

WHAT'S AHEAD

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18

CHEMISTRY OF THE ENVIRONMENT

18.1 | Earth's Atmosphere



The richness of life on Earth, represented in the section-opening photograph, is made possible by our planet's supportive atmosphere, the energy received from the Sun, and an abundance of water. These are the signature environmental features believed to be necessary for life.

As technology has advanced and human population has increased, humans have put new and greater stresses on the environment. Paradoxically, the very technology that enables population growth also provides the tools to help understand and manage the environment in a beneficial way. Chemistry is often at the heart of environmental issues. The economic growth of both developed and developing nations depends critically on chemical processes that range from treatment of water supplies to the extraction of fossil fuels. 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 preceding chapters to an understanding of how our environment operates and how human activities affect it. To understand and protect 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 actions as consumers turn on the same choices made by leading experts and governmental leaders: each decision should reflect the costs versus the benefits of our choices. Unfortunately, the environmental impacts of our decisions are often subtle and not immediately evident.

By the end of this section, you should be able to

- Describe the regions of Earth's atmosphere.
- Calculate concentrations of gases in parts per million (ppm).
- Describe the processes of photodissociation and photoionization.

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 examine some of the important characteristics of our planet's atmosphere.

The temperature of the atmosphere varies with altitude ([Figure 18.1](#)), and 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 10 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 above Earth, an altitude that defines the upper limit of the troposphere, which we call the *tropopause*.

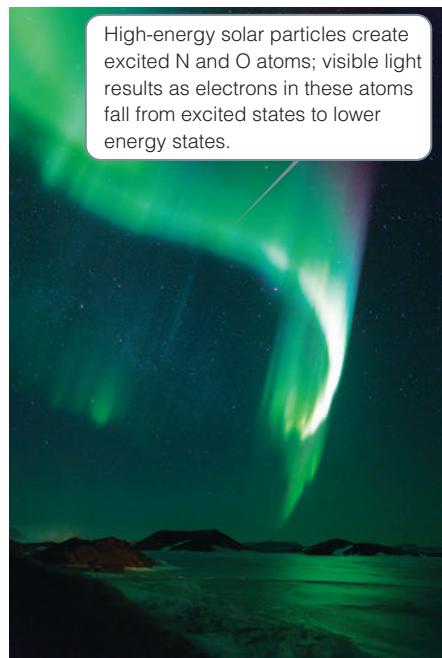
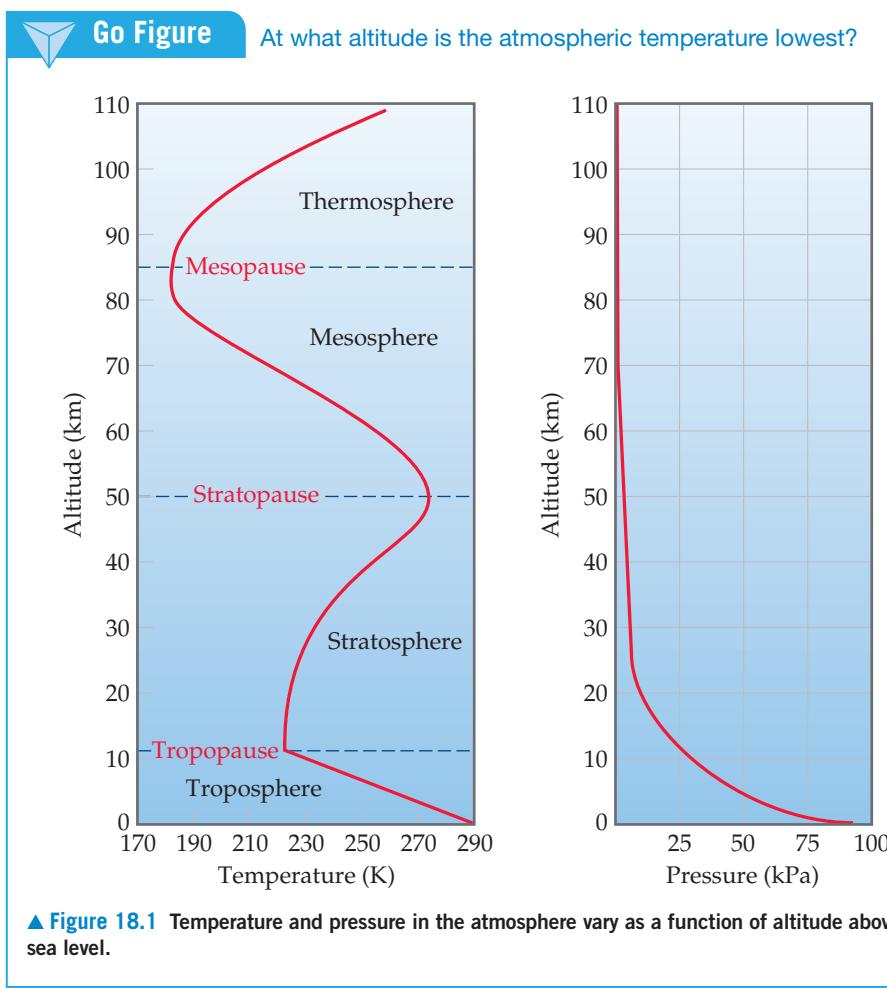
Above the tropopause, air temperature increases with altitude, reaching a maximum of about 275 K at about 50 km. The region from 10 km to 50 km is the **stratosphere**, and above it are the *mesosphere* and *thermosphere*. Notice in Figure 18.1 that the temperature extremes that form the boundaries between 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.

Atmospheric pressure decreases with increasing elevation (Figure 18.1), declining 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 101.3 kPa at sea level to 3.1×10^{-4} kPa at 100 km, to only 1.3×10^{-7} kPa at 200 km.

The troposphere and stratosphere together account for 99.9% of the mass of the atmosphere, 75% of which is the mass in the troposphere. Nevertheless, the thin upper atmosphere plays many important roles in determining the conditions of life at the surface.

Composition of the Atmosphere

Earth's atmosphere is constantly bombarded by radiation and energetic particles from the Sun. This barrage of energy has profound chemical and physical effects, especially in the upper regions of the atmosphere, above about 80 km ([Figure 18.2](#)). In addition, because of Earth's gravitational field, heavier atoms and molecules tend to sink in the atmosphere, leaving lighter atoms and molecules at the top of the atmosphere. (This is



▲ Figure 18.2 The aurora borealis (northern lights).

why, as just noted, 75% of the atmosphere's mass is in the troposphere.) Because of all these factors, the composition of the atmosphere is not uniform.

Table 18.1 shows the composition of dry air near sea level. Note that although traces of many substances are present, N₂ and O₂ make up about 99% of sea-level air. The noble gases and CO₂ make up most of the remainder.

When applied to substances in aqueous solution, the concentration unit *parts per million* (ppm) refers to grams of substance per million grams of solution. When dealing

TABLE 18.1 The Major Components of Dry Air near Sea Level

Component*	Content (mole fraction)	Molar Mass (g/mol)
Nitrogen	0.78084	28.013
Oxygen	0.20948	31.998
Argon	0.00934	39.948
Carbon dioxide	0.000400	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.

TABLE 18.2 Sources and Typical Concentrations of Some Minor Atmospheric Constituents

Constituent	Sources	Typical Concentration
Carbon dioxide, CO ₂	Decomposition of organic matter, release from oceans, fossil fuel combustion	400 ppm throughout troposphere
Carbon monoxide, CO	Decomposition of organic matter, industrial processes, fossil fuel combustion	0.05 ppm in unpolluted air; 1–50 ppm in urban areas
Methane, CH ₄	Decomposition of organic matter, natural-gas seepage, livestock emissions	1.82 ppm throughout troposphere
Nitric oxide, NO	Atmospheric electrical discharges, internal combustion engines, combustion of organic matter	0.01 ppm in unpolluted air; 0.2 ppm in smog
Ozone, O ₃	Atmospheric electrical discharges, diffusion from the stratosphere, photochemical smog	0–0.01 ppm in unpolluted air; 0.5 ppm in photochemical smog
Sulfur dioxide, SO ₂	Volcanic gases, forest fires, bacterial action, fossil fuel combustion, industrial processes	0–0.01 ppm in unpolluted air; 0.1–2 ppm in polluted urban areas

with gases, however, 1 ppm means one part by *volume* in 1 million volumes of the whole. Because volume is proportional to number of moles 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 1 mol of that constituent in 1 million moles of air; that is, the concentration in parts per million is equal to the mole fraction times 10^6 . For example, Table 18.1 lists the mole fraction of CO₂ in the atmosphere as 0.000400, which means its concentration in parts per million is $0.000400 \times 10^6 = 400$ ppm.

Other minor constituents of the troposphere, in addition to CO₂, are listed in **Table 18.2**.

Before we consider the chemical processes that occur in the atmosphere, let's review some of the properties of the two major components, N₂ and O₂. Recall that the N₂ molecule possesses a triple bond between the nitrogen atoms. This very strong bond (bond energy 941 kJ/mol) is largely responsible for the very low reactivity of N₂. The bond energy in O₂ is only 495 kJ/mol, making O₂ much more reactive than N₂. For example, oxygen reacts with many substances to form oxides.

Sample Exercise 18.1

Calculating Concentration from Partial Pressure

What is the concentration, in parts per million, of water vapor in a sample of air if the partial pressure of the water is 0.11 kPa and the total pressure of the air is 98.0 kPa?

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:

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

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

$$X_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P_t} = \frac{0.11 \text{ kPa}}{98.0 \text{ kPa}} = 0.0011$$

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 4.3 ppm. What is the partial pressure of the CO if the total air pressure is 92.7 kPa?

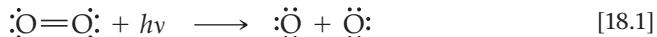
Photochemical Reactions in the Atmosphere

Although 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 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. If it were not for these photochemical processes, plant and animal life as we know it could not exist on Earth.

The Sun emits radiant energy over a wide range of wavelengths (Figure 18.3). 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. The energy of each photon is given by $E = h\nu$, where h is Planck constant and ν is the radiation frequency. For a chemical change to occur when radiation strikes atoms or molecules, two conditions must be met. First, the incoming photons must have sufficient energy to break a chemical bond or remove an electron from the atom or molecule. Second, the atoms or molecules being bombarded 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.

