with some chemical change.

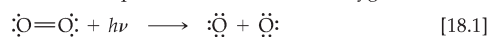
The rupture of a chemical bond resulting from absorption of a photon by a molecule is called **photodissociation**.

**Figure 18.3 The solar spectrum.** Shown in this graph is the amount of sunlight (in light energy per area per time, known as flux) at different wavelengths that reaches the top of Earth's atmosphere. For comparison, the corresponding data for the amount of sunlight that reaches sea level is shown. The atmosphere absorbs much of the ultraviolet and visible light emitted by the Sun.



No ions are formed when the bond between two atoms is cleaved by photodissociation. Instead, half the bonding electrons stay with one of the atoms and half stay with the other atom. The result is two neutral particles.

One of the most important processes occurring in the upper atmosphere above about 120-km elevation is the photodissociation of the oxygen molecule:



The minimum energy required to cause this change is determined by the bond energy (or *dissociation energy*) of  $\text{O}_2$ , 495 kJ/mol. In Sample Exercise 18.2 we calculate the longest wavelength photon having sufficient energy to photodissociate the  $\text{O}_2$  molecule.

### SAMPLE EXERCISE 18.2 | Calculating the Wavelength Required to Break a Bond

What is the maximum wavelength of light, in nanometers, that has enough energy per photon to dissociate the  $\text{O}_2$  molecule?

#### SOLUTION

**Analyze:** We are asked to determine the wavelength of a photon that has just enough energy to break the  $\text{O}=\text{O}$  double bond in  $\text{O}_2$ .

**Plan:** We first need to calculate the energy required to break the  $\text{O}=\text{O}$  double bond in one molecule, and then find the wavelength of a photon of this energy.

**Solve:** The dissociation energy of  $\text{O}_2$  is 495 kJ/mol. Using this value and Avogadro's number, we can calculate the amount of energy needed to break the bond in a single  $\text{O}_2$  molecule:

$$\left(495 \times 10^3 \frac{\text{J}}{\text{mol}}\right) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}}\right) = 8.22 \times 10^{-19} \frac{\text{J}}{\text{molecule}}$$

We next use the Planck relationship,  $E = h\nu$ ,  $\infty$  (Equation 6.2) to calculate the frequency,  $\nu$ , of a photon that has this amount of energy:

$$\nu = \frac{E}{h} = \frac{8.22 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 1.24 \times 10^{15} \text{ s}^{-1}$$

Finally, we use the relationship between the frequency and wavelength of light  $\infty$  (Section 6.1) to calculate the wavelength of the light:

$$= \frac{c}{\nu} = \left(\frac{3.00 \times 10^8 \text{ m/s}}{1.24 \times 10^{15} \text{ /s}}\right) \left(\frac{10^9 \text{ nm}}{1 \text{ m}}\right) = 242 \text{ nm}$$

Thus, light of wavelength 242 nm, which is in the ultraviolet region of the electromagnetic spectrum, has sufficient energy per photon to photodissociate an  $\text{O}_2$  molecule. Because photon energy increases as wavelength *decreases*, any photon of wavelength *shorter* than 242 nm will have sufficient energy to dissociate  $\text{O}_2$ .

#### PRACTICE EXERCISE

The bond energy in  $\text{N}_2$  is 941 kJ/mol (Table 8.4). What is the longest wavelength a photon can have and still have sufficient energy to dissociate  $\text{N}_2$ ?

**Answer:** 127 nm

Fortunately for us,  $\text{O}_2$  absorbs much of the high-energy, short-wavelength radiation from the solar spectrum before that radiation reaches the lower atmosphere. As it does, atomic oxygen,  $:\ddot{\text{O}}:$ , is formed. At higher elevations the dissociation of  $\text{O}_2$  is very extensive. At 400 km, for example, only 1% of the oxygen is in the form of  $\text{O}_2$ ; the other 99% is atomic oxygen. At 130 km,  $\text{O}_2$  and atomic oxygen are just about equally abundant. Below 130 km,  $\text{O}_2$  is more abundant than atomic oxygen because most of the solar energy has been absorbed in the upper atmosphere.

The dissociation energy of  $\text{N}_2$  is very high (Table 8.4). As shown in the Practice Exercise in Sample Exercise 18.2, only photons of very short wavelength possess sufficient energy to dissociate  $\text{N}_2$ . Furthermore,  $\text{N}_2$  does not readily absorb photons, even when they possess sufficient energy. As a result, very little atomic nitrogen is formed in the upper atmosphere by photodissociation of  $\text{N}_2$ .

### Photoionization

In 1901 Guglielmo Marconi received a radio signal in St. John's, Newfoundland, that had been transmitted from Land's End, England, some 2900 km away. Because people at the time thought radio waves traveled in straight lines, they assumed that the curvature of Earth's surface would make radio communication over large distances impossible. Marconi's successful experiment suggested that Earth's atmosphere in some way substantially affects radio-wave propagation. His discovery led to intensive study of the upper atmosphere. In about 1924, the existence of electrons in the upper atmosphere was established by experimental studies.

For each electron present in the upper atmosphere, there must be a corresponding positively charged particle. The electrons in the upper atmosphere result mainly from the **photoionization** of molecules, caused by solar radiation. Photoionization occurs when a molecule absorbs radiation and the absorbed energy causes an electron to be ejected from the molecule. The molecule then becomes a positively charged ion. For photoionization to occur, therefore, a molecule must absorb a photon, and the photon must have enough energy to remove an electron.  $\infty$  (Section 7.4)

**TABLE 18.2** ■ Ionization Processes, Ionization Energies, and Maximum Wavelengths Capable of Causing Ionization

Process	Ionization Energy (kJ/mol)	$\lambda_{\max}$ (nm)
$\text{N}_2 + h\nu \longrightarrow \text{N}_2^+ + \text{e}^-$	1495	80.1
$\text{O}_2 + h\nu \longrightarrow \text{O}_2^+ + \text{e}^-$	1205	99.3
$\text{O} + h\nu \longrightarrow \text{O}^+ + \text{e}^-$	1313	91.2
$\text{NO} + h\nu \longrightarrow \text{NO}^+ + \text{e}^-$	890	134.5

Some of the more important ionization processes occurring in the atmosphere above about 90 km are shown in Table 18.2  $\blacktriangleleft$ , together with the ionization energies and  $\lambda_{\max}$ , the maximum wavelength of a photon capable of causing ionization. Photons with energies sufficient to cause ionization have wavelengths in the high-energy end of the ultraviolet region of the electromagnetic spectrum. These wavelengths are completely filtered out of the radiation reaching Earth, because they are absorbed by the upper atmosphere.

## 18.3 OZONE IN THE UPPER ATMOSPHERE

While  $\text{N}_2$ ,  $\text{O}_2$ , and atomic oxygen absorb photons having wavelengths shorter than 240 nm, ozone,  $\text{O}_3$ , is the key absorber of photons having wavelengths ranging from 240 to 310 nm, in the ultraviolet region of the electromagnetic spectrum. Ozone protects us from these harmful high-energy photons, which would otherwise penetrate to Earth's surface. Let's consider how ozone forms in the upper atmosphere and how it absorbs photons.

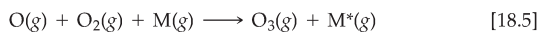
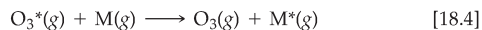
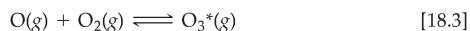
Below an altitude of 90 km, most of the short-wavelength radiation capable of photoionization has been absorbed. Radiation capable of dissociating the  $\text{O}_2$  molecule is sufficiently intense, however, for photodissociation of  $\text{O}_2$  (Equation 18.1) to remain important down to an altitude of 30 km. In the region between 30 and 90 km, the concentration of  $\text{O}_2$  is much greater than that of atomic oxygen. Therefore, the oxygen atoms that form in this region undergo frequent collisions with  $\text{O}_2$  molecules, resulting in the formation of ozone,  $\text{O}_3$ :



The asterisk over the  $\text{O}_3$  denotes that the ozone molecule contains an excess of energy. The reaction in Equation 18.2 releases 105 kJ/mol. This energy must be transferred away from the  $\text{O}_3^*$  molecule in a very short time or else the molecule will fly apart again into  $\text{O}_2$  and  $\cdot\ddot{\text{O}}$ —a decomposition that is the reverse of the process by which  $\text{O}_3^*$  is formed.

An energy-rich  $\text{O}_3^*$  molecule can release its excess energy by colliding with another atom or molecule and transferring some of the excess energy to it. Let's represent the atom or molecule with which  $\text{O}_3^*$  collides as M. (Usually M is  $\text{N}_2$  or  $\text{O}_2$  because these are the most abundant molecules in the atmosphere.)

The formation of  $O_3^*$  and the transfer of excess energy to M are summarized by the following equations (where O atoms are shown without valence electrons):



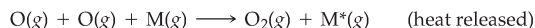
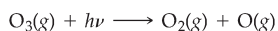
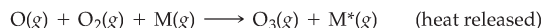
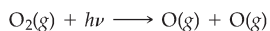
The rate at which  $O_3$  forms according to Equations 18.3 and 18.4 depends on two factors that vary in opposite directions with increasing altitude. First, the formation of  $O_3^*$ , according to Equation 18.3, depends on the presence of O atoms. At low altitudes most of the radiation energetic enough to dissociate  $O_2$  has been absorbed; thus, the formation of O is favored at higher altitudes. Second, both Equations 18.3 and 18.4 depend on molecular collisions. [∞ \(Section 14.5\)](#) The concentration of molecules is greater at low altitudes, and so the frequency of collisions between O and  $O_2$  (Equation 18.3) and between  $O_3^*$  and M (Equation 18.4) are both greater at lower altitudes. Because these processes vary with altitude in opposite directions, the highest rate of  $O_3$  formation occurs in a band at an altitude of about 50 km, near the stratopause [Figure 18.1(a)]. Overall, roughly 90% of Earth's ozone is found in the stratosphere, between the altitudes of 10 and 50 km.

Once formed, an ozone molecule does not last long. Ozone is capable of absorbing solar radiation, which decomposes the molecule back into  $O_2$  and O. Because only 105 kJ/mol is required for this process, photons of wavelength shorter than 1140 nm are sufficiently energetic to photodissociate  $O_3$ . However, most of the output from the Sun is concentrated in the visible and ultraviolet portions of the electromagnetic spectrum (Figure 18.3). Photons with wavelengths shorter than about 300 nm are energetic enough to break many kinds of single chemical bonds. Thus, the "ozone shield" is essential for our continued well-being. The ozone molecules that form this essential shield against high-energy radiation represent only a tiny fraction of the oxygen atoms present in the stratosphere, however, because they are continually destroyed even as they are formed.

### GIVE IT SOME THOUGHT

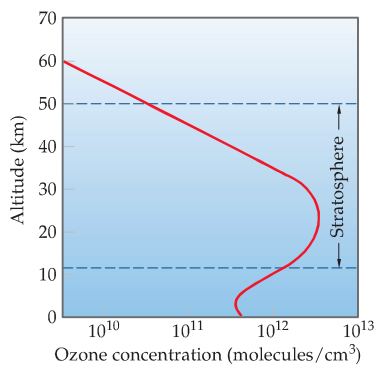
Look at Figure 18.3. Based on the relative areas under the curves, what fraction of the radiation with wavelengths in the ultraviolet portion of the spectrum is absorbed by the upper atmosphere?

The photodecomposition of ozone reverses the reaction that forms it. We thus have a cyclic process of ozone formation and decomposition, summarized as follows:

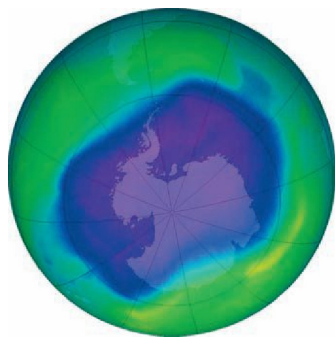


The first and third processes are photochemical; they use a solar photon to initiate a chemical reaction. The second and fourth processes are exothermic chemical reactions. The net result of all four processes is a cycle in which solar radiant energy is converted into thermal energy. The ozone cycle in the stratosphere is responsible for the rise in temperature that reaches its maximum at the stratopause, as illustrated in Figure 18.1(a).





▲ **Figure 18.4 Ozone depletion.** Variation in ozone concentration in the atmosphere, as a function of altitude.



▲ **Figure 18.5 Map of the total ozone present in the Southern Hemisphere, taken on September 24, 2006 from an orbiting satellite.** The different colors represent different ozone concentrations. The center area, which is over Antarctica, is the ozone hole—the area of lowest ozone.

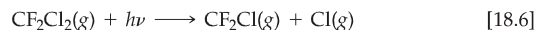
The scheme described for the formation and decomposition of ozone molecules accounts for some, but not all, of the facts about the ozone layer. Many chemical reactions occur that involve substances other than just oxygen. We must also consider the effects of turbulence and winds that mix up the stratosphere. A very complicated picture results. The overall result of ozone formation and removal reactions, coupled with atmospheric turbulence and other factors, is to produce an ozone profile in the upper atmosphere as shown on the left in Figure 18.4, with a maximum ozone concentration occurring at an altitude of about 30 km.

### Depletion of the Ozone Layer

The ozone layer protects Earth's surface from damaging ultraviolet radiation. Satellite monitoring of ozone, which began in 1978, has revealed a depletion of ozone in the stratosphere that is particularly severe over Antarctica, a phenomenon known as the *ozone hole* (Figure 18.5). The first scientific paper on this phenomenon appeared in 1985.

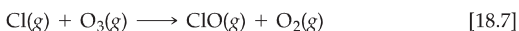
In 1995 the Nobel Prize in Chemistry was awarded to F. Sherwood Rowland, Mario Molina, and Paul Crutzen for their studies of ozone depletion. In 1970 Crutzen showed that naturally occurring nitrogen oxides catalytically destroy ozone. Rowland and Molina recognized in 1974 that chlorine from **chlorofluorocarbons** (CFCs) may deplete the ozone layer. These substances, principally  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ , have been widely used as propellants in spray cans, as refrigerant and air-conditioner gases, and as foaming agents for plastics. They are virtually unreactive in the lower atmosphere. Furthermore, they are relatively insoluble in water and are therefore not removed from the atmosphere by rainfall or by dissolution in the oceans. Unfortunately, the lack of reactivity that makes them commercially useful also allows them to survive in the atmosphere and to diffuse eventually into the stratosphere. It is estimated that several million tons of chlorofluorocarbons are now present in the atmosphere.

As CFCs diffuse into the stratosphere, they are exposed to high-energy radiation, which can cause photodissociation. The C—Cl bonds are considerably weaker than the C—F bonds (Table 8.4). As a result, free chlorine atoms are formed readily in the presence of light with wavelengths in the range of 190 to 225 nm, as shown in this equation for  $\text{CF}_2\text{Cl}_2$ :



Calculations suggest that chlorine atom formation occurs at the greatest rate at an altitude of about 30 km, the altitude at which ozone is at its highest concentration.

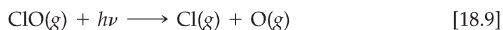
Atomic chlorine reacts rapidly with ozone to form chlorine monoxide (ClO) and molecular oxygen ( $\text{O}_2$ ):



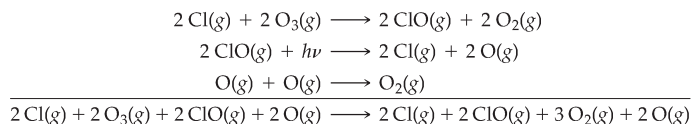
Equation 18.7 follows a second-order rate law with a very large rate constant:

$$\text{Rate} = k[\text{Cl}][\text{O}_3] \quad k = 7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \quad [18.8]$$

Under certain conditions the ClO generated in Equation 18.7 can react to regenerate free Cl atoms. One way that this can happen is by photodissociation of the ClO:



The Cl atoms generated in Equations 18.6 and 18.9 can react with more  $\text{O}_3$ , according to Equation 18.7. The result is a sequence of reactions that accomplishes the Cl atom-catalyzed decomposition of  $\text{O}_3$  to  $\text{O}_2$ , as shown in the following multistep mechanism:



The equation can be simplified by eliminating like species from each side to give



Because the rate of Equation 18.7 increases linearly with [Cl], the rate at which ozone is destroyed increases as the quantity of Cl atoms increases. Thus, the greater the amount of CFCs that diffuse into the stratosphere, the faster the destruction of the ozone layer. Rates of diffusion of molecules from the troposphere into the stratosphere are slow. Nevertheless, a thinning of the ozone layer over the South Pole has been observed, particularly during the months of September and October (Figure 18.5).

Because of the environmental problems associated with CFCs, steps have been taken to limit their manufacture and use. A major step was the signing in 1987 of the Montreal Protocol on Substances That Deplete the Ozone Layer, in which participating nations agreed to reduce CFC production. More stringent limits were set in 1992, when representatives of approximately 100 nations agreed to ban the production and use of CFCs by 1996. Since then, the size of the ozone hole has leveled off. Nevertheless, because CFCs are unreactive and because they diffuse so slowly into the stratosphere, scientists estimate that ozone depletion will continue for many years to come.  $\infty$  (Section 1.4, “Chemistry Put to Work: The Hole Story”)

What substances have replaced CFCs? At this time the main alternatives are hydrofluorocarbons, compounds in which C—H bonds replace the C—Cl bonds of CFCs. One such compound in current use is  $\text{CH}_2\text{FCF}_3$ , known as HFC-134a.

There are no naturally occurring CFCs, but some natural sources contribute chlorine and bromine to the atmosphere, and, just like halogens from CFC, these naturally occurring Cl and Br atoms can participate in ozone-depleting reactions. The principal naturally occurring sources are methyl bromide and methyl chloride,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ . It is estimated that these molecules contribute less than a third to the total Cl and Br in the atmosphere; the remaining two-thirds is a result of human activities. Volcanoes are a source of HCl, but, generally, the HCl they release reacts with water in the troposphere and does not make it to the upper atmosphere.



#### GIVE IT SOME THOUGHT

What process involving CFCs generates a substance that initiates the catalytic decomposition of ozone? Identify the catalyst.

## 18.4 CHEMISTRY OF THE TROPOSPHERE

The troposphere consists primarily of  $\text{N}_2$  and  $\text{O}_2$ , which together make up 99% of Earth’s atmosphere at sea level (Table 18.1). Other gases, although present only at very low concentrations, can have major effects on our environment. Table 18.3  $\blacktriangledown$  lists the major sources and typical concentrations of some of the important minor constituents of the troposphere. Many of these substances occur to only a slight extent in the natural environment but exhibit much higher concentrations in certain areas because of human activities. In this section we will discuss the most important characteristics of a few of these substances and their chemical roles as air pollutants. As we will see, most form as either a direct or an indirect result of our widespread use of combustion reactions.

TABLE 18.3 ■ Sources and Typical Concentrations of Some Minor Atmospheric Constituents

Minor Constituent	Sources	Typical Concentrations
Carbon dioxide, CO <sub>2</sub>	Decomposition of organic matter; release from the oceans; fossil-fuel combustion	375 ppm throughout the troposphere
Carbon monoxide, CO	Decomposition of organic matter; industrial processes; fossil-fuel combustion	0.05 ppm in unpolluted air; 1–50 ppm in urban traffic areas
Methane, CH <sub>4</sub>	Decomposition of organic matter; natural-gas seepage	1.77 ppm throughout the troposphere
Nitric oxide, NO	Electrical discharges; internal combustion engines; combustion of organic matter	0.01 ppm in unpolluted air; 0.2 ppm in smog
Ozone, O <sub>3</sub>	Electrical discharges; diffusion from the stratosphere; photochemical smog	0 to 0.01 ppm in unpolluted air; 0.5 ppm in photochemical smog
Sulfur dioxide, SO <sub>2</sub>	Volcanic gases; forest fires; bacterial action; fossil-fuel combustion; industrial processes	0 to 0.01 ppm in unpolluted air; 0.1–2 ppm in polluted urban environment

TABLE 18.4 ■ Median Concentrations of Atmospheric Pollutants in a Typical Urban Atmosphere

Pollutant	Concentration (ppm)
Carbon monoxide	10
Hydrocarbons	3
Sulfur dioxide	0.08
Nitrogen oxides	0.05
Total oxidants (ozone and others)	0.02

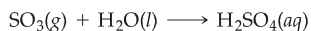
### Sulfur Compounds and Acid Rain

Sulfur-containing compounds are present to some extent in the natural, unpolluted atmosphere. They originate in the bacterial decay of organic matter, in volcanic gases, and from other sources listed in Table 18.3. The amount of sulfur-containing compounds released into the atmosphere worldwide from natural sources is about  $24 \times 10^{12}$  g per year, which is less than the amount from human activities (about  $79 \times 10^{12}$  g per year). Sulfur compounds, chiefly sulfur dioxide, SO<sub>2</sub>, are among the most unpleasant and harmful of the common pollutant gases. Table 18.4 shows the concentrations of several pollutant gases in a typical urban environment (not one that is particularly affected by smog). According to these data, the level of sulfur dioxide is 0.08 ppm or higher about half the time. This concentration is considerably lower than that of other pollutants, notably carbon monoxide. Nevertheless, SO<sub>2</sub> is regarded as the most serious health hazard among the pollutants shown, especially for people with respiratory difficulties.

Combustion of coal accounts for about 65% of the SO<sub>2</sub> released annually in the United States. The majority of this amount is from coal-burning electrical power plants, which generate about 50% of our electricity. The extent to which SO<sub>2</sub> emissions are a problem in the burning of coal depends on the level of its sulfur concentration. Because of concern about SO<sub>2</sub> pollution, low-sulfur coal is in greater demand and is thus more expensive. Much of the coal from east of the Mississippi is relatively high in sulfur content, up to 6% by mass. Much of the coal from the western states has a lower sulfur content. This coal, however, also has a lower heat content per unit mass of coal, so the difference in sulfur content per unit of heat produced is not as large as is often assumed.

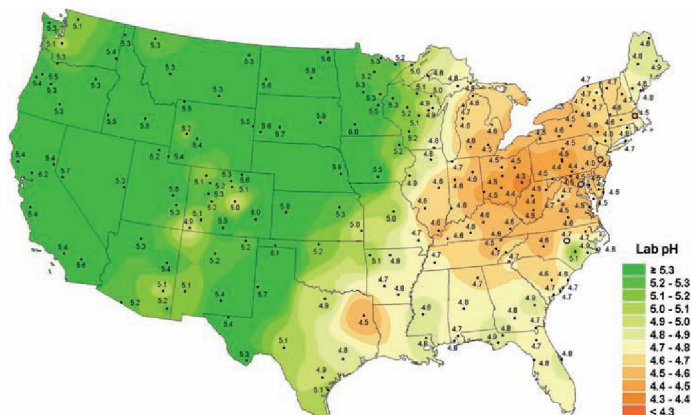
China, which gets 70 percent of its total energy from coal, is the world's largest generator of SO<sub>2</sub>, producing about  $24 \times 10^{12}$  g of SO<sub>2</sub> annually by official Chinese counts and as much as  $34 \times 10^{12}$  g by other counts. As a result, that nation has a major problem with SO<sub>2</sub> pollution.

Sulfur dioxide is harmful to both human health and property; furthermore, atmospheric SO<sub>2</sub> can be oxidized to SO<sub>3</sub> by several pathways (such as reaction with O<sub>2</sub> or O<sub>3</sub>). When SO<sub>3</sub> dissolves in water, it produces sulfuric acid, H<sub>2</sub>SO<sub>4</sub>:



Many of the environmental effects ascribed to SO<sub>2</sub> are actually due to H<sub>2</sub>SO<sub>4</sub>.

The presence of SO<sub>2</sub> in the atmosphere and the sulfuric acid that it produces result in the phenomenon of **acid rain**. (Nitrogen oxides, which form nitric acid, are also major contributors to acid rain.) Uncontaminated rainwater is



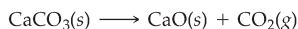
▲ **Figure 18.6** pH values from freshwater sites across the United States, 2005. The numbered dots indicate the locations of monitoring stations.

naturally acidic and generally has a pH value of about 5.6. The primary source of this natural acidity is  $\text{CO}_2$ , which reacts with water to form carbonic acid,  $\text{H}_2\text{CO}_3$ . Acid rain typically has a pH value of about 4. This acidity has affected many lakes in northern Europe, the northern United States, and Canada, reducing fish populations and affecting other parts of the ecological network within the lakes and surrounding forests.

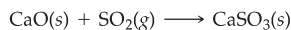
The pH of most natural waters containing living organisms is between 6.5 and 8.5, but as Figure 18.6▲ shows, freshwater pH values are far below 6.5 in many parts of the continental United States. At pH levels below 4.0, all vertebrates, most invertebrates, and many microorganisms are destroyed. The lakes that are most susceptible to damage are those with low concentrations of basic ions, such as  $\text{HCO}_3^-$ , that buffer them against changes in pH. More than 300 lakes in New York State contain no fish, and 140 lakes in Ontario, Canada, are devoid of life. The acid rain that appears to have killed the organisms in these lakes originates hundreds of kilometers upwind in the Ohio Valley and Great Lakes regions. Some of these regions are recovering as sulfur emissions from fossil fuel combustion decrease, in part because of the Clean Air Act, which has resulted in a reduction of more than 40% in  $\text{SO}_2$  emissions from power plants since 1980.

Because acids react with metals and with carbonates, acid rain is corrosive both to metals and to stone building materials. Marble and limestone, for example, whose major constituent is  $\text{CaCO}_3$ , are readily attacked by acid rain (Figure 18.7▶). Billions of dollars each year are lost because of corrosion due to  $\text{SO}_2$  pollution.

One way to reduce the quantity of  $\text{SO}_2$  released into the environment is to remove sulfur from coal and oil before it is burned. Although difficult and expensive, several methods have been developed for removing  $\text{SO}_2$  from the gases formed when coal and oil are combusted. Powdered limestone ( $\text{CaCO}_3$ ), for example, can be injected into the furnace of a power plant, where it decomposes into lime ( $\text{CaO}$ ) and carbon dioxide:



The  $\text{CaO}$  then reacts with  $\text{SO}_2$  to form calcium sulfite:



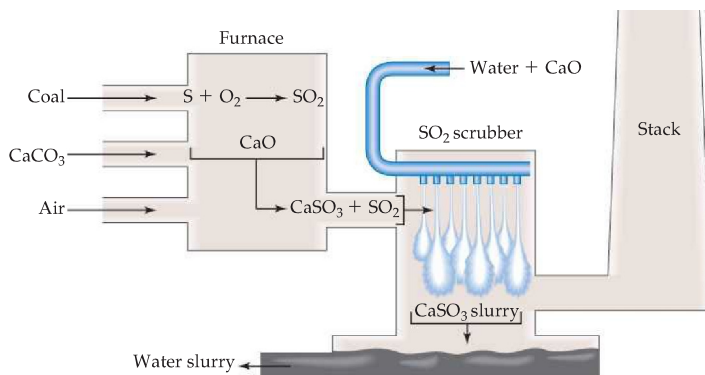
(a)



(b)

▲ **Figure 18.7** Damage from acid rain. (a) This statue at the Field Museum in Chicago shows the effects of corrosion from acid rain and atmospheric pollutants. (b) The same statue after restoration.

► **Figure 18.8 Common method for removing SO<sub>2</sub> from combusted fuel.** Powdered limestone decomposes into CaO, which reacts with SO<sub>2</sub> to form CaSO<sub>3</sub>. The CaSO<sub>3</sub> and any unreacted SO<sub>2</sub> enter a purification chamber called a scrubber, where a shower of CaO and water converts the remaining SO<sub>2</sub> into CaSO<sub>3</sub> and precipitates the CaSO<sub>3</sub> into a watery residue called a slurry.



The solid particles of CaSO<sub>3</sub> as well as much of the unreacted SO<sub>2</sub> can be removed from the furnace gas by passing it through an aqueous suspension of lime (Figure 18.8▲). Not all the SO<sub>2</sub> is removed, however, and given the enormous quantities of coal and oil burned worldwide, pollution by SO<sub>2</sub> will probably remain a problem for some time.

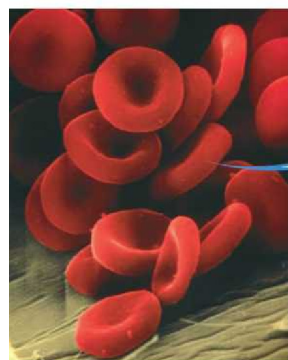
### GIVE IT SOME THOUGHT

What chemical behavior associated with sulfur oxides gives rise to acid rain?

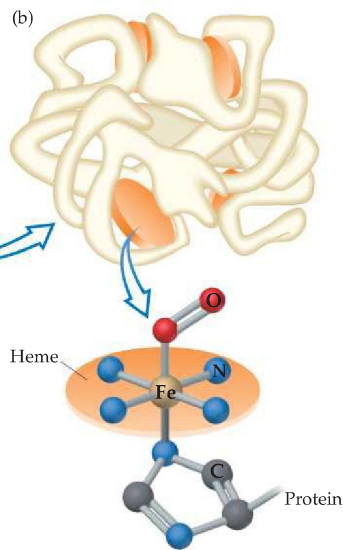
### Carbon Monoxide

Carbon monoxide is formed by the incomplete combustion of carbon-containing material, such as fossil fuels. In terms of total mass, CO is the most abundant of all the pollutant gases. The level of CO present in unpolluted air is very low, approximately 0.05 ppm. The estimated total amount of CO in the atmosphere is about  $5.2 \times 10^{14}$  g. In the United States alone, roughly  $1 \times 10^{14}$  g of CO is produced each year, about two-thirds of which comes from automobiles.