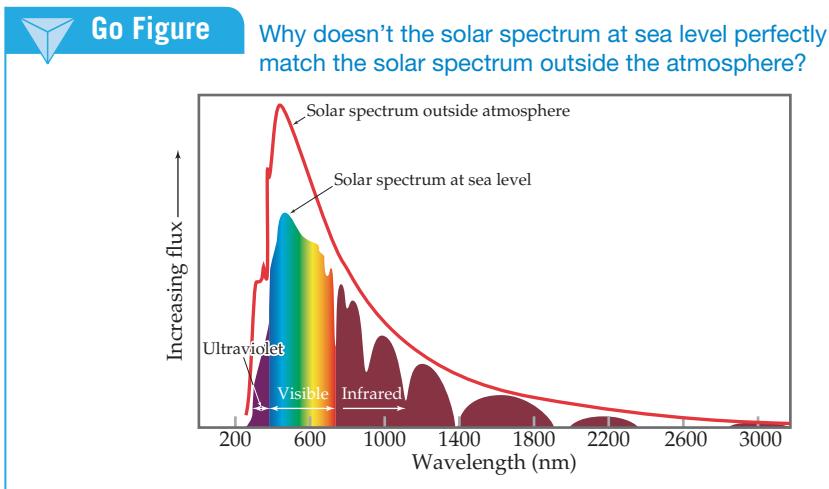
Photodissociation The rupture of a chemical bond resulting from absorption of a photon by a molecule is called **photodissociation**. No ions are formed when the bond between two atoms is cleaved by photodissociation. Instead, half the bonding electrons stay with one atom and half stay with the other atom. The result is two electrically neutral particles.

One of the most important processes occurring above an altitude of about 120 km is photodissociation of the oxygen molecule:



The minimum energy required to cause this change is determined by the bond energy (or *dissociation energy*) of O_2 , 495 kJ/mol.

Fortunately for us, 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, O, is formed. The dissociation of O_2 is very extensive at higher elevations. At 400 km, for example, only 1% of the oxygen is in the form of O_2 ; 99% is atomic oxygen. At 130 km, O_2 and atomic oxygen are just about equally abundant. Below 130 km, O_2 is more abundant than atomic oxygen because most of the solar energy has been absorbed in the upper atmosphere.



▲ Figure 18.3 The solar spectrum above Earth's atmosphere compared to that at sea level.

The more structured curve at sea level is due to gases in the atmosphere absorbing specific wavelengths of light. “Flux,” the unit on the vertical axis, is light energy per area per unit of time.



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 O₂ molecule?

SOLUTION

Analyze We are asked to determine the wavelength of a photon that has just enough energy to break the O=O double bond in O₂.

Solve

The dissociation energy of O₂ 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 O₂ molecule:

Plan We first need to calculate the energy required to break the O=O double bond in one molecule and then find the wavelength of a photon of this energy.

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

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

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

Finally, we use the relationship between frequency and wavelength to calculate the wavelength of the light:

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

Comment Thus, light of wavelength 242 nm, which is in the ultraviolet region of the electromagnetic spectrum, has sufficient energy per photon to photodissociate an O₂ molecule. Because photon energy increases as wavelength *decreases*, any photon of wavelength *shorter* than 242 nm will have sufficient energy to dissociate O₂.

► Practice Exercise

The bond dissociation energy of the Br—Br bond is 193 kJ/mol. What wavelength of light has just enough energy to cause Br—Br bond dissociation?

- (a) 620 nm (b) 310 nm (c) 148 nm (d) 6200 nm (e) 563 nm

The dissociation energy of N₂ is very high, 941 kJ/mol. As you should have seen in working out Practice Exercise 2 of Sample Exercise 18.2, only photons having a wavelength shorter than 127 nm possess sufficient energy to dissociate N₂. Furthermore, N₂ 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 N₂.

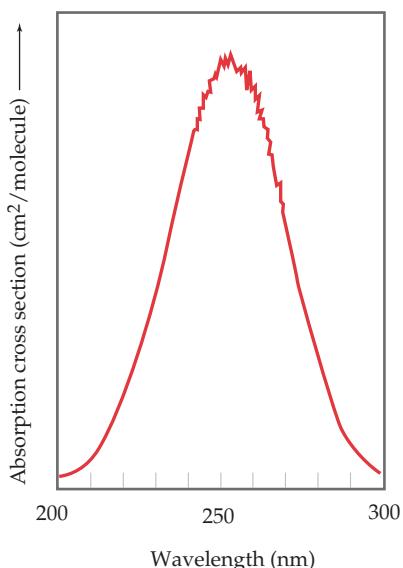
Photoionization Other photochemical processes besides photodissociation occur in the upper atmosphere, although their discovery has taken many twists and turns. In 1901, Guglielmo Marconi received a radio signal in St. John's, Newfoundland, that had been transmitted from Land's End, England, 2900 km 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.

The electrons in the upper atmosphere result mainly from **photoionization**, which occurs when a molecule in the upper atmosphere absorbs solar 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. Notice that this is a very different process from photodissociation.



Go Figure

In what region of the electromagnetic spectrum does ozone most strongly absorb light: (a) IR, (b) visible, or (c) UV?



▲ Figure 18.4 The absorption spectrum of ozone.

TABLE 18.3 Photoionization Reactions for Four Components of the Atmosphere

Process	Ionization Energy (kJ/mol)	λ_{\max} (nm)
$N_2 + h\nu \longrightarrow N_2^+ + e^-$	1495	80.1
$O_2 + h\nu \longrightarrow O_2^+ + e^-$	1205	99.3
$O + h\nu \longrightarrow O^+ + e^-$	1313	91.2
$NO + h\nu \longrightarrow NO^+ + e^-$	890	134.5

Four important photoionization processes occurring in the atmosphere above about 90 km are shown in **Table 18.3**. Photons of any wavelength shorter than the maximum lengths given in the table have enough energy to cause photoionization. A look back at Figure 18.3 shows you that virtually all of these high-energy photons are filtered out of the radiation reaching Earth because they are absorbed by the upper atmosphere.

Ozone in the Stratosphere

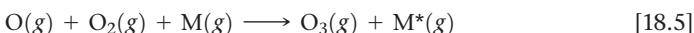
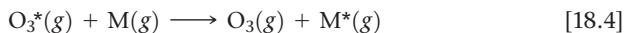
Although N_2 , O_2 , and atomic oxygen absorb photons having wavelengths shorter than 240 nm, ozone, O_3 , is the key absorber of photons whose wavelengths range from 240 to 310 nm, in the ultraviolet region of the electromagnetic spectrum, as illustrated in **Figure 18.4**. Ozone in the upper atmosphere 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.

By the time radiation from the Sun reaches an altitude of 90 km above Earth's surface, most of the short-wavelength radiation capable of photoionization has been absorbed. Nevertheless, radiation capable of dissociating the O_2 molecule is sufficiently intense for photodissociation of 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 O_2 is much greater than the concentration of atomic oxygen. Consequently, the oxygen atoms formed by photodissociation of O_2 in this region frequently collide with O_2 molecules and form ozone:



The asterisk on O_3 denotes that the product contains an excess of energy, because the reaction is exothermic. The 105 kJ/mol that is released must be transferred away from the O_3^* molecule quickly or else the molecule will fly apart into O_2 and atomic O—a decomposition that is the reverse of the reaction by which O_3^* is formed.

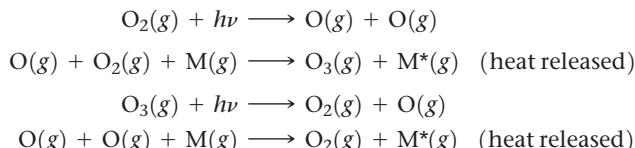
An energy-rich O_3^* molecule can release its excess energy by colliding with another atom or molecule and transferring some of the excess energy to it. Let's use M to represent the atom or molecule with which O_3^* collides. (Usually, M is N_2 or O_2 because these are the most abundant molecules in the atmosphere.) The formation of O_3^* and the transfer of excess energy to M are summarized by the equations



The rate at which the reactions of Equations 18.3 and 18.4 proceed depends on two factors that vary in opposite directions with increasing altitude. First, the formation of O_3^* (Equation 18.3) depends on the presence of O atoms. At low altitudes, most of the radiation energetic enough to dissociate O_2 molecules into O atoms has been absorbed; thus, O atoms are not very plentiful at low altitudes. Second, Equations 18.3 and 18.4 both depend on molecular collisions. The concentration of molecules is greater at low altitudes, and so the rates of both reactions are greater at lower altitudes.

Because these two effects vary with altitude in opposite directions, the highest rate of O₃ formation occurs in a band at an altitude of about 50 km, near the stratopause (Figure 18.1). Overall, roughly 90% of Earth's ozone is found in the stratosphere.

The photodissociation of ozone reverses the reaction that forms it. We thus have a cycle of ozone formation and decomposition, summarized on the next page:



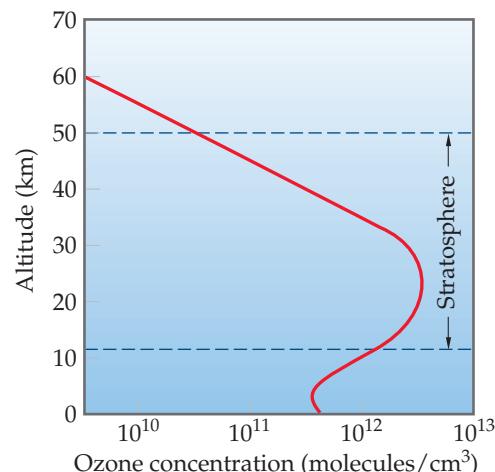
The first and third processes are photochemical; they use a solar photon to initiate a chemical reaction. The second and fourth are exothermic chemical reactions. The net result of the four reactions is a cycle in which solar radiant energy is converted into thermal energy. The ozone cycle in the stratosphere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

The reactions of the ozone cycle account for some, but not all, of the facts about the ozone layer. Many chemical reactions occur that involve substances other than oxygen. We must also consider the effects of turbulence and winds that mix up the stratosphere. A complicated picture results. The overall result of ozone formation and removal reactions, coupled with atmospheric turbulence and other factors, is to produce the upper-atmosphere ozone profile shown in **Figure 18.5**, with a maximum ozone concentration occurring at an altitude of about 25 km. This band of relatively high ozone concentration is referred to as the “ozone layer” or the “ozone shield.”