Carbon monoxide is a relatively unreactive molecule and consequently poses no direct threat to vegetation or materials. It does affect humans, however. It has the unusual ability to bind very strongly to **hemoglobin**, the iron-containing protein in red blood cells [Figure 18.9(a)◀] that transports oxygen in blood. Hemoglobin consists of four protein chains held together by weak intermolecular forces in a cluster [Figure 18.9(b)]. Each protein chain has a heme molecule within its folds. A schematic structure of heme is shown in Figure 18.9(c). Note that iron is situated in the center of a plane of four nitrogen atoms. A hemoglobin molecule in the lungs picks up an O<sub>2</sub> molecule, which reacts with the iron atom to form a species called *oxyhemoglobin*, abbreviated as HbO<sub>2</sub>.



(a)



▲ **Figure 18.9 Hemoglobin binds O<sub>2</sub> and CO.** Red blood cells (a) contain hemoglobin (b). The hemoglobin contains four heme units, each of which can bind an O<sub>2</sub> molecule (c). When exposed to CO, the heme binds CO in preference to O<sub>2</sub>.

As the blood circulates, the oxygen molecule is released in tissues as needed for cell metabolism, that is, for the chemical processes occurring in the cell. [Section 17.2, “Chemistry and Life: Blood as a Buffered Solution”](#)

Like  $O_2$ , CO also binds very strongly to the iron in hemoglobin. The complex is called *carboxyhemoglobin* and is represented as COHb. The equilibrium binding constant of human hemoglobin for CO is about 210 times greater than that for  $O_2$ . As a result, a relatively small quantity of CO can inactivate a substantial fraction of the hemoglobin in the blood for oxygen transport. For example, a person breathing air that contains only 0.1% of CO takes in enough CO after a few hours of breathing to convert up to 60% of the hemoglobin into COHb, thereby reducing the blood’s normal oxygen-carrying capacity by 60%.

Under normal conditions a nonsmoker breathing unpolluted air has about 0.3 to 0.5% COHb in the bloodstream. This amount arises mainly from the production of small quantities of CO in the course of normal body chemistry and from the small amount of CO present in clean air. Exposure to higher concentrations of CO causes the COHb level to increase, which in turn leaves fewer Hb sites to which  $O_2$  can bind. If the level of COHb becomes too high, oxygen transport is effectively shut down and death occurs. Because CO is colorless and odorless, CO poisoning occurs with very little warning. Improperly ventilated combustion devices, such as kerosene lanterns and stoves, thus pose a potential health hazard (Figure 18.10 ▶).

### Nitrogen Oxides and Photochemical Smog

Nitrogen oxides are primary components of smog, a phenomenon with which city dwellers are all too familiar. The term *smog* refers to a particularly unpleasant condition of pollution in certain urban environments that occurs when weather conditions produce a relatively stagnant air mass. The smog made famous by Los Angeles, but now common in many other urban areas as well, is more accurately described as **photochemical smog** because photochemical processes play a major role in its formation (Figure 18.11 ▶).

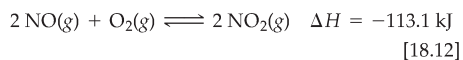
The majority of nitrogen oxide emissions (about 50%) comes from cars, buses, and other forms of transportation. Nitric oxide, NO, forms in small quantities in the cylinders of internal combustion engines by the direct combination of nitrogen and oxygen:



As noted in the “Chemistry Put to Work” box in Section 15.7, the equilibrium constant  $K$  for this reaction increases from about  $10^{-15}$  at 300 K (near room temperature) to about 0.05 at 2400 K (approximately the temperature in the cylinder of an engine during combustion). Thus, the reaction is more favorable at higher temperatures. In fact, some NO is formed in any high-temperature combustion. As a result, electrical power plants are also major contributors to nitrogen oxide pollution.

Before the installation of pollution-control devices on automobiles, typical emission levels of  $NO_x$  were 4 grams per mile (g/mi). (The  $x$  is either 1 or 2 because both NO and  $NO_2$  are formed, although NO predominates.) Starting in 2004, the auto emission standards for  $NO_x$  call for a phased-in reduction to 0.07 g/mi by 2009. Table 18.5 ▶ summarizes the federal standards for hydrocarbons and  $NO_x$  emissions since 1975 as well as the more restrictive standards enforced in California.

In air, nitric oxide (NO) is rapidly oxidized to nitrogen dioxide ( $NO_2$ ):



▲ **Figure 18.10 Carbon monoxide warnings.** Kerosene lamps and stoves have warning labels concerning use in enclosed spaces, such as an indoor room. Incomplete combustion can produce colorless, odorless carbon monoxide, CO, which is toxic.



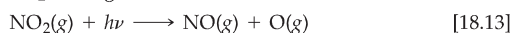
▲ **Figure 18.11 Photochemical smog.** Smog is produced largely by the action of sunlight on automobile exhaust gases.

**TABLE 18.5** ■ National Tailpipe Emission Standards\*

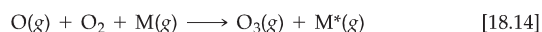
Year	Hydrocarbons (g/mi)	Nitrogen Oxides (g/mi)
1975	1.5 (0.9)	3.1 (2.0)
1980	0.41 (0.41)	2.0 (1.0)
1985	0.41 (0.41)	1.0 (0.4)
1990	0.41 (0.41)	1.0 (0.4)
1995	0.41 (0.25)	0.4 (0.4)
2004	0.075 (0.05)	0.07 (0.05)

\*California standards in parentheses

The equilibrium constant for this reaction decreases from about  $10^{12}$  at 300 K to about  $10^{-5}$  at 2400 K. The photodissociation of  $\text{NO}_2$  initiates the reactions associated with photochemical smog. The dissociation of  $\text{NO}_2$  into  $\text{NO}$  and  $\text{O}$  requires 304 kJ/mol, which corresponds to a photon wavelength of 393 nm. In sunlight, therefore,  $\text{NO}_2$  undergoes dissociation to  $\text{NO}$  and  $\text{O}$ :



The atomic oxygen formed undergoes several possible reactions, one of which gives ozone, as described earlier:



Ozone is a key component of photochemical smog. Although it is an essential UV screen in the upper atmosphere, ozone is an undesirable pollutant in the troposphere. It is extremely reactive and toxic, and breathing air that contains appreciable amounts of ozone can be especially dangerous for asthma sufferers, exercisers, and the elderly. We therefore have two ozone problems: excessive amounts in many urban environments, where it is harmful, and depletion in the stratosphere, where it is vital.

In addition to nitrogen oxides and carbon monoxide, an automobile engine also emits unburned *hydrocarbons* as pollutants. These organic compounds, which are composed entirely of carbon and hydrogen, are the principal components of gasoline (Section 25.3) and are major ingredients of smog. A typical engine without effective emission controls emits about 10 to 15 grams of these compounds per mile. Current standards require that hydrocarbon emissions be less than 0.075 grams per mile. Hydrocarbons are also emitted naturally from living organisms (see “A Closer Look” box later in this section).

Reduction or elimination of smog requires that the essential ingredients for its formation be removed from automobile exhaust. Catalytic converters are designed to drastically reduce the levels of  $\text{NO}_x$  and hydrocarbons, two of the major ingredients of smog.  $\infty$  (Section 14.7, “Chemistry Put to Work: Catalytic Converters”)



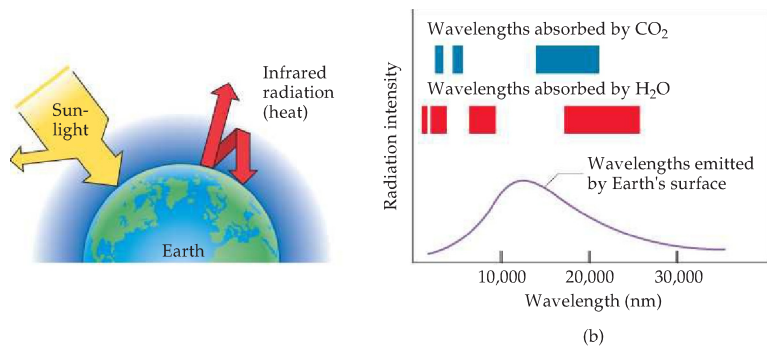
#### GIVE IT SOME THOUGHT

What photochemical reaction involving nitrogen oxides initiates the formation of photochemical smog?

### Water Vapor, Carbon Dioxide, and Climate

We have seen how the atmosphere makes life as we know it possible on Earth by screening out harmful short-wavelength radiation. In addition, the atmosphere is essential in maintaining a reasonably uniform and moderate temperature on the surface of the planet. The two atmospheric components of greatest importance in maintaining Earth's surface temperature are carbon dioxide and water. Without them, the average surface temperature of Earth would be 254 K, a temperature too low to sustain life.

Earth is in overall thermal balance with its surroundings. This means that Earth radiates energy into space at a rate equal to the rate at which it absorbs energy from the Sun. The Sun has a surface temperature of about 6000 K. As seen from outer space, Earth is relatively cold (254 K). The temperature of an object determines the distribution of wavelengths in the radiation it emits.  $\infty$  (Section 6.2) Why does Earth, viewed from outside its atmosphere, appear so much colder than the temperature we usually experience at its surface? The troposphere is transparent to visible light but not to infrared radiation. Figure 18.12  $\blacktriangleright$  shows the distribution of radiation from Earth's surface and the wavelengths absorbed by atmospheric water vapor and carbon dioxide. According to the graph, these atmospheric gases absorb much of the outgoing radiation from Earth's surface. In doing so, they help to maintain a livable uniform temperature at the surface by holding in, as it were, the infrared radiation, that we feel as heat.



◀ **Figure 18.12 Why Earth appears so cold from outer space.** (a) Carbon dioxide and water in the atmosphere absorb certain wavelengths of infrared radiation, which helps keep energy from escaping from Earth's surface. (b) The distribution of the wavelengths absorbed by CO<sub>2</sub> and H<sub>2</sub>O compared to the wavelengths emitted by Earth's surface.

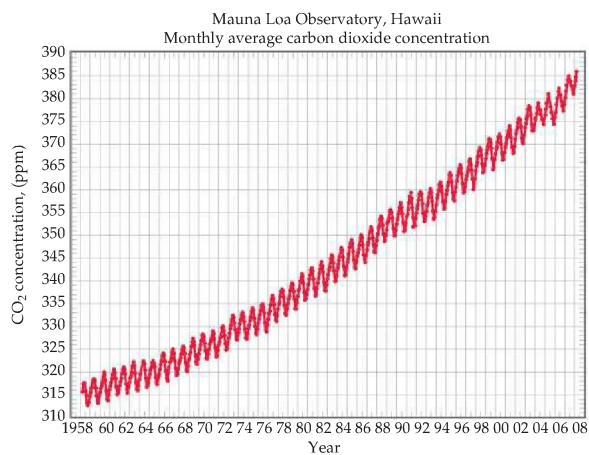
The influence of H<sub>2</sub>O, CO<sub>2</sub>, and certain other atmospheric gases on Earth's temperature is called the *greenhouse effect*, because these heat-trapping gases act much like the glass of a greenhouse. Correspondingly, these gases are called *greenhouse gases*.

Water vapor makes the largest contribution to the greenhouse effect. The partial pressure of water vapor in the atmosphere varies greatly from place to place and time to time, but it is generally highest near Earth's surface and drops off very sharply with increased elevation. Because water vapor absorbs infrared radiation so strongly, it plays the major role in maintaining the atmospheric temperature at night, when the surface is emitting radiation into space and not receiving energy from the Sun. In very dry desert climates, where the water-vapor concentration is unusually low, it may be extremely hot during the day but very cold at night. In the absence of an extensive layer of water vapor to absorb and then radiate part of the infrared radiation back to Earth, the surface loses this radiation into space and cools off very rapidly.

Carbon dioxide plays a secondary, but very important, role in maintaining the surface temperature. The worldwide combustion of fossil fuels, principally coal and oil, on a prodigious scale in the modern era has sharply increased the carbon dioxide level of the atmosphere. To get a sense of the amount of CO<sub>2</sub> produced, for example, by the combustion of hydrocarbons and other carbon-containing substances, which are the components of fossil fuels, consider the combustion of butane, C<sub>4</sub>H<sub>10</sub>. Combustion of 1.00 g of C<sub>4</sub>H<sub>10</sub> produces 3.03 g of CO<sub>2</sub>. (Section 3.6) Similarly, a gallon (3.78 L) of gasoline (density = 0.70 g/mL and approximate composition C<sub>8</sub>H<sub>18</sub>) produces about 8 kg (18 lb) of CO<sub>2</sub>. Combustion of fossil fuels releases about  $2.2 \times 10^{16}$  g (24 billion tons) of CO<sub>2</sub> into the atmosphere annually with the largest quantity coming from transportation vehicles.

Much CO<sub>2</sub> is absorbed into oceans or used by plants in photosynthesis. Nevertheless, we are now generating CO<sub>2</sub> much faster than it is being absorbed or used. Chemists have monitored atmospheric CO<sub>2</sub> concentrations since 1958. Analysis of air trapped in ice cores taken from Antarctica and Greenland makes it possible to determine the atmospheric levels of CO<sub>2</sub> during the past 160,000 years. These measurements reveal that the level of CO<sub>2</sub> remained fairly constant from the last Ice Age, some 10,000 years ago, until roughly the beginning of the Industrial Revolution, about 300 years ago. Since that time, the concentration of CO<sub>2</sub> has increased by about 30% to a current high of about 386 ppm (Figure 18.13 ▶).

▼ **Figure 18.13 Rising CO<sub>2</sub> levels.** The concentration of atmospheric CO<sub>2</sub> has risen more than 15% since the late 1950s. These data were recorded at the Mauna Loa Observatory in Hawaii by monitoring the absorption of infrared radiation. The sawtooth shape of the graph is due to regular seasonal variations in CO<sub>2</sub> concentration for each year.





A consensus is emerging among scientists that this increase in the concentration of  $\text{CO}_2$  in the atmosphere is already perturbing Earth's climate and that it may be responsible for the observed increase in the average global air temperature of  $0.3^\circ\text{C}$  to  $0.6^\circ\text{C}$  over the past century. Scientists often use the term climate change instead of global warming to refer to this effect, because as the Earth's temperature increases, it affects winds and ocean currents in ways that can cool some areas and warm others.

On the basis of present and expected future rates of fossil-fuel use, the atmospheric  $\text{CO}_2$  level is expected to double from its present level sometime between 2050 and 2100. Computer models predict that this increase will result in an average global temperature increase of  $1^\circ\text{C}$  to  $3^\circ\text{C}$ . Major changes in global climate could result from a temperature change of this magnitude. Because so many factors go into determining climate, we cannot predict with certainty what changes will occur. Clearly, however, humanity has acquired the potential, by changing the concentration of  $\text{CO}_2$  and other heat-trapping gases in the atmosphere, to substantially alter the climate of the planet.