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 these molecules are continually destroyed even as they are formed.

Go Figure

Estimate the ozone concentration in moles per liter for the peak value in this graph.



▲ Figure 18.5 Variation in ozone concentration in the atmosphere as a function of altitude.

Self-Assessment Exercises

- 18.1** Would you expect the ratio of atmospheric helium to argon to be larger in the troposphere or the mesosphere?
(a) Troposphere
(b) Mesosphere
- 18.2** Which equation best represents the photoionization of ozone?
(a) O₃ + hν → O₃⁺ + e⁻
(b) O₃ + e⁻ → O₃⁻ + hν
(c) O₃ + hν → O₂ + O
- 18.3** Based on its Lewis structure, which molecule will have stronger oxygen-oxygen bonds, O₂ or O₃?
(a) Oxygen
(b) Ozone

Exercises

- 18.4** **(a)** How are the boundaries between the regions of the atmosphere determined? **(b)** Explain why the stratosphere, which is about 35 km thick, has a smaller total mass than the troposphere, which is about 12 km thick.
- 18.5** The Environmental Protection Agency (EPA) has established air quality standards. For ozone (O₃), the 8-hour average concentration permitted under the standards is 0.085 parts per million (ppm). **(a)** Calculate the partial pressure of ozone at 0.085 ppm if the atmospheric pressure is 100 kPa. **(b)** How many ozone molecules are in 1.0 L of air? Assume T = 25 °C.
- 18.6** **(a)** From the data in Table 18.1, what is the concentration of helium in the atmosphere in ppm? **(b)** What is the concentration of helium in the atmosphere in atoms per liter, assuming an atmospheric pressure of 101 kPa and a temperature of 298 K?

- 18.7** In CH_3I the C—I bond-dissociation energy is 241 kJ/mol. In $\text{C}_6\text{H}_5\text{I}$ the C—I bond-dissociation energy is 280 kJ/mol. What is the range of wavelengths of photons that can cause C—I bond rupture in one molecule but not in the other?
- 18.8** Why is the photodissociation of N_2 in the atmosphere relatively unimportant compared with the photodissociation of O_2 ?

- 18.9** The ultraviolet spectrum can be divided into three regions based on wavelength: UV-A (315–400 nm), UV-B (280–315 nm), and UV-C (100–280 nm). **(a)** Photons from which region have the highest energy and therefore are the most harmful to living tissue? **(b)** In the absence of ozone, which of these three regions, if any, are absorbed by the atmosphere? **(c)** When appropriate concentrations of ozone are present in the stratosphere, is all of the UV light absorbed before reaching the Earth's surface? If not, which region or regions are not filtered out?

18.1 (b) 18.2 (a) 18.3 (a)

Answers to Self-Assessment Exercises



18.2 | Human Activities and Earth's Atmosphere



Both natural and *anthropogenic* (human-caused) events can modify Earth's atmosphere. One impressive natural event was the eruption of Mount Pinatubo in June 1991. The volcano ejected approximately 10 km^3 of material into the stratosphere, causing a 10% drop in the amount of sunlight reaching Earth's surface during the next 2 years. That drop in sunlight led to a temporary 0.5°C drop in Earth's surface temperature. The volcanic particles that made it to the stratosphere remained there for approximately 3 years, *raising* the temperature of the stratosphere by several degrees due to

light absorption. Measurements of the stratospheric ozone concentration showed significantly increased ozone decomposition in this 3-year period.

By the end of this section, you should be able to

- Describe the origins and behavior of sulfur oxides and nitrogen oxides as air pollutants, including the generation of acid rain and photochemical smog.
- Describe how water and carbon dioxide cause an increase in atmospheric temperature near Earth's surface.

The Ozone Layer and Its Depletion

The ozone layer protects Earth's surface from the damaging ultraviolet (UV) radiation. Therefore, if the concentration of ozone in the stratosphere decreases substantially, more UV radiation will reach Earth's surface, causing unwanted photochemical reactions, including reactions correlated with skin cancer. 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 18.6). The first scientific paper on this phenomenon appeared in 1985, and the National Aeronautics and Space Administration (NASA) maintains an "Ozone Hole Watch" website with daily updates and data from 1999 to the present.

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 CFCl_3 and CF_2Cl_2 , do not occur in nature and 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 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. Because C—Cl bonds are considerably weaker than C—F bonds, free chlorine atoms are formed readily in the presence of light with wavelengths in the range from 190 to 225 nm, as shown in this typical reaction:



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 and molecular oxygen:



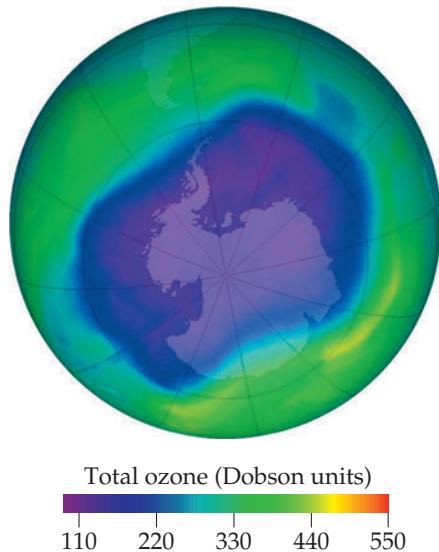
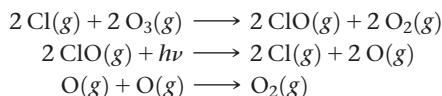
This reaction follows a second-order rate law with a very large rate constant:

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

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 ClO:



The Cl atoms generated in Equations 18.6 and 18.9 can react with more O_3 , according to Equation 18.7. The result is a sequence of reactions that accomplishes the Cl-catalyzed decomposition of O_3 to O_2 :



▲ Figure 18.6 Ozone present in the Southern Hemisphere, September 24, 2006. The data were taken from an orbiting satellite. This day had the lowest stratospheric ozone concentration yet recorded. One "Dobson unit" corresponds to 2.69×10^{16} ozone molecules in a 1 cm^2 column of atmosphere.

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



Because the rate of Equation 18.7 increases linearly with $[\text{Cl}]$, the rate at which ozone is destroyed increases as the quantity of Cl atoms increases. Thus, the higher the concentration of CFCs in the stratosphere, the faster the destruction of the ozone layer. Even though troposphere-to-stratosphere diffusion rates are slow, a substantial thinning of the ozone layer over the South Pole has been observed, particularly during September and October (Figure 18.6).

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, with some exceptions for “essential uses.” Since then, the production of CFCs has indeed dropped precipitously. Images such as that shown in Figure 18.6 taken annually reveal that the depth and size of the ozone hole has begun to slowly decline. Nevertheless, because CFCs are unreactive and because they diffuse so slowly into the stratosphere, scientists estimate that it will take many decades for ozone concentrations in the stratosphere to return to pre-1980 levels. What substances have replaced CFCs? At this time, the main alternatives are hydrofluorocarbons (HFCs), compounds in which C—H bonds replace the C—Cl bonds of CFCs. One such compound in current use is CH_2FCF_3 , known as HFC-134a. While the HFCs are a big improvement over the CFCs because they contain no C—Cl bonds, it turns out that they are potent greenhouse warming gases, with which we will deal shortly.

There are no naturally occurring CFCs, but some natural sources contribute chlorine and bromine to the atmosphere, and, just like halogens from CFCs, these naturally occurring Cl and Br atoms can participate in ozone-depleting reactions. The principal natural sources are bromomethane and chloromethane, which are emitted from the oceans. It is estimated that these molecules contribute less than a third of 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.

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 18.2. The amount of these compounds released into the atmosphere worldwide from natural sources is about 24×10^{12} g per year, less than the amount from human activities, about 80×10^{12} g per year (principally related to combustion of fuels).

Sulfur compounds, chiefly sulfur dioxide, SO_2 , 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 (where by *typical* we mean one that is not 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_2 is regarded as the most serious health hazard among the pollutants shown, especially for people with respiratory difficulties.

Combustion of coal and oil accounts for about two thirds of the anthropogenic SO_2 released annually worldwide. The majority of this amount is from coal-burning electrical power plants, which generate about 50% of our electricity. The extent to which SO_2 emissions are a problem when coal is burned depends on the amount of sulfur in the coal. Because of concern about SO_2 pollution, low-sulfur coal is in greater demand and is thus more expensive.

Sulfur dioxide is harmful to both human health and property; furthermore, atmospheric SO_2 can be oxidized to SO_3 by several pathways (such as reaction with O_2 or O_3). When SO_3 dissolves in water, it produces sulfuric acid:

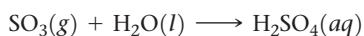
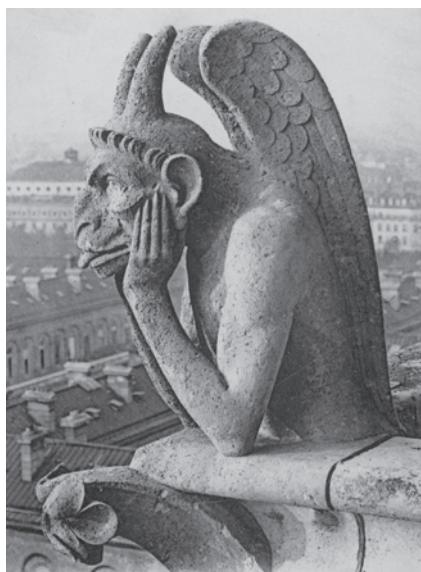


TABLE 18.4 Median Concentrations of Atmospheric Pollutants in a Typical Urban Atmosphere

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



◀ **Figure 18.7** Damage from acid rain. The right photograph, recently taken, shows how the statue has lost detail in its carvings.

Many of the environmental effects ascribed to SO_2 are actually due to H_2SO_4 .