The global warming threat posed by atmospheric  $\text{CO}_2$  has sparked considerable research into ways of capturing the gas at its largest combustion sources and storing it deep underground or under the seafloor. There is also much interest in developing new ways to use  $\text{CO}_2$  as a chemical feedstock.



### A Closer Look

#### OTHER GREENHOUSE GASES

Although  $\text{CO}_2$  receives most of the attention, other gases in total make an approximately equal contribution to the greenhouse effect. These gases include methane,  $\text{CH}_4$ , the hydrofluorocarbons (HFCs) such as  $\text{CH}_2\text{FCF}_3$ , and the chlorofluorocarbons (CFCs) such as  $\text{CF}_2\text{Cl}_2$ . The HFCs have replaced CFCs in a host of applications including refrigerants and air-conditioner gases. (Section 18.3) Although they do not contribute to the depletion of the ozone layer, HFCs are nevertheless strong greenhouse gases. Their total concentration in the atmosphere is still small (40 parts per trillion), but this amount is increasing about 10% per year. Thus, these substances are becoming increasingly important contributors to the greenhouse effect.

Methane already makes a significant contribution to the greenhouse effect. Each methane molecule has about 25 times the greenhouse effect of a  $\text{CO}_2$  molecule. Studies of atmospheric gas trapped long ago in the Greenland and Antarctic ice sheets show that the concentration of methane in the atmosphere has increased during the industrial age, from preindustrial values in the range of 0.3 to 0.7 ppm to the present value of about 1.8 ppm. The major sources of methane are associated with agriculture and fossil fuel use.

Methane is formed in biological processes that occur in low-oxygen environments. Anaerobic bacteria, which flourish in swamps and landfills, near the roots of rice plants, and in the digestive systems of cows and other ruminant animals, produce methane (Figure 18.14). It also leaks into the atmosphere during natural-gas extraction and transport (see "Chemistry Put to Work" box, Section 10.5). It is estimated that about two-thirds of present-day methane emissions, which are increasing by about 1% per year, are related to human activities.

Methane has a half-life in the atmosphere of about 10 years, whereas  $\text{CO}_2$  is much longer-lived. This might at

first seem a good thing, but there are indirect effects to consider. Some methane is oxidized in the stratosphere, producing water vapor, a powerful greenhouse gas that is otherwise virtually absent from the stratosphere. In the troposphere methane is attacked by reactive species such as OH radicals or nitrogen oxides, eventually producing other greenhouse gases such as  $\text{O}_3$ . It has been estimated that the climate-changing effects of  $\text{CH}_4$  are more than half those of  $\text{CO}_2$ . Given this large contribution, important reductions of the greenhouse effect could be achieved by reducing methane emissions or capturing the emissions for use as a fuel.



▲ **Figure 18.14 Methane production.** Ruminant animals, such as cows and sheep, produce methane in their digestive systems. In Australia sheep and cattle produce about 14% of the country's total greenhouse emissions.

The approximately 115 million tons of CO<sub>2</sub> used annually by the global chemical industry is but a small fraction of the approximately 24 billion tons of annual CO<sub>2</sub> emissions. However, the use of CO<sub>2</sub> as a raw material will probably never be great enough to reduce its atmospheric concentration.

### GIVE IT SOME THOUGHT

Explain why nighttime temperatures remain higher in locations where there is higher humidity.

## 18.5 THE WORLD OCEAN

Water is the most common liquid on Earth. It covers 72% of Earth's surface and is essential to life. Our bodies are about 65% water by mass. Because of extensive hydrogen bonding, water has unusually high melting and boiling points and a high heat capacity. ∞ (Section 11.2) Water's highly polar character is responsible for its exceptional ability to dissolve a wide range of ionic and polar-covalent substances. Many reactions occur in water, including reactions in which H<sub>2</sub>O itself is a reactant. Recall, for example, that H<sub>2</sub>O can participate in acid-base reactions as either a proton donor or a proton acceptor. ∞ (Section 16.3) In Chapter 20 we will see that H<sub>2</sub>O can also participate in oxidation-reduction reactions as either a donor or an acceptor of electrons. All these properties play a role in our environment.

### Seawater

The vast layer of salty water that covers so much of the planet is connected and is generally constant in composition. For this reason, oceanographers speak of a world ocean rather than of the separate oceans we learn about in geography books. The world ocean is huge. Its volume is  $1.35 \times 10^9$  km<sup>3</sup>. Almost all the water on Earth, 97.2%, is in the world ocean. Of the remaining 2.8%, 2.1% is in the form of ice caps and glaciers. All the freshwater—in lakes, rivers, and groundwater—amounts to only 0.6%. Most of the remaining 0.1% is in brackish (salty) water, such as that in the Great Salt Lake in Utah.

Seawater is often referred to as saline water. The **salinity** of seawater is the mass in grams of dry salts present in 1 kg of seawater. In the world ocean the salinity averages about 35. To put it another way, seawater contains about 3.5% dissolved salts by mass. The list of elements present in seawater is very long. Most, however, are present only in very low concentrations. Table 18.6 ▼ lists the 11 ionic species that are most abundant in seawater.

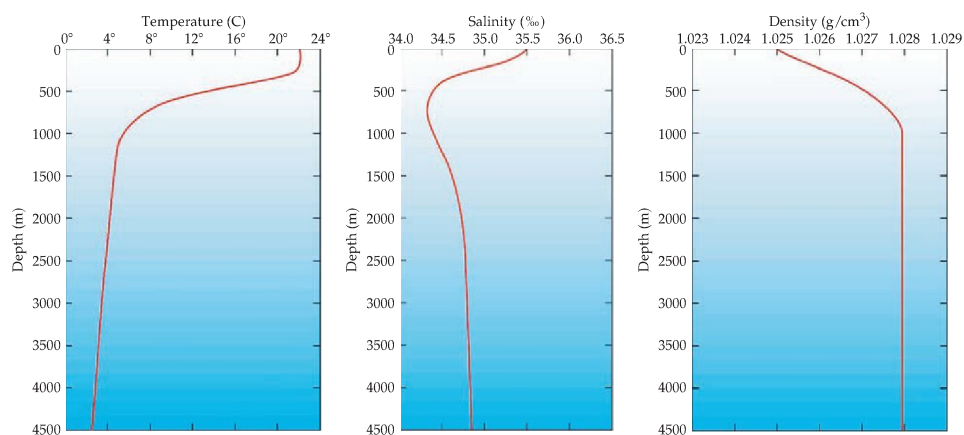
The properties of seawater—its salinity, density, and temperature—vary as a function of depth (Figure 18.15 ▼). Sunlight penetrates well only 200 m into the sea; the region between 200 m and 1000 m deep is the “twilight zone,” where visible light is faint. Below 1000 m in depth, the ocean is pitch-black and cold, about 4 °C. The transport of heat, salt, and other chemicals throughout the ocean is influenced by these changes in the physical properties of seawater, and in turn the changes in the way heat and substances are transported affects ocean currents and the global climate.

The sea is so vast that if a substance is present in seawater to the extent of only 1 part per billion (ppb, that is,  $1 \times 10^{-6}$  g per kilogram of water), there is still  $1 \times 10^{12}$  kg of it in the world ocean. Nevertheless, the ocean is rarely used as a source of raw

**TABLE 18.6** ■ Ionic Constituents of Seawater Present in Concentrations Greater than 0.001 g/kg (1 ppm)

Ionic Constituent	g/kg Seawater	Concentration (M)
Chloride, Cl <sup>-</sup>	19.35	0.55
Sodium, Na <sup>+</sup>	10.76	0.47
Sulfate, SO <sub>4</sub> <sup>2-</sup>	2.71	0.028
Magnesium, Mg <sup>2+</sup>	1.29	0.054
Calcium, Ca <sup>2+</sup>	0.412	0.010
Potassium, K <sup>+</sup>	0.40	0.010
Carbon dioxide*	0.106	$2.3 \times 10^{-3}$
Bromide, Br <sup>-</sup>	0.067	$8.3 \times 10^{-4}$
Boric acid, H <sub>3</sub> BO <sub>3</sub>	0.027	$4.3 \times 10^{-4}$
Strontium, Sr <sup>2+</sup>	0.0079	$9.1 \times 10^{-5}$
Fluoride, F <sup>-</sup>	0.0013	$7.0 \times 10^{-5}$

\*CO<sub>2</sub> is present in seawater as HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>.



▲ **Figure 18.15** Average temperature, salinity, and density of seawater as a function of depth.

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materials because the cost of extracting the desired substances is too high. Only three substances are obtained from seawater in commercially important amounts: sodium chloride, bromine (from bromide salts), and magnesium (from its salts).

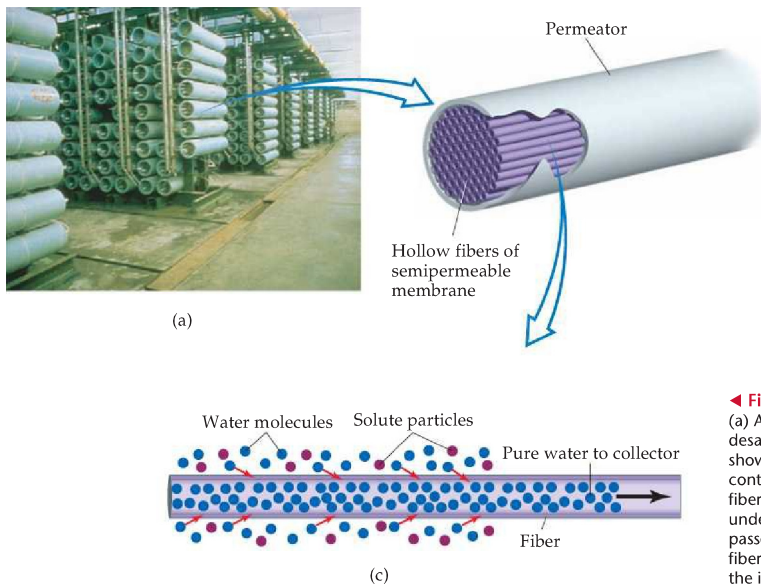
Absorption of  $\text{CO}_2$  by the ocean plays a large role in global climate. Carbon dioxide reacts with water to form carbonic acid,  $\text{H}_2\text{CO}_3$  (Section 16.6), and so as  $\text{CO}_2$  from the atmosphere is absorbed by the world ocean, the concentration of  $\text{H}_2\text{CO}_3$  in the ocean increases. Most of the carbon in the ocean, however, is in the form of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions. These ions form a buffer system that maintains the ocean's average pH between 8.0 and 8.3. The buffering capacity of the world ocean is predicted to decrease as the concentration of  $\text{CO}_2$  in the atmosphere increases, because of the increase in  $\text{H}_2\text{CO}_3$  concentration. With less buffering capacity, the carbonate ion can precipitate out as  $\text{CaCO}_3$ , one of the main ingredients in seashells. Thus, both acid-base equilibrium reactions and solubility equilibrium reactions (Section 17.4) form a complicated web of interactions that tie the ocean to the atmosphere and to the global climate.

### Desalination

Because of its high salt content, seawater is unfit for human consumption and for most of the uses to which we put water. In the United States the salt content of municipal water supplies is restricted by health codes to no more than about 500 ppm (0.05% by mass). This amount is much lower than the 3.5% dissolved salts present in seawater and the 0.5% or so present in brackish water found underground in some regions. The removal of salts from seawater or brackish water to make the water usable is called **desalination**.

Water can be separated from dissolved salts by *distillation* because water is a volatile substance and the salts are nonvolatile. (Section 13.5: "A Closer Look: Ideal Solutions with Two or More Volatile Components") The principle of distillation is simple enough, but carrying out the process on a large scale presents many problems. As water is distilled from seawater, for example, the salts become more and more concentrated and eventually precipitate out.

Seawater can also be desalinated using **reverse osmosis**. Recall that osmosis is the net movement of solvent molecules, but not solute molecules, through a semipermeable membrane. (Section 13.5) In osmosis the solvent passes from the more dilute solution into the more concentrated one. However, if sufficient external pressure is applied, osmosis can be stopped and, at still higher pressures, reversed. When this occurs, solvent passes from the more concentrated into the more dilute solution. In a modern reverse-osmosis facility tiny



◀ **Figure 18.16 Reverse osmosis.**

(a) A room inside a reverse-osmosis desalination plant. (b) Each cylinder shown in (a) is called a permeator and contains several million tiny hollow fibers. (c) When seawater is introduced under pressure into a permeator, water passes through the fiber wall into the fibers and is thereby separated from all the ions initially present in the seawater.

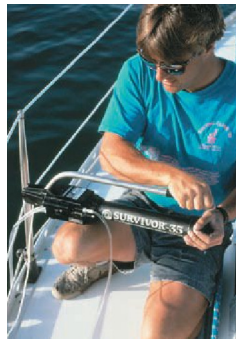
hollow fibers are used as the semipermeable membrane. Water is introduced under pressure into the fibers, and desalinated water is recovered, as illustrated in Figure 18.16 ▲.

Research and development into improving desalination technologies is ongoing, and already an estimated 11,000 desalination plants exist in some 120 countries around the world. The world's largest desalination plant is located in Jubail, Saudi Arabia. This plant provides 50% of that country's drinking water by using reverse osmosis to desalinate seawater from the Persian Gulf. Such plants are becoming increasingly common in the United States. The largest, near Tampa Bay, Florida, is scheduled to be functional in 2008 and will produce 35 million gallons of drinking water a day by reverse osmosis when fully constructed. Small-scale, manually operated reverse-osmosis desalinators are now also available for use in camping and traveling, and at sea (Figure 18.17 ►).

## 18.6 FRESHWATER

The United States is fortunate in its abundance of freshwater— $1.7 \times 10^{15}$  liters (660 trillion gallons) is the estimated reserve, which is renewed by rainfall. An estimated  $9 \times 10^{11}$  liters of freshwater is used every day in the United States. Most of this is used for agriculture (41%) and hydroelectric power (39%), with small amounts for industry (6%), household needs (6%), and drinking water (1%). An adult needs about 2 liters of water per day for drinking. In the United States our daily use of water per person far exceeds this subsistence level, amounting to an average of about 300 L/day for personal consumption and hygiene. We use about 8 L/person for cooking and drinking, about 120 L/person for cleaning (bathing, laundering, and housecleaning), 80 L/person for flushing toilets, and 80 L/person for watering lawns.

The total amount of freshwater on Earth is not a very large fraction of the total water present. Indeed, freshwater is one of our most precious resources. It forms by evaporation from the oceans and the land. The water vapor that accumulates in the atmosphere is transported by global atmospheric circulation, eventually returning to Earth as rain, snow, and other forms of precipitation.



▲ **Figure 18.17 A portable desalination device.** This hand-operated water desalinator works by reverse osmosis. It can produce 4.5 L (1.2 gal) of pure water from seawater in an hour.

As rain falls and as water runs off the land on its way to the oceans, it dissolves a variety of cations (mainly  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Fe}^{2+}$ ), anions (mainly  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ ), and gases (principally  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$ ). As we use water, it becomes laden with additional dissolved material, including the wastes of human society. As our population and output of environmental pollutants increase, we find that we must spend ever-increasing amounts of money and resources to guarantee a supply of freshwater.

### Dissolved Oxygen and Water Quality

The amount of dissolved  $\text{O}_2$  in water is an important indicator of water quality. Water fully saturated with air at 1 atm and  $20^\circ\text{C}$  contains about 9 ppm of  $\text{O}_2$ . Oxygen is necessary for fish and most other aquatic life. Cold-water fish require that the water contain at least 5 ppm of dissolved oxygen for survival. Aerobic bacteria consume dissolved oxygen to oxidize organic materials and so meet their energy requirements. The organic material that the bacteria are able to oxidize is said to be **biodegradable**. This oxidation occurs by a complex set of chemical reactions, and the organic material disappears gradually.

Excessive quantities of biodegradable organic materials in water are detrimental because they deplete the water of the oxygen necessary to sustain normal animal life. Typical sources of these biodegradable materials, which are called *oxygen-demanding wastes*, include sewage, industrial wastes from food-processing plants and paper mills, and effluent (liquid waste) from meatpacking plants.

In the presence of oxygen, the carbon, hydrogen, nitrogen, sulfur, and phosphorus in biodegradable material end up mainly as  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and phosphates. The formation of these oxidation products sometimes reduces the amount of dissolved oxygen to the point where aerobic bacteria can no longer survive. Anaerobic bacteria then take over the decomposition process, forming  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ , and other products, several of which contribute to the offensive odors of some polluted waters.

Plant nutrients, particularly nitrogen and phosphorus, contribute to water pollution by stimulating excessive growth of aquatic plants. The most visible results of excessive plant growth are floating algae and murky water. More significantly, however, as plant growth becomes excessive, the amount of dead and decaying plant matter increases rapidly, a process called *eutrophication* (Figure 18.18 ◀). The decay of plants consumes  $\text{O}_2$  as the plants are biodegraded, leading to the depletion of oxygen in the water. Without sufficient supplies of oxygen, the water, in turn, cannot sustain any form of animal life. The most significant sources of nitrogen and phosphorus compounds in water are domestic sewage (phosphate-containing detergents and nitrogen-containing body wastes), runoff from agricultural land (fertilizers containing both nitrogen and phosphorus), and runoff from livestock areas (animal wastes containing nitrogen).



▲ **Figure 18.18 Eutrophication.**

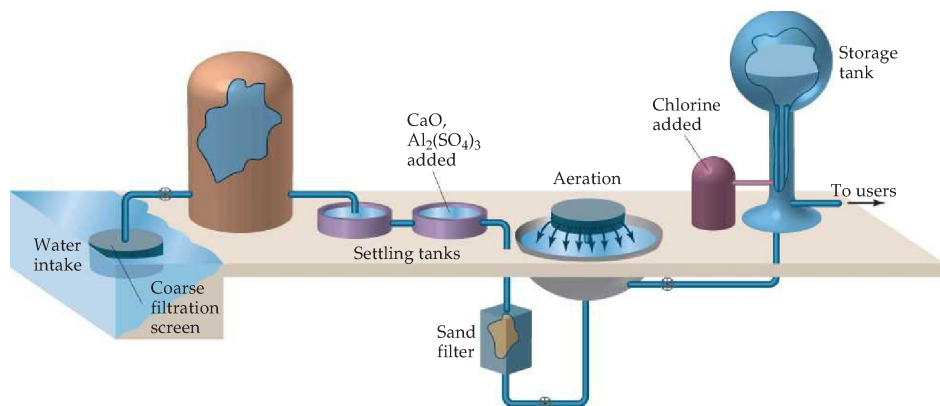
The growth of algae and duckweed in this pond is due to agricultural wastes. The wastes feed the growth of the algae and weeds, which deplete the oxygen in the water, a process called eutrophication. A eutrophic lake cannot support fish.

### GIVE IT SOME THOUGHT

One common test for water quality involves measuring dissolved oxygen, storing the water in a closed container at a constant temperature for five days, and then remeasuring the dissolved oxygen. If such a test shows a considerable decrease in dissolved oxygen over the five-day period, what can we conclude about the nature of the pollutants present?

### Treatment of Municipal Water Supplies

The water needed for domestic uses, agriculture, and industrial processes is taken either from naturally occurring lakes, rivers, and underground sources or from reservoirs. Much of the water that finds its way into municipal water

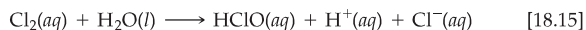


▲ Figure 18.19 Common steps in treating water for a public water system.

systems is “used” water: It has already passed through one or more sewage systems or industrial plants. Consequently, this water must be treated before it is distributed to our faucets. Municipal water treatment usually involves five steps: coarse filtration, sedimentation, sand filtration, aeration, and sterilization. Figure 18.19▲ shows a typical treatment process.

After coarse filtration through a screen, the water is allowed to stand in large settling tanks in which finely divided sand and other minute particles can settle out. To aid in removing very small particles, the water may first be made slightly basic by adding  $\text{CaO}$ . Then  $\text{Al}_2(\text{SO}_4)_3$  is added. The aluminum sulfate reacts with  $\text{OH}^-$  ions to form a spongy, gelatinous precipitate of  $\text{Al}(\text{OH})_3$  ( $K_{sp} = 1.3 \times 10^{-33}$ ). This precipitate settles slowly, carrying suspended particles down with it, thereby removing nearly all finely divided matter and most bacteria. The water is then filtered through a sand bed. Following filtration, the water may be sprayed into the air to hasten the oxidation of dissolved organic substances.

The final stage of the operation normally involves treating the water with a chemical agent to ensure the destruction of bacteria. Ozone is most effective, but it must be generated at the place where it is used. Chlorine,  $\text{Cl}_2$ , is therefore more convenient. Chlorine can be shipped in tanks as a liquefied gas and dispensed from the tanks through a metering device directly into the water supply. The amount used depends on the presence of other substances with which the chlorine might react and on the concentrations of bacteria and viruses to be removed. The sterilizing action of chlorine is probably due not to  $\text{Cl}_2$  itself, but to hypochlorous acid, which forms when chlorine reacts with water:



As many as a billion people worldwide lack access to clean water. According to the United Nations, 95% of the world’s cities still dump raw sewage into their water supplies. Thus, it should come as no surprise to know that 80% of all the health maladies in developing countries can be traced back to water-borne diseases associated with unsanitary water.

One promising development is a device called the LifeStraw (Figure 18.20▶). When a person sucks water through the straw, the water first encounters a textile prefilter with a mesh opening of  $100 \mu\text{m}$  followed by a second textile filter with a mesh opening of  $15 \mu\text{m}$ . These filters remove debris and even clusters of bacteria. The water next encounters a chamber of iodine-impregnated beads, where bacteria, viruses, and parasites are killed. Finally, the water passes through granulated active carbon, which removes the smell of iodine as well as the parasites that have not been taken by the prefilter or killed by the iodine.

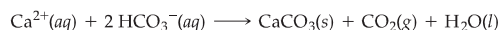


▲ Figure 18.20 LifeStraw. A LifeStraw is a drinking straw that purifies water as it is drunk.

## A Closer Look

## WATER SOFTENING

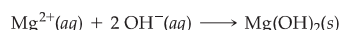
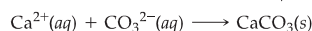
Water containing a relatively high concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and other divalent cations is called **hard water**. Although the presence of these ions is generally not a health threat, they can make water unsuitable for some household and industrial uses. For example, these ions react with soaps to form an insoluble soap scum, the stuff of bathtub rings. In addition, mineral deposits may form when water containing these ions is heated. When water containing calcium ions and bicarbonate ions is heated, some carbon dioxide is driven off. As a result, the solution becomes less acidic and insoluble calcium carbonate forms:



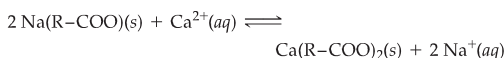
The solid  $\text{CaCO}_3$  coats the surface of hot-water systems and teakettles, thereby reducing heating efficiency. These deposits, called *scale*, can be especially serious in boilers where water is heated under pressure in pipes running through a furnace. Formation of scale reduces the efficiency of heat transfer and reduces the flow of water through pipes (Figure 18.21 ▼).

The removal of the ions that cause hard water is called *water softening*. Not all municipal water supplies require water softening. In those that do, the water is generally taken from underground sources in which it has had considerable contact with limestone,  $\text{CaCO}_3$ , and other minerals containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$ . The **lime-soda process** is used for

large-scale municipal water-softening operations. The water is treated with lime,  $\text{CaO}$  [or slaked lime,  $\text{Ca}(\text{OH})_2$ ], and soda ash,  $\text{Na}_2\text{CO}_3$ . These chemicals precipitate  $\text{Ca}^{2+}$  as  $\text{CaCO}_3$  ( $K_{sp} = 4.5 \times 10^{-9}$ ) and  $\text{Mg}^{2+}$  as  $\text{Mg}(\text{OH})_2$  ( $K_{sp} = 1.6 \times 10^{-12}$ ):



**Ion exchange** is a typical household method for water softening. In this procedure the hard water is passed through a bed of an ion-exchange resin: plastic beads with covalently bound anion groups such as  $-\text{COO}^{-}$  or  $-\text{SO}_3^{-}$ . These negatively charged groups have  $\text{Na}^{+}$  ions attached to balance their charges. The  $\text{Ca}^{2+}$  and other cations in the hard water are attracted to the anionic groups and displace the lower-charged  $\text{Na}^{+}$  into the water. Thus, one type of ion is exchanged for another. To maintain charge balance, 2  $\text{Na}^{+}$  enter the water for each  $\text{Ca}^{2+}$  removed. If we represent the resin with its anionic site as  $\text{R}-\text{COO}^{-}$ , we can write the equation for the process as follows:



Water softened in this way contains an increased concentration of  $\text{Na}^{+}$ . Although  $\text{Na}^{+}$  does not form precipitates or cause other problems associated with hard-water cations, individuals concerned about their sodium intake, such as those who have high blood pressure (hypertension), should avoid drinking water softened in this way.

When all the available  $\text{Na}^{+}$  have been displaced from the ion-exchange resin, the resin is regenerated by flushing it with a concentrated solution of  $\text{NaCl}$ . Homeowners can do this by charging their units with large amounts of  $\text{NaCl}(\text{s})$ , which can be purchased at most grocery stores. The high concentration of  $\text{Na}^{+}$  forces the equilibrium shown in the earlier equation to shift to the left, causing the  $\text{Na}^{+}$  to displace the hard-water cations, which are flushed down the drain.



◀ **Figure 18.21 Scale formation.** A section of water pipe that has been coated on the inside with  $\text{CaCO}_3$  and other insoluble salts deposited from hard water.

## 18.7 GREEN CHEMISTRY

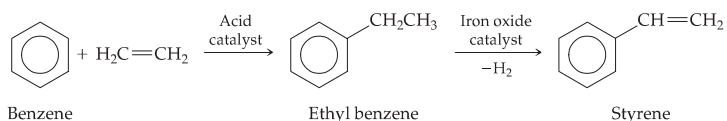
The planet on which we live is, to a large extent, a closed system, one that exchanges energy but not matter with its environment. If humankind is to thrive in the future, all the processes we carry out should be in balance with Earth's natural processes and physical resources. This goal requires that no toxic materials are released to the environment, that our needs are met with renewable resources, and that we consume the least possible amount of energy. Although the chemical industry is but a small part of human activity, chemical processes are involved in nearly all aspects of modern life. Chemistry is therefore at the heart of efforts to accomplish these goals.

**Green chemistry** is an initiative that promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment. Some of the major principles that govern green chemistry are the following:

- The potential hazards of substances should be a major consideration in the design of chemical processes. It is better to prevent waste than to treat or clean it up after it has been created.

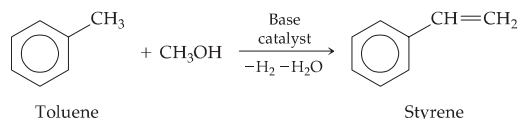
- The methods employed in synthesizing substances should generate as little waste product as possible.
- Chemical processes should be designed to be as energy efficient as possible, avoiding high temperatures and pressures. Thus, catalysts should be sought that facilitate reactions under mild reaction conditions.
- The raw materials for chemical processes should be renewable whenever technically and economically feasible.

To illustrate how green chemistry works in practice, consider the manufacture of styrene, a very important building block in the formation of many polymers, including the expanded polystyrene packages used to pack eggs and restaurant takeout food. The global demand for styrene is more than 25 million metric tons per year. For many years styrene has been produced in a two-step process. In the first step, benzene and ethylene react in the presence of a solid catalyst, forming ethyl benzene. In the second step, the ethyl benzene is mixed with high temperature steam and passed over an iron oxide catalyst at 625 °C yielding styrene:



This process has several shortcomings. One is that both benzene, which is formed from crude oil, and ethylene, which is formed from natural gas, are high-priced starting materials for a product that should be a low-priced commodity. From an environmental point of view, the high toxicity of benzene and the high energy cost overall for the process are both undesirable.

Researchers at Exelus Inc. have demonstrated a process that bypasses some of these shortcomings. The two-step process is replaced by a one-step process in which toluene is reacted with methanol at 425 °C over a special catalyst:



The new process saves money because toluene and methanol are less expensive than benzene and ethylene, and the reaction conditions require much lower energy input. Additional benefits are that the methanol could be produced from biomass, and that benzene is replaced by less toxic toluene. The hydrogen formed in the reaction can be recycled as a source of energy. This example demonstrates how finding the right catalyst was key in discovering the new process.

Let's consider some other examples in which green chemistry can operate to improve environmental quality.

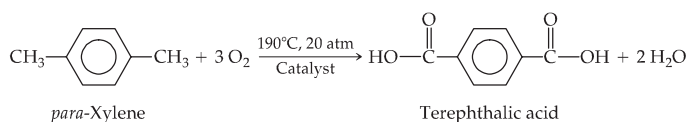
### Solvents and Reagents

A major area of concern in chemical processes is the use of volatile organic compounds as solvents for reactions. Generally, the solvent in which a reaction is run is not consumed in the reaction, and there are unavoidable releases of solvent into the atmosphere even in the most carefully controlled processes. Further, the solvent may be toxic or may decompose to some extent during the reaction, thus creating waste products. The use of supercritical fluids (Section 11.4: "Chemistry Put to Work: Supercritical Fluid Extraction") represents a way to replace conventional solvents with other reagents. Recall that a supercritical fluid is an unusual state of matter that has properties of both a gas and a liquid. ∞ (Section 11.4) Water and carbon dioxide are the two most popular choices as supercritical fluid solvents. One recently developed industrial process,



for example, replaces chlorofluorocarbon solvents with liquid or supercritical  $\text{CO}_2$  in the production of polytetrafluoroethylene ( $[\text{CF}_2\text{CF}_2]_n$ , sold as Teflon<sup>®</sup>). The chlorofluorocarbon solvents have harmful effects on Earth's ozone layer (Section 18.3). Though  $\text{CO}_2$  is a greenhouse gas, no new  $\text{CO}_2$  need be manufactured for use as a supercritical fluid solvent.