The presence of SO_2 in the atmosphere and the sulfuric acid it produces result in the phenomenon of **acid rain**. (Nitrogen oxides, which form nitric acid, are also major contributors to acid rain.) Uncontaminated rainwater generally has a pH value of about 5.6. The primary source of this natural acidity is CO_2 , which reacts with water to form carbonic acid, H_2CO_3 . Acid rain typically has a pH value of about 4. This shift toward greater 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 in the lakes and surrounding forests.

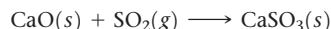
The pH of most natural waters containing living organisms is between 6.5 and 8.5. At pH levels below 4.0, all vertebrates, most invertebrates, and many microorganisms are destroyed. The lakes most susceptible to damage are those with low concentrations of basic ions, such as HCO_3^- , that would act as a buffer to minimize changes in pH.

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 CaCO_3 , are readily attacked by acid rain (Figure 18.7). Billions of dollars each year are lost because of corrosion due to SO_2 pollution.

Although difficult and expensive, several methods to reduce the quantity of SO_2 released into the environment have been developed. Powdered limestone (CaCO_3), for example, can be injected into the furnace of a power plant, where it decomposes into lime (CaO) and carbon dioxide:



The CaO then reacts with SO_2 to form calcium sulfite:



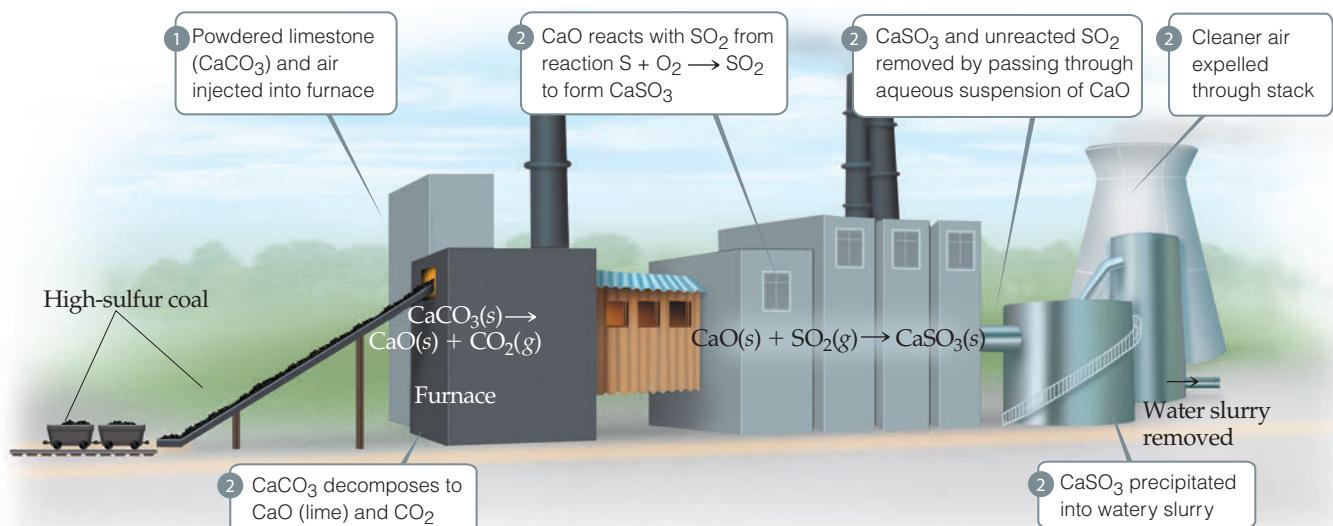
The solid particles of CaSO_3 , as well as much of the unreacted SO_2 , can be removed from the furnace gas by passing it through an aqueous suspension of CaO (Figure 18.8). Not all the SO_2 is removed, however, and given the enormous quantities of coal and oil burned worldwide, pollution by SO_2 will probably remain a problem for some time.

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 the pollution condition that occurs in certain urban environments when weather conditions produce a relatively stagnant air mass. Smog is more accurately described as **photochemical smog** because photochemical processes play a major role in its formation (Figure 18.9).

**Go Figure**

What is the major solid product resulting from removal of SO₂ from furnace gas?



▲ Figure 18.8 One method for removing SO₂ from combusted fuel.



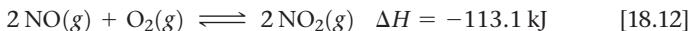
▲ Figure 18.9 Photochemical smog is produced largely by the action of sunlight on vehicle exhaust gases, as illustrated in this photo of Beijing, China.

Nitric oxide, NO, forms in small quantities in the cylinders of internal combustion engines in the reaction



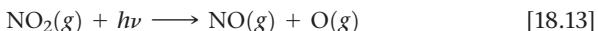
As noted in the Chemistry Put to Work box in Section 15.5, the equilibrium constant for this reaction increases from about 10^{-15} at 300 K to about 0.05 at 2400 K (approximate temperature in the cylinder of an engine during combustion). Thus, the reaction is more favorable at higher temperatures.

In air, nitric oxide is rapidly oxidized to nitrogen dioxide:

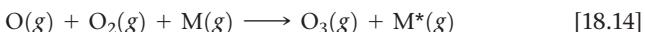


The equilibrium constant for this reaction decreases from about 10^{12} at 300 K to about 10^{-5} at 2400 K.

The photodissociation of NO₂ initiates the reactions associated with photochemical smog. Dissociation of NO₂ requires 304 kJ/mol, which corresponds to a photon wavelength of 393 nm. In sunlight, therefore, NO₂ dissociates to NO and O:



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



Although it is essential to screen out harmful UV radiation 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 its presence is vital.

In addition to nitrogen oxides and carbon monoxide, a car engine also emits unburned *hydrocarbons* as pollutants. These organic compounds are the principal components of petrol and of many compounds we use as fuel (propane, C₃H₈, and butane, C₄H₁₀; for example), but are major ingredients of smog. 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 ingredients essential to its formation be removed from car exhaust. Catalytic converters reduce the levels of NO_x and hydrocarbons, two of the major ingredients of smog. (See the Chemistry Put to Work: Catalytic Converters in Section 14.7.)

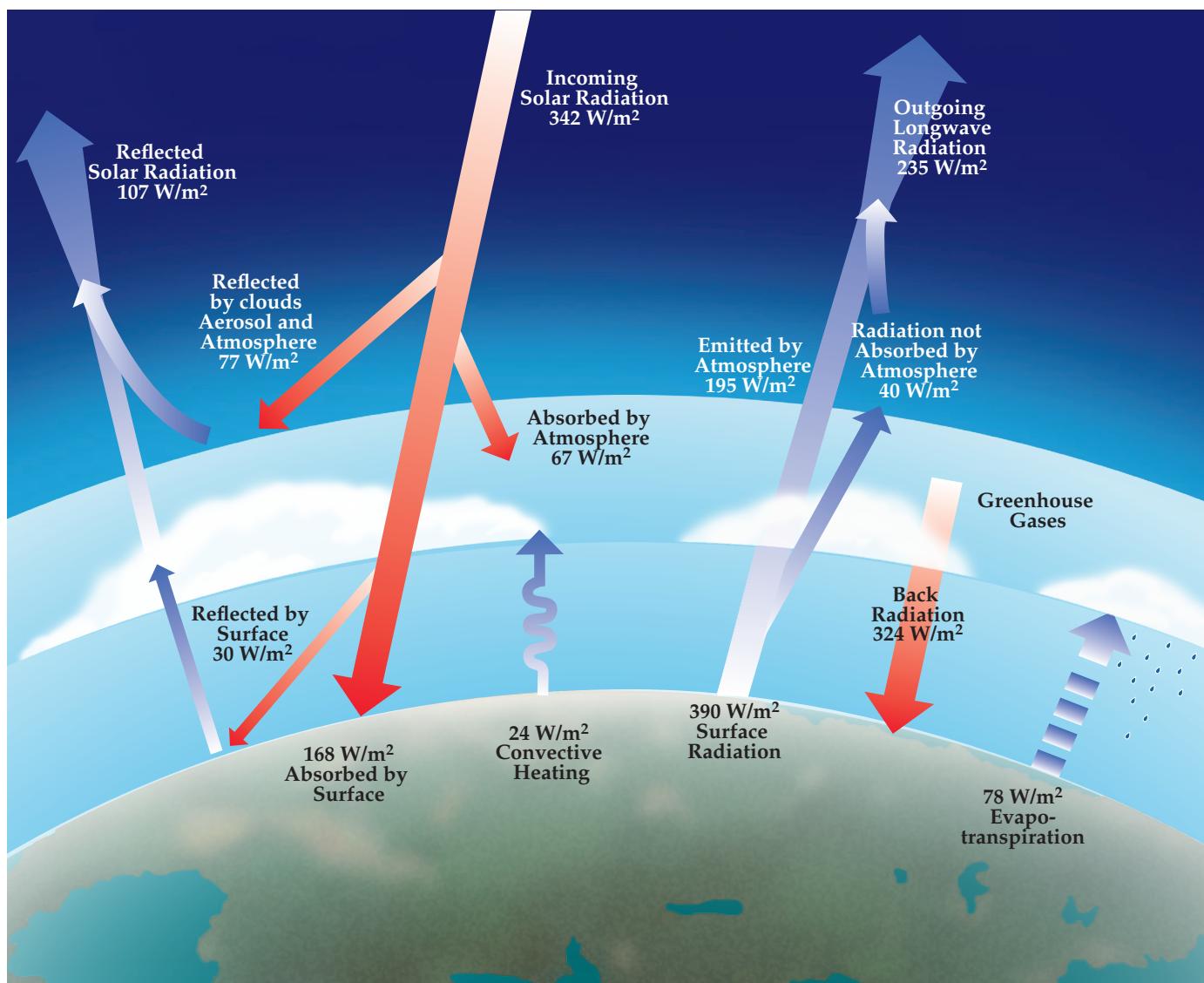
Greenhouse Gases: Water Vapor, Carbon Dioxide, and Climate

In addition to screening out harmful short-wavelength radiation, the atmosphere is essential in maintaining a reasonably uniform and moderate temperature on Earth's surface. Earth is in overall thermal balance with its surroundings. This means that the planet radiates energy into space at a rate equal to the rate at which it absorbs energy from the Sun. **Figure 18.10** shows the flow of energy into and out of Earth, and **Figure 18.11** shows the fraction of infrared radiation leaving the surface that is absorbed