As a further example, *para*-xylene is oxidized to form terephthalic acid, which in turn is used to make polyethylene terephthalate (PET) plastic and polyester fiber (Section 12.6, Table 12.5):



This commercial process requires pressurization and a relatively high temperature. Oxygen is the oxidizing agent, and acetic acid ( $\text{CH}_3\text{COOH}$ ) is the solvent. An alternative route employs supercritical water as the solvent (Table 11.5) and hydrogen peroxide as the oxidant. This alternative process has several potential advantages, most particularly the elimination of acetic acid as solvent and the use of a different oxidizing agent. Whether it can successfully replace the existing commercial process, however, depends on many factors, which will require further study.

### GIVE IT SOME THOUGHT

We noted earlier that increasing carbon dioxide levels contribute to global warming, which seems like a bad thing, but now we are saying that using carbon dioxide in industrial processes is a good thing for the environment. Explain this seeming contradiction.

### Other Processes

Many processes that are important in modern society use chemicals not found in nature. Let's briefly examine two of these processes, dry cleaning and the coating of automotive bodies to prevent corrosion, and consider alternatives being developed to reduce harmful environmental impacts.

Dry cleaning of clothing typically uses a chlorinated organic solvent such as tetrachloroethylene ( $\text{Cl}_2\text{C}=\text{CCl}_2$ ), which may cause cancer in humans. The widespread use of this and related solvents in dry cleaning, metal cleaning, and other industrial processes has contaminated groundwater in some areas. Alternative dry-cleaning methods that employ liquid  $\text{CO}_2$ , along with special cleaning agents, are being successfully commercialized (Figure 18.22 ◀).

The metal bodies of cars are coated extensively during manufacture to prevent corrosion. One of the key steps is the electrodeposition of a layer of metal ions that creates an interface between the vehicle body and the polymeric coatings that serve as the undercoat for painting. In the past, lead was the metal of choice for inclusion in the electrodeposition mixture. Because lead is highly toxic, however, its use in other paints and coatings has been virtually eliminated, and a relatively nontoxic yttrium hydroxide alternative to lead has been developed as an automotive coating (Figure 18.23 ▶). When this coating is subsequently heated, the hydroxide is converted to the oxide, producing an insoluble ceramiclike coating. ∞∞ (Section 12.4)

### The Challenges of Water Purification

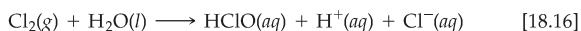
Access to clean water is essential to the workings of a stable, thriving society. We have seen in the previous section that disinfection of water is an important step in water treatment for human consumption. Water disinfection is one of the greatest



▲ **Figure 18.22 Green chemistry for your clothes.** This dry-cleaning apparatus employs liquid  $\text{CO}_2$  as the solvent.

public health innovations in human history. It has dramatically decreased the incidences of waterborne bacterial diseases such as cholera and typhus. But this great benefit comes at a price.

In 1974 scientists in both Europe and the United States discovered that chlorination of water produces a group of by-products that had previously gone undetected. These by-products are called *trihalomethanes* (THMs) because all have a single carbon atom and three halogen atoms:  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$ . These and many other chlorine- and bromine-containing organic substances are produced by the reaction of aqueous chlorine with organic materials present in nearly all natural waters, as well as with substances that are by-products of human activity. Recall that chlorine dissolves in water to form  $\text{HClO}$ , which is the active oxidizing agent  $\infty$  (Section 7.8):

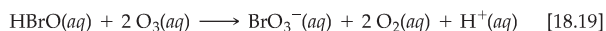


$\text{HClO}$  in turn reacts with organic substances to form the THMs. Bromine enters through the reaction of  $\text{HClO}$  with dissolved bromide ion:



$\text{HBrO}(\text{aq})$  halogenates organic substances analogously to  $\text{HClO}(\text{aq})$ .

Some THMs and other halogenated organic substances are suspected carcinogens; others interfere with the body's endocrine system. As a result, the World Health Organization and the Environmental Protection Agency (EPA) have placed concentration limits of  $80 \mu\text{g}/\text{L}$  (80 ppb) on the total quantity of such substances in drinking water. The goal is to reduce the levels of THMs and related substances in the drinking water supply while preserving the antibacterial effectiveness of the water treatment. In some cases simply lowering the concentration of chlorine may provide adequate disinfection while reducing the concentrations of THMs formed. Alternative oxidizing agents, such as ozone ( $\text{O}_3$ ) or chlorine dioxide ( $\text{ClO}_2$ ), produce less of the halogenated substances, but they have their own disadvantages. For example, each is capable of oxidizing aqueous bromide, as shown here for ozone:



As we have seen,  $\text{HBrO}(\text{aq})$  is capable of reacting with dissolved organic substances to form halogenated organic compounds. Furthermore, bromate ion has been shown to cause cancer in animal tests.

There seem to be no completely satisfactory alternatives to chlorination or ozonation at present. The risks of cancer from THMs and related substances in municipal water are very low, however, compared to the risks of cholera, typhus, and gastrointestinal disorders from untreated water. When the water supply is cleaner to begin with, less disinfectant is needed; thus, the danger of contamination through disinfection is reduced. Once the THMs are formed, their concentrations in the water supply can be reduced by aeration because the THMs are more volatile than water. Alternatively, they can be removed by adsorption onto activated charcoal or other adsorbents.



▲ **Figure 18.23 Green chemistry for your car.** An automobile body receives a corrosion-protection coating containing yttrium in place of lead.

**SAMPLE INTEGRATIVE EXERCISE** | Putting Concepts Together

(a) Acids from acid rain or other sources are no threat to lakes in areas where the rock is limestone (calcium carbonate), which can neutralize the excess acid. Where the rock is granite, however, no such neutralization occurs. How does the limestone neutralize the acid? (b) Acidic water can be treated with basic substances to increase the pH, although such a procedure is usually only a temporary cure. Calculate the minimum mass of lime, CaO, needed to adjust the pH of a small lake ( $V = 4 \times 10^9$  L) from 5.0 to 6.5. Why might more lime be needed?

**SOLUTION**

**Analyze:** We need to remember what a neutralization reaction is, and calculate the amount of a substance needed to effect a certain change in pH.

**Plan:** For (a), we need to think about how acid can react with calcium carbonate, which evidently does not happen with acid and granite. For (b), we need to think about what reaction would happen with acid and CaO and do stoichiometric calculations. From the proposed change in pH, we can calculate the change in proton concentration needed and then figure out how much CaO it would take to do the reaction.

**Solve:**

(a) The carbonate ion, which is the anion of a weak acid, is basic.  $\infty$  (Sections 16.2 and 16.7) Thus, the carbonate ion,  $\text{CO}_3^{2-}$ , reacts with  $\text{H}^+(\text{aq})$ . If the concentration of  $\text{H}^+(\text{aq})$  is small, the major product is the bicarbonate ion,  $\text{HCO}_3^-$ . If the concentration of  $\text{H}^+(\text{aq})$  is higher, however,  $\text{H}_2\text{CO}_3$  forms and decomposes to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .  $\infty$  (Section 4.3)

(b) The initial and final concentrations of  $\text{H}^+(\text{aq})$  in the lake are obtained from their pH values:

$$[\text{H}^+]_{\text{initial}} = 10^{-5.0} = 1 \times 10^{-5} \text{ M} \quad \text{and} \quad [\text{H}^+]_{\text{final}} = 10^{-6.5} = 3 \times 10^{-7} \text{ M}$$

Using the volume of the lake, we can calculate the number of moles of  $\text{H}^+(\text{aq})$  at both pH values:

$$(1 \times 10^{-5} \text{ mol/L})(4.0 \times 10^9 \text{ L}) = 4 \times 10^4 \text{ mol}$$

$$(3 \times 10^{-7} \text{ mol/L})(4.0 \times 10^9 \text{ L}) = 1 \times 10^3 \text{ mol}$$

Hence, the change in the amount of  $\text{H}^+(\text{aq})$  is  $4 \times 10^4 \text{ mol} - 1 \times 10^3 \text{ mol} \approx 4 \times 10^4 \text{ mol}$ .

Let's assume that all the acid in the lake is completely ionized, so that only the free  $\text{H}^+(\text{aq})$  measured by the pH needs to be neutralized. We will need to neutralize at least that much acid, although there may be a great deal more acid in the lake than that.

The oxide ion of CaO is very basic.  $\infty$  (Section 16.5) In the neutralization reaction 1 mol of  $\text{O}^{2-}$  reacts with 2 mol of  $\text{H}^+$  to form  $\text{H}_2\text{O}$ . Thus,  $4 \times 10^4 \text{ mol}$  of  $\text{H}^+$  requires the following number of grams of CaO:

$$(4 \times 10^4 \text{ mol H}^+) \left( \frac{1 \text{ mol CaO}}{2 \text{ mol H}^+} \right) \left( \frac{56.1 \text{ g CaO}}{1 \text{ mol CaO}} \right) = 1 \times 10^6 \text{ g CaO}$$

This amounts to slightly more than a ton of CaO. That would not be very costly because CaO is an inexpensive base, selling for less than \$100 per ton when purchased in large quantities. The amount of CaO calculated above, however, is the very minimum amount needed because there are likely to be weak acids in the water that must also be neutralized. This liming procedure has been used to adjust the pH of some small lakes to bring their pH into the range necessary for fish to live. The lake in our example would be about a half mile long, a half mile wide, and have an average depth of 20 ft.

## CHAPTER REVIEW

## SUMMARY AND KEY TERMS

**Sections 18.1 and 18.2** In these sections we examined the physical and chemical properties of Earth's atmosphere. The complex temperature variations in the atmosphere give rise to four regions, each with characteristic properties. The lowest of these regions, the **troposphere**, extends

from Earth's surface up to an altitude of about 12 km. Above the troposphere, in order of increasing altitude, are the **stratosphere**, mesosphere, and thermosphere. In the upper reaches of the atmosphere, only the simplest chemical species can survive the bombardment of highly

energetic particles and radiation from the Sun. The average molecular weight of the atmosphere at high elevations is lower than that at Earth's surface because the lightest atoms and molecules diffuse upward and also because of **photodissociation**, which is the breaking of bonds in molecules because of the absorption of light. Absorption of radiation may also lead to the formation of ions via **photoionization**.

**Section 18.3** Ozone is produced in the upper atmosphere from the reaction of atomic oxygen with  $O_2$ . Ozone is itself decomposed by absorption of a photon or by reaction with an active species such as Cl. **Chlorofluorocarbons** can undergo photodissociation in the stratosphere, introducing atomic chlorine, which is capable of catalytically destroying ozone. A marked reduction in the ozone level in the upper atmosphere would have serious adverse consequences because the ozone layer filters out certain wavelengths of ultraviolet light that are not removed by any other atmospheric component.

**Section 18.4** In the troposphere the chemistry of trace atmospheric components is of major importance. Many of these minor components are pollutants. Sulfur dioxide is one of the more noxious and prevalent examples. It is oxidized in air to form sulfur trioxide, which, upon dissolving in water, forms sulfuric acid. The oxides of sulfur are major contributors to **acid rain**. One method of preventing the escape of  $SO_2$  from industrial operations is to react the  $SO_2$  with CaO to form calcium sulfite ( $CaSO_3$ ).

Carbon monoxide (CO) is found in high concentrations in automobile engine exhaust and in cigarette smoke. CO is a health hazard because it can form a strong bond with **hemoglobin** and thus reduce the capacity for blood to transfer oxygen from the lungs.

**Photochemical smog** is a complex mixture of components in which both nitrogen oxides and ozone play important roles. Smog components are generated mainly in automobile engines, and smog control consists largely of controlling auto emissions.

Carbon dioxide and water vapor are the major components of the atmosphere that strongly absorb infrared radiation.  $CO_2$  and  $H_2O$  are therefore critical in maintaining Earth's temperature. The concentrations of  $CO_2$  and other so-called greenhouse gases in the atmosphere are thus important in determining worldwide climate. Because of the

extensive combustion of fossil fuels (coal, oil, and natural gas), the concentration of carbon dioxide in the atmosphere is steadily increasing.

**Section 18.5** Seawater contains about 3.5% by mass of dissolved salts and is described as having a **salinity** of 35. Seawater's density and salinity vary with depth. Because most of the world's water is in the oceans, humans may eventually look to the seas for freshwater. **Desalination** is the removal of dissolved salts from seawater or brackish water to make it fit for human consumption. Desalination may be accomplished by distillation or by **reverse osmosis**.

**Section 18.6** Freshwater contains many dissolved substances, including dissolved oxygen, which is necessary for fish and other aquatic life. Substances that are decomposed by bacteria are said to be **biodegradable**. Because the oxidation of biodegradable substances by aerobic bacteria consumes dissolved oxygen, these substances are called oxygen-demanding wastes. The presence of an excess amount of oxygen-demanding wastes in water can sufficiently deplete the dissolved oxygen to kill fish and produce offensive odors. Plant nutrients can contribute to the problem by stimulating the growth of plants that become oxygen-demanding wastes when they die.

The water available from freshwater sources may require treatment before it can be used domestically. The several steps generally used in municipal water treatment include coarse filtration, sedimentation, sand filtration, aeration, sterilization, and sometimes water softening. Water softening is required when the water contains ions such as  $Mg^{2+}$  and  $Ca^{2+}$ , which react with soap to form soap scum. Water containing such ions is called **hard water**. The **lime-soda process**, which involves adding CaO and  $Na_2CO_3$  to hard water, is sometimes used for large-scale municipal water softening. Individual homes usually rely on **ion exchange**, a process by which hard-water ions are exchanged for  $Na^+$  ions.

**Section 18.7** The **green chemistry** initiative promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment. The areas in which the principles of green chemistry can operate to improve environmental quality include choices of solvents and reagents for chemical reactions, development of alternative processes, and improvements in existing systems and practices.

## KEY SKILLS

- Describe the regions of Earth's atmosphere in terms of how temperature varies with altitude.
- Describe the composition of the atmosphere in terms of the major components in dry air at sea level.
- Calculate concentrations of gases in parts per million (ppm).
- Describe the processes of photodissociation and photoionization and their role in the upper atmosphere.
- Use bond energies and ionization energies to calculate the minimum frequency or maximum wavelength needed to cause photodissociation or photoionization.
- Explain the role of ozone in the upper atmosphere.
- Explain how chlorofluorocarbons (CFCs) are involved in depleting the ozone layer.