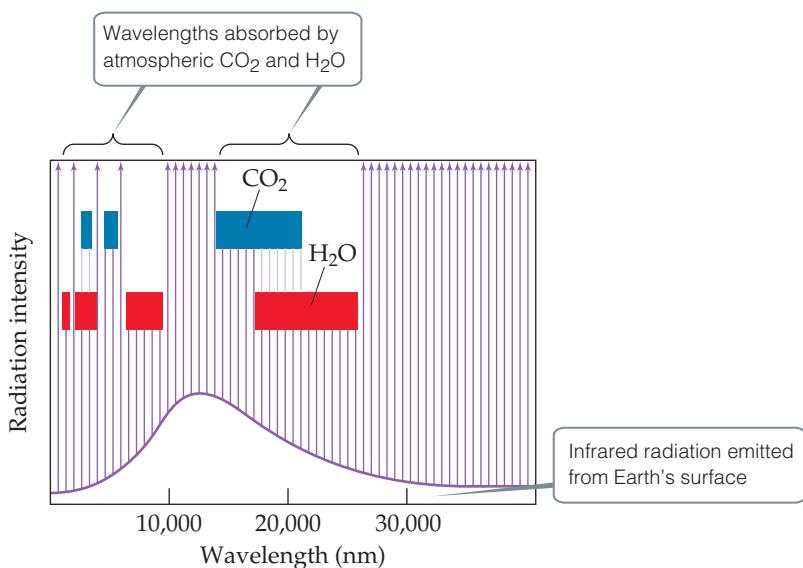


Go Figure

What is the total amount of energy absorbed by the surface? What fraction of that energy is emitted upward as infrared radiation?



▲ **Figure 18.10** Earth's thermal balance. The amount of radiation reaching the surface of the planet is equal to the amount radiated back into space.



▲ Figure 18.11 Portions of the infrared radiation emitted by Earth's surface that are absorbed by atmospheric CO₂ and H₂O.

by atmospheric water vapor and carbon dioxide. In absorbing this radiation, these two atmospheric gases help maintain a livable uniform temperature at the surface by holding in, as it were, the infrared radiation, which we feel as heat.

The influence of H₂O, CO₂, and certain other atmospheric gases on Earth's temperature is called the *greenhouse effect* because in trapping infrared radiation these gases act much like the glass of a greenhouse. The gases themselves 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 is generally highest near Earth's surface and drops off with increasing 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 low, it may be extremely hot during the day but very cold at night. In the absence of a 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 carbon dioxide levels in the atmosphere. To get a sense of the amount of CO₂ 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, C₄H₁₀. Combustion of 1.00 g of C₄H₁₀ produces 3.03 g of CO₂. Combustion of fossil fuels releases about 2.2×10^{16} g of CO₂ into the atmosphere annually, with the largest quantity coming from transportation vehicles.

Sample Exercise 18.3

Estimating the Quantity of CO₂ Released from Combustion of Gasoline

What mass of carbon dioxide is produced when 5.0 liters of petrol is combusted? The approximate density and composition of petrol are 0.70 g/mL and C₈H₁₈, respectively.

SOLUTION

Analyze We are asked to calculate the mass of CO₂ produced when 5.0 liters of octane (C₈H₁₈) reacts with oxygen to form carbon dioxide and water.

Solve

First, convert the volume from liters to mL.

Plan We first must determine the mass in grams of C₈H₁₈ in 5.0 liters of gasoline. We then write a balanced chemical equation for the combustion of C₈H₁₈ and use it to determine the theoretical yield of CO₂.

$$(5.0 \text{ liters}) \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) = 5.0 \times 10^3 \text{ mL}$$

Next, use the density of octane to calculate its mass in grams.

$$(5.0 \times 10^3 \text{ mL}) \left(\frac{0.70 \text{ g}}{\text{mL}} \right) = 3.5 \times 10^3 \text{ g}$$

To calculate the theoretical yield of carbon dioxide, we must write a balanced chemical equation for the combustion of C₈H₁₈ (octane):



Using the balanced equation and the mass of C₈H₁₈, we can calculate the theoretical yield of CO₂.

$$(3.5 \times 10^3 \text{ g C}_8\text{H}_{18}) \left(\frac{1 \text{ mol C}_8\text{H}_{18}}{114.2 \text{ g C}_8\text{H}_{18}} \right) \left(\frac{16 \text{ mol CO}_2}{2 \text{ mol C}_8\text{H}_{18}} \right) \left(\frac{44 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) \\ = 1.1 \times 10^4 \text{ g CO}_2$$

So we see that for every five liters of octane burned 11 kg of CO₂ are produced.

► Practice Exercise

A typical propane, C₃H₈, tank for an outdoor grill contains 5 kg of propane. What mass of CO₂

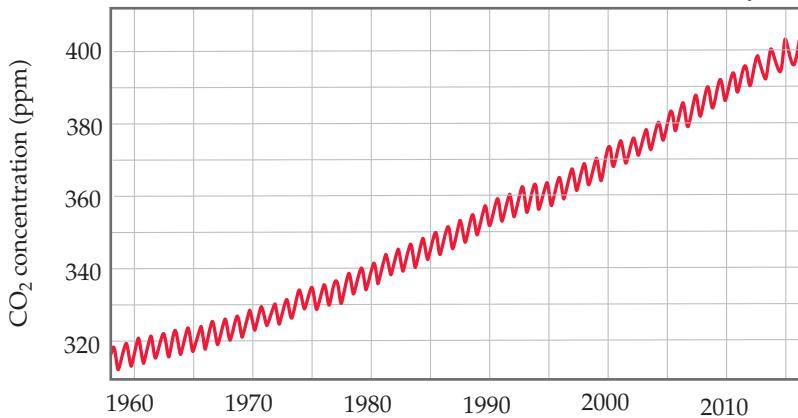
is produced by combusting the propane in such a tank?

Much CO₂ is absorbed into oceans or used by plants. Nevertheless, we are now generating CO₂ much faster than it is being absorbed or used. Analysis of air trapped in ice cores taken from Antarctica and Greenland makes it possible to determine the atmospheric levels of CO₂ during the past 160,000 years. These measurements reveal that the level of CO₂ 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 CO₂ has increased by about 30% to a current high of about 400 ppm (Figure 18.12). Climate scientists believe that the CO₂ level has not been this high since 3 to 5 million years ago.

**Go Figure**

What is the source of the steady increase in slope of this curve over time?

Carbon dioxide concentration at Mauna Loa Observatory



▲ Figure 18.12 Rising CO₂ levels. The sawtooth shape of the graph is due to regular seasonal variations in CO₂ concentration for each year.

The consensus among climate scientists is that the increase in atmospheric CO₂ is perturbing Earth's climate and is very likely playing a role in the observed increase in the average global air temperature of 0.3–0.6 °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, winds and ocean currents are affected in ways that cool some areas and warm others.

On the basis of present and expected future rates of fossil-fuel use, the atmospheric CO₂ 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 °C to 3 °C. Because so many factors go into determining climate, we cannot predict with certainty what changes will occur because of this warming. Clearly, however, atmospheric concentrations of CO₂ and other heat-trapping gases are rising as a result of human activity. The effects of these changes on the climate are already being felt, and if left unchecked they have the potential to substantially alter the climate of the planet.

The climate change threat posed by atmospheric CO₂ has sparked considerable research into ways of capturing the gas at its largest combustion sources and storing it under ground or under the seafloor. There is also much interest in developing new ways to use CO₂ as a chemical feedstock. However, the approximately 115 million tons of CO₂ used annually by the global chemical industry is but a small fraction of the approximately 24 billion tons of annual CO₂ emissions. The use of CO₂ as a raw material will probably never be great enough to significantly reduce its atmospheric concentration.

A CLOSER LOOK Other Greenhouse Gases

Although CO₂ receives most of the attention, other gases contribute to the greenhouse effect, including methane, CH₄, hydrofluorocarbons (HFCs), and chlorofluorocarbons (CFCs).

HFCs have replaced CFCs in a host of applications, including refrigerants and air-conditioner gases. Although they do not contribute to the depletion of the ozone layer, HFCs are nevertheless potent greenhouse gases. For example, one of the by-product molecules from production of HFCs that are used in commerce is HCF₃, which is estimated to have a global warming potential, gram for gram, more than 14,000 times that of CO₂. The total concentration of HFCs in the atmosphere has been 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. Studies of atmospheric gas trapped long ago in the Greenland and Antarctic ice sheets show that the atmospheric methane concentration has increased from preindustrial values 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 18.13). It also leaks into the atmosphere during natural-gas extraction and transport. 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 CO₂ is much longer-lived. This might seem a good thing, but there are indirect effects to consider. Methane is oxidized in the stratosphere, producing water vapor, a powerful greenhouse gas that



▲ **Figure 18.13** Methane production. Ruminant animals, such as cows and sheep, produce methane in their digestive systems.

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 O₃. It has been estimated that on a per-molecule level, the global warming potential of CH₄ is about 21 times that of CO₂. 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.

Related Exercises: 18.72, 18.74

Self-Assessment Exercises

- 18.10** What photochemical reaction involving nitrogen oxides initiates the formation of photochemical smog?
- $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$
 - $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$
 - $\text{NO}_2(g) + h\nu \longrightarrow \text{NO}(g) + \text{O}(g)$
- 18.11** What part of the electromagnetic spectrum is absorbed by water vapor in the atmosphere?
- Ultraviolet radiation
 - Visible radiation
 - Infrared radiation

Exercises

- 18.12** Which of the following reactions in the stratosphere cause an increase in temperature there?
- $\text{O}(g) + \text{O}_2(g) \longrightarrow \text{O}_3^*(g)$
 - $\text{O}_3^*(g) + \text{M}(g) \longrightarrow \text{O}_3(g) + \text{M}^*(g)$
 - $\text{O}_2(g) + h\nu \longrightarrow 2\text{O}(g)$
 - $\text{O}(g) + \text{N}_2(g) \longrightarrow \text{NO}(g) + \text{N}(g)$
 - All of these
- 18.13** (a) What is the difference between chlorofluorocarbons and hydrofluorocarbons? (b) Why are hydrofluorocarbons potentially less harmful to the ozone layer than CFCs?
- 18.14** (a) When chlorine atoms react with atmospheric ozone, what are the products of the reaction? (b) Based on average bond enthalpies, would you expect a photon capable of dissociating a C—Cl bond to have sufficient energy to dissociate a C—Br bond? (c) Would you expect the substance CFBr_3 to accelerate depletion of the ozone layer?
- 18.15** Why is rainwater naturally acidic, even in the absence of polluting gases such as SO_2 ?
- 18.16** Copper exposed to air and water may be oxidized. The green oxidized product is referred to as “patina”. (a) Write a balanced chemical equation to show the reaction of copper
- to copper (II) ions with oxygen and protons from acid rain. (b) Would you expect some kind of “patina” on a silver surface? Explain.
- 18.17** An important reaction in the formation of photochemical smog is the photodissociation of 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.
- 18.18** The atmosphere of Mars is 96% CO_2 , with a pressure of approximately 0.6 kPa at the surface. Based on measurements taken over a period of several years by the Rover Environmental Monitoring Station (REMS), the average daytime temperature at the REMS location on Mars is -5.7°C , while the average nighttime temperature is -79°C . This daily variation in temperature is much larger than what we experience on Earth. What factor plays the largest role in this wide temperature variation, the composition or the density of the atmosphere?

18.10 (c) 18.11 (c)

Answers to Self-Assessment Exercises

18.3 | Earth's Water



Earth is called The Blue Planet because of the abundance of water on its surface.

Indeed, water 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. 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_2O itself is a reactant. Recall, for example, that H_2O can participate in acid-base reactions as either a proton donor or a proton acceptor. All these properties play a role in our environment.

By the end of this section you should be able to

- Appreciate the complexity of the global water cycle

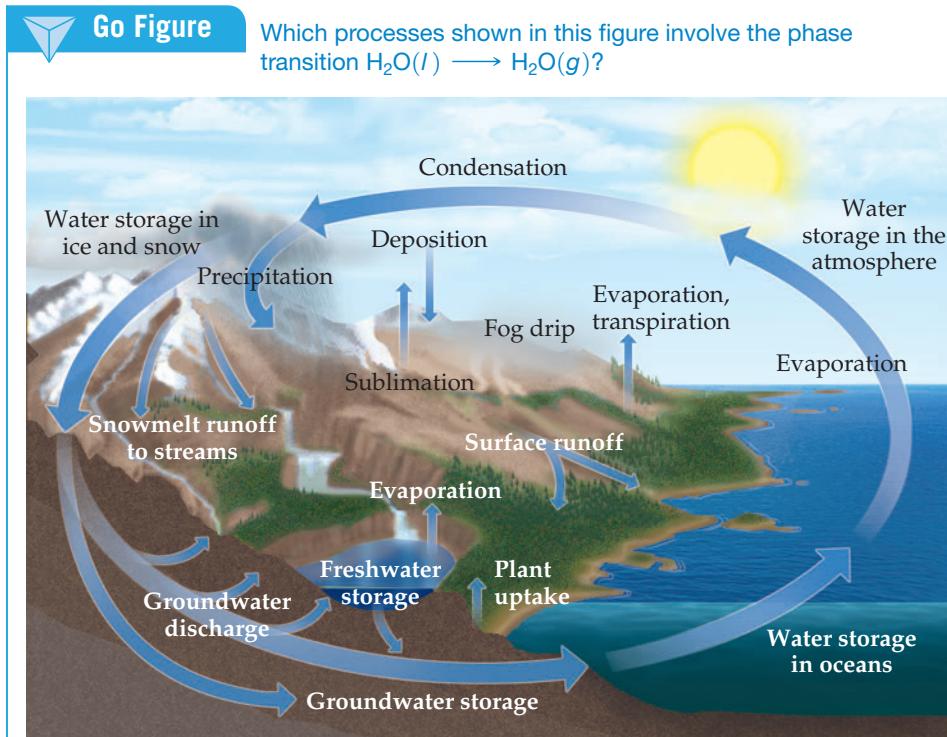
The Global Water Cycle

All the water on Earth is connected in a global water cycle (Figure 18.14). Most of the processes depicted here rely on the phase changes of water. For instance, warmed by the Sun, liquid water in the oceans evaporates into the atmosphere as water vapor and condenses into liquid water droplets that we see as clouds. Water droplets in the clouds can crystallize to ice, which can precipitate as hail or snow. Once on the ground, the hail or snow melts to liquid water, which soaks into the ground. If conditions are right, it is also possible for ice on the ground to sublime to water vapor in the atmosphere. Because the processes occurring on the surface (evaporation, sublimation) are endothermic and those occurring in the atmosphere (condensation, crystallization) are exothermic they act to transfer heat absorbed by the surface into the atmosphere.

Salt Water: Earth's Oceans and Seas

The vast layer of salty water that covers so much of the planet is in actuality one large connected body 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, having a volume of $1.35 \times 10^9 \text{ km}^3$ and containing 97.2% of all the water on Earth. Of the remaining 2.8%, 2.1% is in the form of ice caps and glaciers. All the freshwater—in lakes, in rivers, and in the ground—amounts to only 0.6%.



▲ Figure 18.14 The global water cycle.

TABLE 18.5 Ionic Constituents of Seawater Present in Concentrations Greater than 0.001 g/kg (1 ppm)

Ionic Constituent	Salinity	Concentration (<i>M</i>)
Chloride, Cl ⁻	19.35	0.55
Sodium, Na ⁺	10.76	0.47
Sulfate, SO ₄ ²⁻	2.71	0.028
Magnesium, Mg ²⁺	1.29	0.054
Calcium, Ca ²⁺	0.412	0.010
Potassium, K ⁺	0.40	0.010
Carbon dioxide*	0.106	2.3 × 10 ⁻³
Bromide, Br ⁻	0.067	8.3 × 10 ⁻⁴
Boric acid, H ₃ BO ₃	0.027	4.3 × 10 ⁻⁴
Strontium, Sr ²⁺	0.0079	9.1 × 10 ⁻⁵
Fluoride, F ⁻	0.0013	7.0 × 10 ⁻⁵

*CO₂ is present in seawater as HCO₃⁻ and CO₃²⁻.

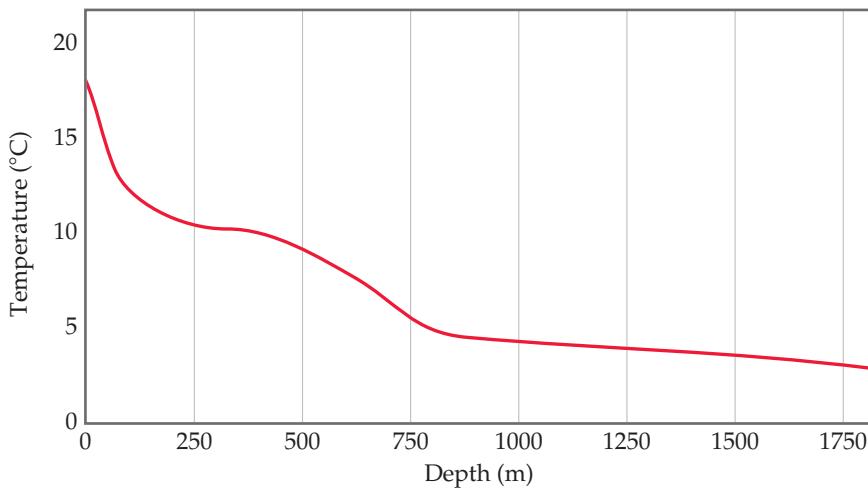
Seawater is often referred to as saline water. The **salinity** of seawater is the mass in grams of dry salts present in 1 kg of seawater. In the world ocean, salinity averages about 35. To put it another way, seawater contains about 3.5% dissolved salts by mass. The list of elements present in seawater is very long. Most, however, are present only in very low concentrations. **Table 18.5** lists the 11 ionic species most abundant in seawater.

Seawater temperature varies as a function of depth (**Figure 18.15**), as does salinity and density. Sunlight penetrates well only 200 m into the water; the region between 200 m and 1000 m deep is the “twilight zone,” where visible light is faint. Below 1000 m, 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.



Go Figure

Based on the temperature variation here would you expect the density of seawater to increase or decrease as the depth increases?



▲ **Figure 18.15** Typical average temperature of mid-latitude seawater as a function of depth.

The sea is so vast that if the concentration of a substance in seawater is 1 part per billion (1×10^{-6} g/kg of water), there is 1×10^{12} kg of the substance in the world ocean. Nevertheless, because of high extracting costs, only three substances are obtained from seawater in commercially important amounts: sodium chloride, bromine (from bromide salts), and magnesium (from its salts).

Absorption of CO_2 by the ocean plays a large role in global climate. Because carbon dioxide and water form carbonic acid, the H_2CO_3 concentration in the ocean increases as the water absorbs atmospheric CO_2 . Most of the carbon in the ocean, however, is in the form of HCO_3^- and CO_3^{2-} ions, which form a buffer system that maintains the ocean's pH between 8.0 and 8.3. The pH of the ocean is predicted to decrease as the concentration of CO_2 in the atmosphere increases, as discussed in the "Chemistry and Life" box on ocean acidification on page 890.

Freshwater and Groundwater

Freshwater is the term used to denote natural waters that have low concentrations (less than 500 ppm) of dissolved salts and solids. Freshwater includes the waters of lakes, rivers, ponds, and streams.

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 18.14).

As water runs off the land on its way to the oceans, it dissolves a variety of cations (mainly Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Fe^{2+}), anions (mainly Cl^- , SO_4^{2-} , and HCO_3^-), and gases (principally O_2 , N_2 , and 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, ever-increasing amounts of money and resources must be spent to guarantee a supply of freshwater.

Approximately 20% of the world's freshwater is under the soil, in the form of *groundwater*. Groundwater resides in *aquifers*, which are layers of porous rock that hold water. The water in aquifers can be very pure, and accessible for human consumption if near the surface (Figure 18.16). Dense underground formations that do not allow water to readily penetrate can hold groundwater for years or even millennia. When their water is removed by drilling and pumping, such aquifers are slow to recharge via the diffusion of surface water.