- Describe the origins and behavior of sulfur oxides, carbon monoxide, and nitrogen oxides as air pollutants, including the generation of acid rain and photochemical smog.
- Describe how water and carbon dioxide in the atmosphere affect atmospheric temperature via the greenhouse effect.
- Explain what is meant by the salinity of water and describe the process of reverse osmosis as a means of desalination.
- List the major cations, anions, and gases present in natural waters and describe the relationship between dissolved oxygen and water quality.
- List the main steps involved in treating water for domestic uses.
- Describe the main goals of green chemistry.

## VISUALIZING CONCEPTS

**18.1** At room temperature (298 K) and 1 atm pressure, one mole of an ideal gas occupies 22.4 L. [∞](#) (Section 10.4)

(a) Looking back at Figure 18.1, do you predict that 1 mole of an ideal gas in the middle of the stratosphere would occupy a greater or smaller volume than 22.4 L?

(b) Looking at Figure 18.1(a), we see that the temperature is lower at 85 km altitude than at 50 km. Does this mean that one mole of an ideal gas would occupy less volume at 85 km than at 50 km? Explain. [Section 18.1]

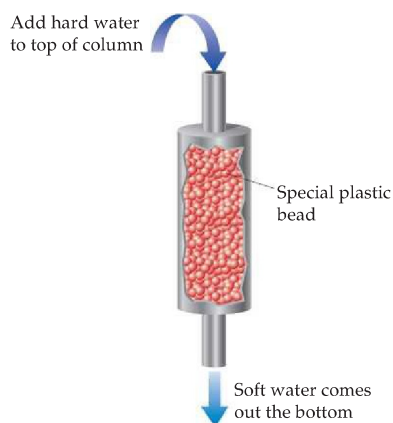
**18.2** Molecules in the upper atmosphere tend to contain double and triple bonds rather than single bonds. Suggest an explanation. [Section 18.2]

**18.3** Why does ozone concentration in the atmosphere vary as a function of altitude (see Figure 18.4)? [Section 18.3]

**18.4** You are working with an artist who has been commissioned to make a sculpture for a big city in the eastern United States. The artist is wondering what material to use to make her sculpture, because she has heard that acid rain in the eastern U.S. might destroy it over time. You take samples of granite, marble, bronze, and other materials, and place them outdoors for a long time in the big city. You periodically examine the appearance and measure the mass of the samples. (a) What observations would lead you to conclude that one, or more, of the materials were well-suited for the sculpture? (b) What chemical process (or processes) is (are) the most likely responsible for any observed changes in the materials? [Section 18.4]

**18.5** How does carbon dioxide interact with the world ocean? [Section 18.5]

**18.6** The following picture represents an ion-exchange column, in which water containing “hard” ions, such as  $\text{Ca}^{2+}$ , is added to the top of the column, and water containing “soft” ions such as  $\text{Na}^+$  come out the bottom. Explain what is happening in the column. [Section 18.6]



**18.7** Describe the basic goals of green chemistry. [Section 18.7]

**18.8** One mystery in environmental science is the imbalance in the “carbon dioxide budget.” Considering only human activities, scientists have estimated that 1.6 billion metric tons of  $\text{CO}_2$  is added to the atmosphere every year because of deforestation (plants use  $\text{CO}_2$ , and fewer plants will leave more  $\text{CO}_2$  in the atmosphere). Another 5.5 billion tons per year is put into the atmosphere because of burning fossil fuels. It is further estimated (again, considering only human activities) that the atmosphere actually takes up about 3.3 billion tons of  $\text{CO}_2$  per year, while the oceans take up 2 billion tons per year, leaving about 1.8 billion tons of  $\text{CO}_2$  per year unaccounted for. This “missing”  $\text{CO}_2$  is assumed to be taken up by the “land.” What do you think might be happening?

## EXERCISES

### Earth’s Atmosphere

**18.9** (a) What is the primary basis for the division of the atmosphere into different regions? (b) Name the regions of the atmosphere, indicating the altitude interval for each one.

**18.10** (a) How are the boundaries between the regions of the atmosphere determined? (b) Explain why the stratosphere, which is more than 20 miles thick, has a smaller total mass than the troposphere, which is less than 10 miles thick.

- 18.11** Air pollution in the Mexico City metropolitan area is among the worst in the world. The concentration of ozone in Mexico City has been measured at 441 ppb (0.441 ppm). Mexico City sits at an altitude of 7400 feet, which means its atmospheric pressure is only 0.67 atm. Calculate the partial pressure of ozone at 441 ppb if the atmospheric pressure is 0.67 atm.
- 18.12** From the data in Table 18.1, calculate the partial pressures of carbon dioxide and argon when the total atmospheric pressure is 96.5 kPa.
- 18.13** The average concentration of carbon monoxide in air in an Ohio city in 2006 was 3.5 ppm. Calculate the number of CO molecules in 1.0 L of this air at a pressure of 755 torr and a temperature of 18 °C.
- 18.14** (a) From the data in Table 18.1, what is the concentration of neon in the atmosphere in ppm? (b) What is the concentration of neon in the atmosphere in molecules per L, assuming an atmospheric pressure of 733 torr and a temperature of 292 K?

## The Upper Atmosphere; Ozone

- 18.15** The dissociation energy of a carbon–bromine bond is typically about 210 kJ/mol. What is the maximum wavelength of photons that can cause C—Br bond dissociation?
- 18.16** In  $\text{CF}_3\text{Cl}$  the C—Cl bond-dissociation energy is 339 kJ/mol. In  $\text{CCl}_4$  the C—Cl bond-dissociation energy is 293 kJ/mol. What is the range of wavelengths of photons that can cause C—Cl bond rupture in one molecule but not in the other?
- 18.17** (a) Distinguish between *photodissociation* and *photoionization*. (b) Use the energy requirements of these two processes to explain why photodissociation of oxygen is more important than photoionization of oxygen at altitudes below about 90 km.
- 18.18** Why is the photodissociation of  $\text{N}_2$  in the atmosphere relatively unimportant compared with the photodissociation of  $\text{O}_2$ ?
- 18.19** What is a hydrofluorocarbon? Why are these compounds potentially less harmful to the ozone layer than CFCs?
- 18.20** Draw the Lewis structure for the chlorofluorocarbon CFC-11,  $\text{CFCl}_3$ . What chemical characteristics of this substance allow it to effectively deplete stratospheric ozone?
- 18.21** (a) Why is the fluorine present in chlorofluorocarbons not a major contributor to depletion of the ozone layer? (b) What are the chemical forms in which chlorine exists in the stratosphere following cleavage of the carbon–chlorine bond?
- 18.22** Would you expect the substance  $\text{CFBr}_3$  to be effective in depleting the ozone layer, assuming that it is present in the stratosphere? Explain.

## Chemistry of the Troposphere

- 18.23** For each of the following gases, make a list of known or possible naturally occurring sources: (a)  $\text{CH}_4$ , (b)  $\text{SO}_2$ , (c) NO, (d) CO.
- 18.24** Why is rainwater naturally acidic, even in the absence of polluting gases such as  $\text{SO}_2$ ?
- 18.25** (a) Write a chemical equation that describes the attack of acid rain on limestone,  $\text{CaCO}_3$ . (b) If a limestone sculpture were treated to form a surface layer of calcium sulfate, would this help to slow down the effects of acid rain? Explain.
- 18.26** The first stage in corrosion of iron upon exposure to air is oxidation to  $\text{Fe}^{2+}$ . (a) Write a balanced chemical equation to show the reaction of iron with oxygen and protons from acid rain. (b) Would you expect the same sort of reaction to occur with a silver surface? Explain.
- 18.27** Alcohol-based fuels for automobiles lead to the production of formaldehyde ( $\text{CH}_2\text{O}$ ) in exhaust gases. Formaldehyde undergoes photodissociation, which contributes to photochemical smog:
- $$\text{CH}_2\text{O} + h\nu \longrightarrow \text{CHO} + \text{H}$$
- The maximum wavelength of light that can cause this reaction is 335 nm. (a) In what part of the electromagnetic spectrum is light with this wavelength found? (b) What is the maximum strength of a bond, in kJ/mol, that can be broken by absorption of a photon of 335-nm light? (c) Compare your answer from part (b) to the appropriate value from Table 8.4. What do you conclude about the C—H bond energy in formaldehyde? (d) Write out the formaldehyde photodissociation reaction, showing Lewis-dot structures.
- 18.28** An important reaction in the formation of photochemical smog is the photodissociation of  $\text{NO}_2$ :
- $$\text{NO}_2 + h\nu \longrightarrow \text{NO}(g) + \text{O}(g)$$
- The maximum wavelength of light that can cause this reaction is 420 nm. (a) In what part of the electromagnetic spectrum is light with this wavelength found? (b) What is the maximum strength of a bond, in kJ/mol, that can be broken by absorption of a photon of 420-nm light? (c) Write out the photodissociation reaction showing Lewis-dot structures.
- 18.29** Explain why increasing concentrations of  $\text{CO}_2$  in the atmosphere affect the quantity of energy leaving Earth but do not affect the quantity entering from the Sun.
- 18.30** (a) With respect to absorption of radiant energy, what distinguishes a greenhouse gas from a nongreenhouse gas? (b)  $\text{CH}_4$  is a greenhouse gas, but Ar is not. How might the molecular structure of  $\text{CH}_4$  explain why it is a greenhouse gas?

## The World Ocean

- 18.31** What is the molarity of  $\text{Na}^+$  in a solution of  $\text{NaCl}$  whose salinity is 5.6 if the solution has a density of 1.03 g/mL?
- 18.32** Phosphorus is present in seawater to the extent of 0.07 ppm by mass. If the phosphorus is present as phosphate,  $\text{PO}_4^{3-}$ , calculate the corresponding molar concentration of phosphate in seawater.
- 18.33** A first-stage recovery of magnesium from seawater is precipitation of  $\text{Mg}(\text{OH})_2$  with  $\text{CaO}$ :
- $$\text{Mg}^{2+}(\text{aq}) + \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Mg}(\text{OH})_2(\text{s}) + \text{Ca}^{2+}(\text{aq})$$
- What mass of  $\text{CaO}$ , in grams, is needed to precipitate 1000 lb of  $\text{Mg}(\text{OH})_2$ ?
- 18.34** Gold is found in seawater at very low levels, about 0.05 ppb by mass. Assuming that gold is worth about \$800 per troy ounce, how many liters of seawater would you have to process to obtain \$1,000,000 worth of gold?
- Assume the density of seawater is 1.03 g/mL and that your gold recovery process is 50% efficient.
- 18.35** Suppose that one wishes to use reverse osmosis to reduce the salt content of brackish water containing 0.22 M total salt concentration to a value of 0.01 M, thus rendering it usable for human consumption. What is the minimum pressure that needs to be applied in the permeators (Figure 18.16) to achieve this goal, assuming that the operation occurs at 298 K? (*Hint:* Refer to Section 13.5.)
- 18.36** Assume that a portable reverse-osmosis apparatus such as that shown in Figure 18.17 operates on seawater, whose concentrations of constituent ions are listed in Table 18.6, and that the desalinated water output has an effective molarity of about 0.02 M. What minimum pressure must be applied by hand pumping at 297 K to cause reverse osmosis to occur? (*Hint:* Refer to Section 13.5.)

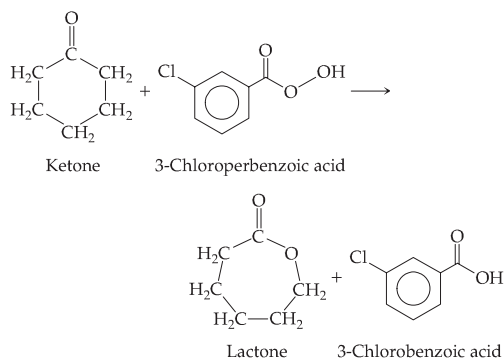
## Freshwater

- 18.37** List the common products formed when an organic material containing the elements carbon, hydrogen, oxygen, sulfur, and nitrogen decomposes (a) under aerobic conditions, (b) under anaerobic conditions.
- 18.38** (a) Explain why the concentration of dissolved oxygen in freshwater is an important indicator of the quality of the water. (b) How is the solubility of oxygen in water affected by increasing temperature?
- 18.39** The organic anion
- $$\text{H}_3\text{C}-(\text{CH}_2)_9-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{SO}_3^-$$
- is found in most detergents. Assume that the anion undergoes aerobic decomposition in the following manner:
- $$2 \text{C}_{18}\text{H}_{29}\text{SO}_3^-(\text{aq}) + 51 \text{O}_2(\text{aq}) \longrightarrow 36 \text{CO}_2(\text{aq}) + 28 \text{H}_2\text{O}(\text{l}) + 2 \text{H}^+(\text{aq}) + 2 \text{SO}_4^{2-}(\text{aq})$$
- What is the total mass of  $\text{O}_2$  required to biodegrade 1.0 g of this substance?
- 18.40** The average daily mass of  $\text{O}_2$  taken up by sewage discharged in the United States is 59 g per person. How many liters of water at 9 ppm  $\text{O}_2$  are totally depleted of oxygen in 1 day by a population of 120,000 people?
- 18.41** Write a balanced chemical equation to describe how magnesium ions are removed in water treatment by the addition of slaked lime,  $\text{Ca}(\text{OH})_2$ .
- 18.42** (a) Which of the following ionic species could be responsible for hardness in a water supply:  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ? (b) What properties of an ion determine whether it will contribute to water hardness?
- 18.43** How many moles of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  should be added to soften 1200 L of water in which  $[\text{Ca}^{2+}] = 5.0 \times 10^{-4} \text{ M}$  and  $[\text{HCO}_3^-] = 7.0 \times 10^{-4} \text{ M}$ ?
- 18.44** The concentration of  $\text{Ca}^{2+}$  in a particular water supply is  $5.7 \times 10^{-3} \text{ M}$ . The concentration of bicarbonate ion,  $\text{HCO}_3^-$ , in the same water is  $1.7 \times 10^{-3} \text{ M}$ . What masses of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  must be added to  $5.0 \times 10^7 \text{ L}$  of this water to reduce the level of  $\text{Ca}^{2+}$  to 20% of its original level?
- 18.45** Ferrous sulfate ( $\text{FeSO}_4$ ) is often used as a coagulant in water purification. The iron(II) salt is dissolved in the water to be purified, then oxidized to the iron(III) state by dissolved oxygen, at which time gelatinous  $\text{Fe}(\text{OH})_3$  forms, assuming the pH is above approximately 6. Write balanced chemical equations for the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by dissolved oxygen, and for the formation of  $\text{Fe}(\text{OH})_3(\text{s})$  by reaction of  $\text{Fe}^{3+}(\text{aq})$  with  $\text{HCO}_3^-(\text{aq})$ .
- 18.46** What properties make a substance a good coagulant for water purification?