The nature of the rock that contains the groundwater has a large influence on the water's chemical composition. If minerals in the rock are water soluble to some extent, ions can leach out of the rock and remain dissolved in the groundwater. Arsenic in the form of HAsO_4^{2-} , H_2AsO_4^- , H_3AsO_4 , and HAsO_3 is found in many groundwater sources across the world, most infamously in Bangladesh, at concentrations poisonous to humans.

Self-Assessment Exercise

- 18.19** Consider the phase diagram for water shown in Figure 11.28 (page 544). In what pressure range and in what temperature range must H_2O exist in order for $\text{H}_2\text{O}(s)$ to sublime to $\text{H}_2\text{O}(g)$?

- (a) $T > 0^\circ\text{C}$ and $P > 0.6 \text{ kPa}$
- (b) $T < 0^\circ\text{C}$ and $P > 0.6 \text{ kPa}$
- (c) $T > 0^\circ\text{C}$ and $P < 0.6 \text{ kPa}$
- (d) $T < 0^\circ\text{C}$ and $P < 0.6 \text{ kPa}$

Exercises

- 18.20** Sulfur is present in seawater to the extent of 0.09 % by mass. Assuming that the sulfur is present as sulfate, SO_4^{2-} , calculate the corresponding molar concentration of SO_4^{2-} in seawater.

- 18.21** The enthalpy of fusion of water is 6.01 kJ/mol. Sunlight striking Earth's surface supplies 168 W per square meter (1 W = 1 watt = 1 J/s). (a) Assuming that melting of ice is due only to energy input from the Sun, calculate how

many grams of ice could be melted from a 1.00 square meter patch of ice over a 12 h day. (b) The specific heat capacity of ice is 2.032 J/g °C. If the initial temperature of a 1.00 square meter patch of ice is –5.0 °C, what is its final temperature after being in sunlight for 12 h, assuming no phase changes and assuming that sunlight penetrates uniformly to a depth of 1.00 cm?

- 18.22** Platinum is found in seawater at very low levels, about 0.23 parts in 10^{12} by mass. How much platinum can be found in the entire ocean (1.3×10^{21} L)? Assume the density of seawater is 1.03 g/mL.

18.19 (d)

Answers to Self-Assessment Exercises



18.4 | Human Activities and Water Quality



At least 8 million tons of plastic end up in the oceans every year, resulting in entanglement and ingestion by marine life and sea birds. At the current rate of pollution, there will be more plastic, by weight, than fish in the oceans by 2050.

All life on Earth depends on the availability of suitable water. Many human activities entail waste disposal into natural waters without any treatment. These practices result in contaminated water that is detrimental to both plant and animal aquatic life.

By the end of this section, you should be able to

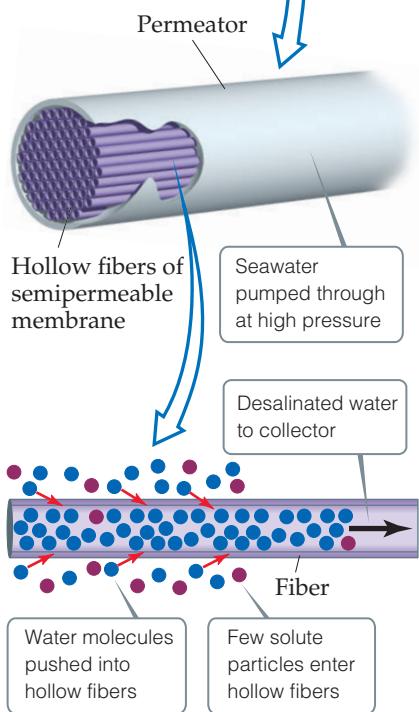
- Understand some main factors that result in the deterioration of water quality and how water can be treated to make it fit for human consumption.

Dissolved Oxygen and Water Quality

The amount of O₂ dissolved in water is an important indicator of water quality. Water fully saturated with air at 101.3 kPa and 20 °C contains about 9 ppm of O₂. Oxygen is necessary for fish and most other aquatic life. Cold-water fish require water containing at



▲ Figure 18.17 Eutrophication. This rapid accumulation of dead and decaying plant matter in a body of water uses up the water's oxygen supply, making the water unsuitable for aquatic animals.



▲ Figure 18.18 Reverse osmosis.

least 5 ppm of dissolved oxygen for survival. Aerobic bacteria consume dissolved oxygen to oxidize organic materials for energy. The organic material the bacteria are able to oxidize is said to be **biodegradable**.

Excessive quantities of biodegradable organic materials in water are detrimental because they remove the oxygen necessary to sustain aquatic 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 liquid waste from meatpacking plants.

In the presence of oxygen, the carbon, hydrogen, nitrogen, sulfur, and phosphorus in biodegradable material end up mainly as CO_2 , HCO_3^- , H_2O , NO_3^- , 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 CH_4 , NH_3 , H_2S , 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. What is more significant, however, is that as plant growth becomes excessive, the amount of dead and decaying plant matter increases rapidly, a process called *eutrophication* (Figure 18.17). The processes by which plants decay consumes O_2 , and without sufficient oxygen, the water cannot sustain 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 contain both nitrogen and phosphorus), and runoff from livestock areas (animal wastes contain nitrogen).

Water Purification: 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 many countries, the salt content of municipal water supplies is restricted by health codes to no more than about 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. 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. Distillation is also an energy-intensive process.

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. 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 reverse osmosis occurs, solvent passes from the more concentrated into the more dilute solution. In a modern reverse-osmosis facility, hollow fibers are used as the semipermeable membrane (Figure 18.18). Saline water (water containing significant salts) is introduced under pressure into the fibers, and desalinated water is recovered.

The world's largest desalination plant, in Jubail, Saudi Arabia, provides 50% of that country's drinking water by using reverse osmosis to desalinate seawater from the Persian Gulf.

Water Purification: Municipal Treatment

The water needed for domestic, agricultural, and industrial use is taken either from lakes, rivers, and underground sources or from reservoirs. Much of the water that finds its way into municipal water systems is “used” water, meaning it has already passed through one or more sewage systems or industrial plants. Consequently, this water must be treated before it is distributed.

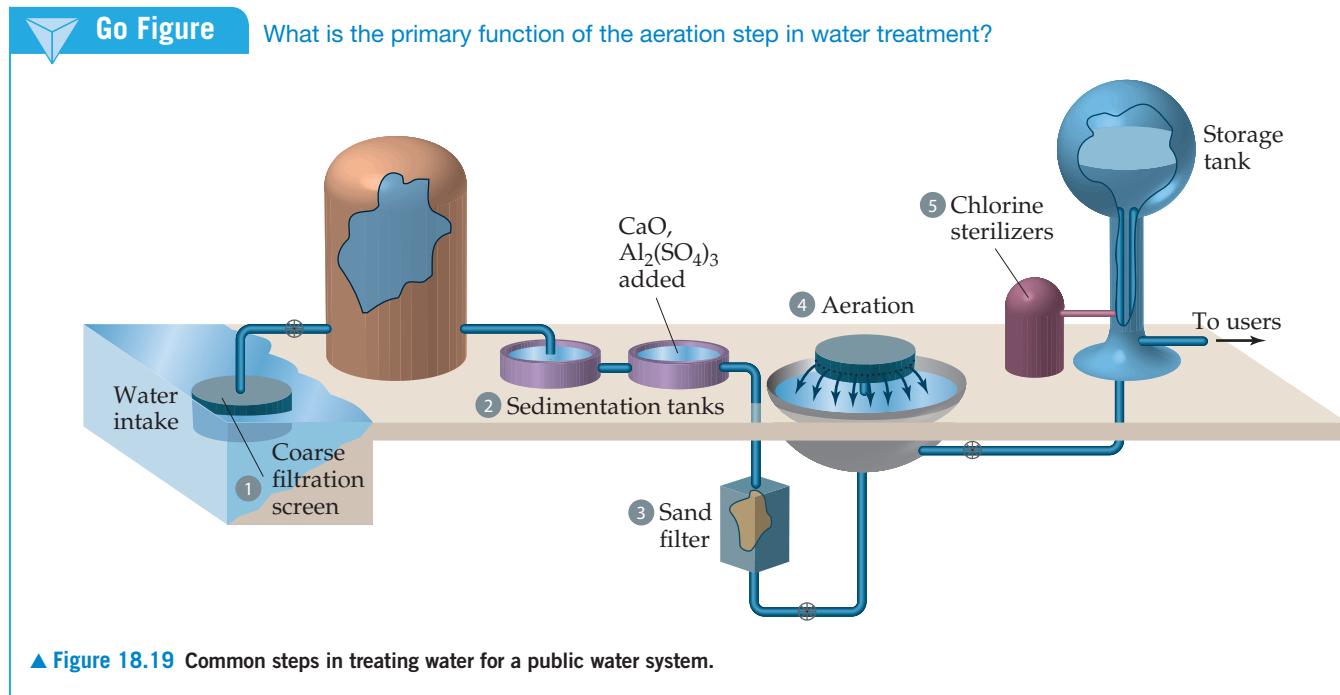
Municipal water treatment usually involves five steps (Figure 18.19).