## Green Chemistry

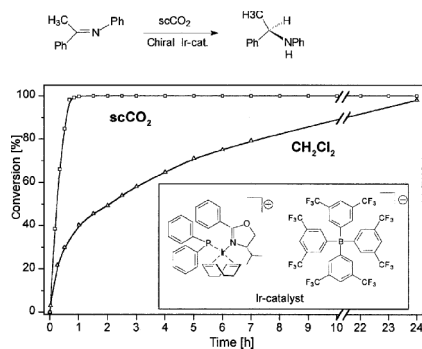
- 18.47** One of the principles of green chemistry is that it is better to use as few steps as possible in making new chemicals. How does this principle relate to energy efficiency?
- 18.48** Discuss how catalysts can make processes more energy efficient.

- 18.49** The Baeyer–Villiger reaction is a classic organic oxidation reaction for converting ketones to lactones, as in this reaction:



The reaction is used in the manufacture of plastics and pharmaceuticals. The reactant 3-chloroperbenzoic acid is somewhat shock sensitive, however, and prone to explode. Also, 3-chlorobenzoic acid is a waste product. An alternative process being developed uses hydrogen peroxide and a catalyst consisting of tin deposited within a solid support. The catalyst is readily recovered from the reaction mixture. (a) What would you expect to be the other product of oxidation of the ketone to lactone by hydrogen peroxide? (b) What principles of green chemistry are addressed by use of the proposed process?

- 18.50** The reaction shown here was performed with an iridium catalyst, both in supercritical  $\text{CO}_2$  ( $\text{scCO}_2$ ) and in the chlorinated solvent  $\text{CH}_2\text{Cl}_2$ . The kinetic data for the reaction in both solvents are plotted in the graph. Why is this a good example of a green chemical reaction?



## ADDITIONAL EXERCISES

- 18.51** A friend of yours has seen each of the following items in newspaper articles and would like an explanation: (a) acid rain, (b) greenhouse gas, (c) photochemical smog, (d) ozone depletion. Give a brief explanation of each term, and identify one or two of the chemicals associated with each.
- 18.52** Suppose that on another planet the atmosphere consists of 17%  $\text{Kr}$ , 38%  $\text{CH}_4$ , and 45%  $\text{O}_2$ . What is the average molar mass at the surface? What is the average molar mass at an altitude at which all the  $\text{O}_2$  is photodissociated?
- 18.53** If an average  $\text{O}_3$  molecule “lives” only 100–200 seconds in the stratosphere before undergoing dissociation, how can  $\text{O}_3$  offer any protection from ultraviolet radiation?
- 18.54** Show how Equations 18.7 and 18.9 can be added to give Equation 18.10. (You may need to multiply one of the reactions by a factor to have them add properly.)
- 18.55** What properties of CFCs make them ideal for various commercial applications but also make them a long-term problem in the stratosphere?
- 18.56** Halons are fluorocarbons that contain bromine, such as  $\text{CBrF}_3$ . They are used extensively as foaming agents for fighting fires. Like CFCs, halons are very unreactive and ultimately can diffuse into the stratosphere. (a) Based on the data in Table 8.4, would you expect photodissociation of Br atoms to occur in the stratosphere? (b) Propose a mechanism by which the presence of halons in the stratosphere could lead to the depletion of stratospheric ozone.
- 18.57** It is estimated that the lifetime for HFCs in the stratosphere is 2–7 years. If HFCs have such long lifetimes, why are they being used to replace CFCs?
- [18.58]** The hydroxyl radical,  $\text{OH}$ , is formed at low altitudes via the reaction of excited oxygen atoms with water:
- $$\text{O}^*(g) + \text{H}_2\text{O}(g) \longrightarrow 2 \text{OH}(g)$$
- (a) Write the Lewis structure for the hydroxyl radical. (*Hint:* It has one unpaired electron.) Once produced, the hydroxyl radical is very reactive. Explain why each of the following series of reactions affects the pollution in the troposphere:
- (b)  $\text{OH} + \text{NO}_2 \longrightarrow \text{HNO}_3$
- (c)  $\text{OH} + \text{CO} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{OOH}$   
 $\text{OOH} + \text{NO} \longrightarrow \text{OH} + \text{NO}_2$
- (d)  $\text{OH} + \text{CH}_4 \longrightarrow \text{H}_2\text{O} + \text{CH}_3$   
 $\text{CH}_3 + \text{O}_2 \longrightarrow \text{OOCH}_3$   
 $\text{OOCH}_3 + \text{NO} \longrightarrow \text{OCH}_3 + \text{NO}_2$
- 18.59** Explain, using Le Châtelier’s principle, why the equilibrium constant for the formation of  $\text{NO}$  from  $\text{N}_2$  and  $\text{O}_2$  increases with increasing temperature, whereas the equilibrium constant for the formation of  $\text{NO}_2$  from  $\text{NO}$  and  $\text{O}_2$  decreases with increasing temperature.



- 18.60** The affinity of carbon monoxide for hemoglobin is about 210 times that of  $O_2$ . Assume a person is inhaling air that contains 125 ppm of CO. If all the hemoglobin leaving the lungs carries either oxygen or CO, calculate the fraction in the form of carboxyhemoglobin.
- 18.61** Natural gas consists primarily of methane,  $CH_4(g)$ . (a) Write a balanced chemical equation for the complete combustion of methane to produce  $CO_2(g)$  as the only carbon-containing product. (b) Write a balanced chemical equation for the incomplete combustion of methane to produce  $CO(g)$  as the only carbon-containing product. (c) At 25 °C and 1.0 atm pressure, what is the minimum quantity of dry air needed to combust 1.0 L of  $CH_4(g)$  completely to  $CO_2(g)$ ?
- 18.62** One of the possible consequences of global warming is an increase in the temperature of ocean water. The oceans serve as a “sink” for  $CO_2$  by dissolving large amounts of it. (a) How would the solubility of  $CO_2$  in the oceans be affected by an increase in the temperature of the water? (b) Discuss the implications of your answer to part (a) for the problem of global warming.
- 18.63** The rate of solar energy striking Earth averages 169 watts per square meter. The rate of energy radiated from Earth’s surface averages 390 watts per square meter. Comparing these numbers, one might expect that the planet would cool quickly, yet it does not. Why not?
- 18.64** The solar power striking Earth every day averages 169 watts per square meter. The peak electrical power usage in New York City is 12,000 megawatts. Considering that present technology for solar energy conversion is only about 10% efficient, from how many square meters of land must sunlight be collected in order to provide this peak power? (For comparison, the total area of the city is  $830 \text{ km}^2$ .)
- 18.65** Write balanced chemical equations for each of the following reactions: (a) The nitric oxide molecule undergoes photodissociation in the upper atmosphere. (b) The nitric oxide molecule undergoes photoionization in the upper atmosphere. (c) Nitric oxide undergoes oxidation by ozone in the stratosphere. (d) Nitrogen dioxide dissolves in water to form nitric acid and nitric oxide.
- 18.66** (a) Explain why  $Mg(OH)_2$  precipitates when  $CO_3^{2-}$  ion is added to a solution containing  $Mg^{2+}$ . (b) Will  $Mg(OH)_2$  precipitate when 4.0 g of  $Na_2CO_3$  is added to 1.00 L of a solution containing 125 ppm of  $Mg^{2+}$ ?
- [18.67]** It has been pointed out that there may be increased amounts of NO in the troposphere as compared with the past because of massive use of nitrogen-containing compounds in fertilizers. Assuming that NO can eventually diffuse into the stratosphere, how might it affect the conditions of life on Earth? Using the index to this text, look up the chemistry of nitrogen oxides. What chemical pathways might NO in the troposphere follow?
- [18.68]** As of the writing of this text, EPA standards limit atmospheric ozone levels in urban environments to 84 ppb. How many moles of ozone would there be in the air above Los Angeles County (area about 4000 square miles; consider a height of 10 m above the ground) if ozone was at this concentration?

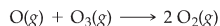
## INTEGRATIVE EXERCISES

- 18.69** The estimated average concentration of  $NO_2$  in air in the United States in 2006 was 0.016 ppm. (a) Calculate the partial pressure of the  $NO_2$  in a sample of this air when the atmospheric pressure is 755 torr (99.1 kPa). (b) How many molecules of  $NO_2$  are present under these conditions at 20 °C in a room that measures  $15 \times 14 \times 8 \text{ ft}$ ?
- [18.70]** In 1986 an electrical power plant in Taylorsville, Georgia, burned 8,376,726 tons of coal, a national record at that time. (a) Assuming that the coal was 83% carbon and 2.5% sulfur and that combustion was complete, calculate the number of tons of carbon dioxide and sulfur dioxide produced by the plant during the year. (b) If 55% of the  $SO_2$  could be removed by reaction with powdered CaO to form  $CaSO_3$ , how many tons of  $CaSO_3$  would be produced?
- 18.71** The water supply for a midwestern city contains the following impurities: coarse sand, finely divided particulates, nitrate ion, trihalomethanes, dissolved phosphorus in the form of phosphates, potentially harmful bacterial strains, dissolved organic substances. Which of the following processes or agents, if any, is effective in removing each of these impurities: coarse sand filtration, activated carbon filtration, aeration, ozonization, precipitation with aluminum hydroxide?
- 18.72** The concentration of  $H_2O$  in the stratosphere is about 5 ppm. It undergoes photodissociation as follows:
- $$H_2O(g) \longrightarrow H(g) + OH(g)$$
- (a) Write out the Lewis-dot structures for both products and reactant.
- (b) Using Table 8.4, calculate the wavelength required to cause this dissociation.
- (c) The hydroxyl radicals, OH, can react with ozone, giving the following reactions:
- $$OH(g) + O_3(g) \longrightarrow HO_2(g) + O_2(g)$$
- $$HO_2(g) + O(g) \longrightarrow OH(g) + O_2(g)$$
- What overall reaction results from these two elementary reactions? What is the catalyst in the overall reaction? Explain.
- 18.73** Bioremediation is the process by which bacteria repair their environment in response, for example, to an oil spill. The efficiency of bacteria for “eating” hydrocarbons depends on the amount of oxygen in the system, pH, temperature, and many other factors. In a certain oil spill, hydrocarbons from the oil disappeared with a first-order rate constant of  $2 \times 10^{-6} \text{ s}^{-1}$ . How many days did it take for the hydrocarbons to decrease to 10% of their initial value?
- 18.74** The standard enthalpies of formation of ClO and  $ClO_2$  are 101 and 102 kJ/mol, respectively. Using these data and the thermodynamic data in Appendix C, calculate the overall enthalpy change for each step in the following catalytic cycle:
- $$ClO(g) + O_3(g) \longrightarrow ClO_2(g) + O_2(g)$$
- $$ClO_2(g) + O(g) \longrightarrow ClO(g) + O_2(g)$$

What is the enthalpy change for the overall reaction that results from these two steps?

**18.75** The main reason that distillation is a costly method for purifying water is the high energy required to heat and vaporize water. **(a)** Using the density, specific heat, and heat of vaporization of water from Appendix B, calculate the amount of energy required to vaporize 1.00 gal of water beginning with water at 20 °C. **(b)** If the energy is provided by electricity costing \$0.085/kWh, calculate its cost. **(c)** If distilled water sells in a grocery store for \$1.26 per gal, what percentage of the sales price is represented by the cost of the energy?

**[18.76]** A reaction that contributes to the depletion of ozone in the stratosphere is the direct reaction of oxygen atoms with ozone:



At 298 K the rate constant for this reaction is  $4.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . **(a)** Based on the units of the rate constant, write the likely rate law for this reaction. **(b)** Would you expect this reaction to occur via a single elementary process? Explain why or why not. **(c)** From the magnitude of the rate constant, would you expect the activation energy of this reaction to be large or small? Explain. **(d)** Use  $\Delta H_f^\circ$  values from Appendix C to estimate the enthalpy change for this reaction. Would this reaction raise or lower the temperature of the stratosphere?

**18.77** Nitrogen dioxide ( $\text{NO}_2$ ) is the only important gaseous species in the lower atmosphere that absorbs visible light. **(a)** Write the Lewis structure(s) for  $\text{NO}_2$ . **(b)** How does this structure account for the fact that  $\text{NO}_2$  dimerizes to form  $\text{N}_2\text{O}_4$ ? Based on what you can find about this dimerization reaction in the text, would you expect to find the  $\text{NO}_2$  that forms in an urban environment to be in the form of dimer? Explain. **(c)** What would you expect as products, if any, for the reaction of  $\text{NO}_2$  with  $\text{CO}$ ? **(d)** Would you expect  $\text{NO}_2$  generated in an urban environment to migrate to the stratosphere? Explain.

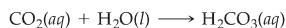
**18.78** The following data was collected for the destruction of  $\text{O}_3$  by  $\text{H}$  ( $\text{O}_3 + \text{H} \rightarrow \text{O}_2 + \text{OH}$ ) at very low concentrations:

Experiment	$[\text{O}_3], \text{M}$	$[\text{H}], \text{M}$	Initial Rate, $\text{M/s}$
1	$5.17 \times 10^{-33}$	$3.22 \times 10^{-26}$	$1.88 \times 10^{-14}$
2	$2.59 \times 10^{-33}$	$3.25 \times 10^{-26}$	$9.44 \times 10^{-15}$
3	$5.19 \times 10^{-33}$	$6.46 \times 10^{-26}$	$3.77 \times 10^{-14}$

- (a)** Write the rate law for the reaction.  
**(b)** Calculate the rate constant.

**18.79** The degradation of  $\text{CF}_3\text{CH}_2\text{F}$  (an HFC) by  $\text{OH}$  radicals in the troposphere is first order in each reactant and has a rate constant of  $k = 1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at 4 °C. If the tropospheric concentrations of  $\text{OH}$  and  $\text{CF}_3\text{CH}_2\text{F}$  are  $8.1 \times 10^5$  and  $6.3 \times 10^8$  molecules  $\text{cm}^{-3}$ , respectively, what is the rate of reaction at this temperature in  $\text{M/s}$ ?

**[18.80]** The Henry's law constant for  $\text{CO}_2$  in water at 25 °C is  $3.1 \times 10^{-2} \text{ M atm}^{-1}$ . **(a)** What is the solubility of  $\text{CO}_2$  in water at this temperature if the solution is in contact with air at normal atmospheric pressure? **(b)** Assume that all of this  $\text{CO}_2$  is in the form of  $\text{H}_2\text{CO}_3$  produced by the reaction between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ :



What is the pH of this solution?

**[18.81]** If the pH of a 1.0-in. rainfall over 1500  $\text{mi}^2$  is 3.5, how many kilograms of  $\text{H}_2\text{SO}_4$  are present, assuming that it is the only acid contributing to the pH?

**[18.82]** The precipitation of  $\text{Al}(\text{OH})_3$  ( $K_{sp} = 1.3 \times 10^{-33}$ ) is sometimes used to purify water. **(a)** Estimate the pH at which precipitation of  $\text{Al}(\text{OH})_3$  will begin if 5.0 lb of  $\text{Al}_2(\text{SO}_4)_3$  is added to 2000 gal of water. **(b)** Approximately how many pounds of  $\text{CaO}$  must be added to the water to achieve this pH?