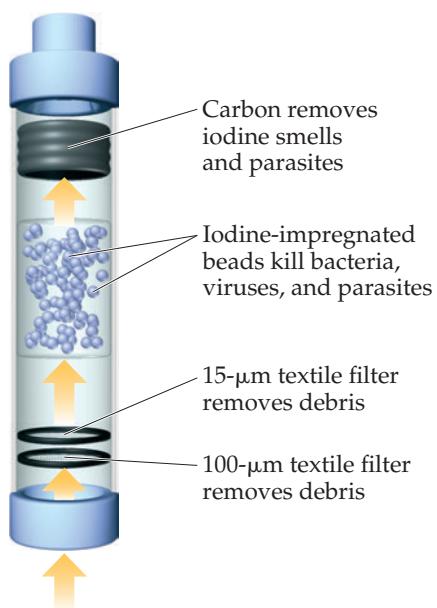
1. After coarse filtration through a screen, the water is allowed to stand in large sedimentation tanks where sand and other minute particles settle out. To aid in removing very small particles, the water may first be made slightly basic with CaO.
2. Then $\text{Al}_2(\text{SO}_4)_3$ is added and reacts with 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.
3. The water is then filtered through a sand bed.
4. Following filtration, the water may be sprayed into the air (aeration) to hasten oxidation of dissolved inorganic ions of iron and manganese, reduce concentrations of any H_2S or NH_3 that may be present, and reduce bacterial concentrations.
5. The final step normally involves treating the water with a chemical agent to ensure the destruction of bacteria. Ozone is more effective, but chlorine is less expensive. Liquefied Cl_2 is dispensed from 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 not due to Cl_2 itself but to hypochlorous acid, which forms when chlorine reacts with water:



It is estimated that about 800 million people worldwide lack access to clean water. According to the United Nations, 95% of the world's cities still dump raw sewage into





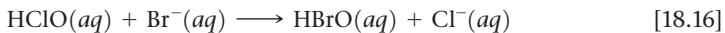
▲ **Figure 18.20** A LifeStraw purifies water as it is drunk.

their water supplies. Thus, it should come as no surprise that 80% of all the health maladies in developing countries can be traced to waterborne 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 filter with a mesh opening of 100 μm followed by a second textile filter with a mesh opening of 15 μm. 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 filters or killed by the iodine. At present the Lifestraw is too costly to permit widespread use in underdeveloped countries, but there is hope that its cost can be greatly reduced. They have been used in acute situations where a natural disaster such as an earthquake or flooding has resulted in the temporary contamination of the drinking water supply.

Water disinfection is one of the greatest public health innovations in human history. It has dramatically decreased the incidences of waterborne bacterial diseases such as cholera and typhus. However, this great benefit comes at a price. In 1974 scientists in Europe and the United States discovered that chlorination of water produces a group of by-products previously undetected. These by-products are called *trihalomethanes* (THMs) because all have a single carbon atom and three halogen atoms: CHCl₃, CHCl₂Br, CHClBr₂, and CHBr₃. These and many other chlorine- and bromine-containing organic substances are produced by the reaction of dissolved chlorine with the 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 the oxidizing agent HClO as shown in Equation 18.15.

The HClO in turn reacts with organic substances to form THMs. Bromine enters the reaction sequence through the reaction of HClO with dissolved bromide ion:



Then both HBrO(aq) and HClO(aq) can halogenate organic substances to form the THMs.

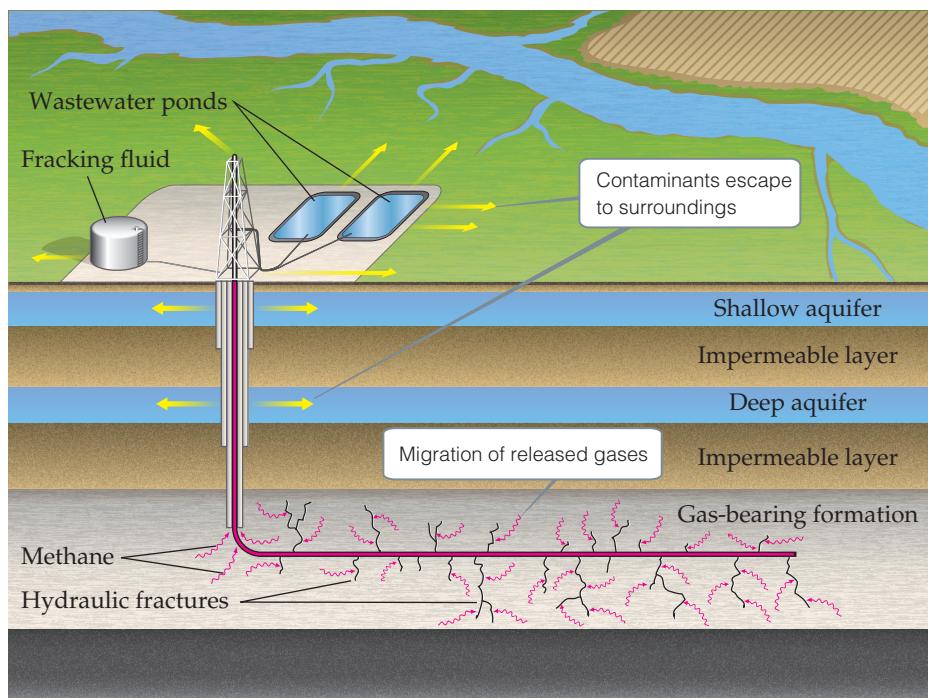
A CLOSER LOOK Fracking and Water Quality

In recent years **fracking**, short for *hydraulic fracturing*, has become widely used to greatly increase the availability of petroleum reserves. In fracking, a large volume of water, typically seven million liters or more, mixed with various additives, is injected at high pressure into wellbores extended horizontally into rock formations (Figure 18.21). The water is laden with sand, ceramic materials, and other additives, including gels, foams, and compressed gases, that serve to increase the yield in the process. The high-pressure fluid finds its way into tiny faults in geological formations, releasing petroleum and natural gas. Fracking has greatly increased petroleum reserves, particularly of natural gas, in many parts of the world.

Unfortunately, the potential for environmental damage from fracking is significant. The large volume of fracking fluid required to create a well must be returned to the surface. Without purification the fluid is rendered unfit for other uses, and becomes a large-scale environmental problem. Often the waste water is allowed to sit in open waste water pits. Because fracturing of rock formations

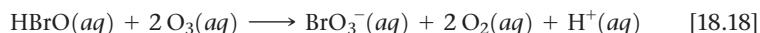
increases the pathways for flows of petroleum and various gases, bodies of underground water that have been serving as municipal water supplies or wells for individual homes in some locales have become contaminated with petroleum, hydrogen sulfide and other toxic substances. The escape of a variety of gases, including methane and other hydrocarbons, from the wellheads contributes to air pollution. In a study published in 2013, methane emissions to the atmosphere during hydraulic fracturing operations in Utah, USA were estimated to be in the range of 6–12% of the amount of methane produced. As related in the Closer Look box on page 880, methane is a potent greenhouse gas.

The many environmental issues surrounding the practice of fracking have generated widespread concern and adverse public reaction. Fracking represents yet one more instance of the conflict between those who advocate the availability of low cost energy and those who are more focused on sustaining long term the quality of the environment.



▲ **Figure 18.21** A schematic of a well site employing fracking. The yellow arrows indicate the avenues through which contaminants enter the environment.

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 have placed concentration limits of $80 \mu\text{g/L}$ (80 ppb) on the total quantity of THMs in drinking water. The goal is to reduce the levels of THMs and other disinfection by-products in the drinking water supply while preserving the antibacterial effectiveness of the water treatment. In some cases, lowering the concentration of chlorine may provide adequate disinfection while reducing the concentrations of THMs formed. Alternative oxidizing agents, such as ozone or chlorine dioxide, produce less of the halogenated substances but have their own disadvantages. For example, each is capable of oxidizing dissolved bromide, as shown here for ozone:



Bromate ion, BrO_3^- , has been shown to cause cancer in animal tests.

At present, there seem to be no completely satisfactory alternatives to chlorination or ozonation, and we are faced with a consideration of benefit versus risk. In this case, the risks of cancer from THMs and related substances in municipal water are very low relative 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 and thus the risk of THMs is lowered. Once THMs form, 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.

- Understand some main factors that result in the deterioration of water quality and how water can be treated to make it fit for human consumption.

CHEMISTRY AND LIFE**Ocean Acidification**

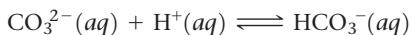
Seawater is a weakly basic solution, with pH values typically between 8.0 and 8.3. This pH range is maintained through a carbonic acid buffer system similar to the one in blood (see Equation 17.10). Because the pH of seawater is higher than that of blood (7.35–7.45), the second dissociation of carbonic acid cannot be neglected and CO_3^{2-} becomes an important aqueous species.

The availability of carbonate ions plays an important role in shell formation for a number of marine organisms, including stony corals (**Figure 18.22**). These organisms, which are referred to as marine *calcifiers* and play an important role in the food chains of nearly all oceanic ecosystems, depend on dissolved Ca^{2+} and CO_3^{2-} ions to form their shells and exoskeletons. The relatively low solubility-product constant of CaCO_3 ,



and the fact that the ocean contains saturated concentrations of Ca^{2+} and CO_3^{2-} mean that CaCO_3 is usually quite stable once formed. In fact, calcium carbonate skeletons of creatures that died millions of years ago are not uncommon in the fossil record.

The concentration of dissolved CO_2 in the ocean is sensitive to changes in atmospheric CO_2 levels. As discussed in Section 18.2, the atmospheric CO_2 concentration has risen by approximately 30% over the past three centuries to the present level of 400 ppm. Human activity has played a prominent role in this increase. Scientists estimate that one-third to one-half of the CO_2 emissions resulting from human activity have been absorbed by Earth's oceans. While this absorption helps mitigate the greenhouse gas effects of CO_2 , the extra CO_2 in the ocean produces carbonic acid, which lowers the pH. Because CO_3^{2-} is the conjugate base of the weak acid HCO_3^- , the carbonate ion readily combines with the hydrogen ion:



This consumption of carbonate ion shifts the CaCO_3 dissolution equilibrium to the right, increasing the solubility of CaCO_3 , which can lead to partial dissolution of calcium carbonate shells and exoskeletons. If the amount of atmospheric CO_2 continues to increase at the present rate, scientists estimate that seawater pH will fall to 7.9 sometime over the next 50 years. While this change might sound small, it has dramatic ramifications for oceanic ecosystems.

Related Exercises: 18.39, 18.42, 18.78



▲ Figure 18.22 Marine calcifiers. Many sea-dwelling organisms use CaCO_3 for their shells and exoskeletons. Examples include stony coral, crustaceans, some phytoplankton, and echinoderms, such as sea urchins and starfish.

Self-Assessment Exercise

- 18.23** Which two elements are largely responsible for fresh water eutrophication?

- (a) S and P
- (b) N and P
- (c) C and S

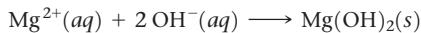
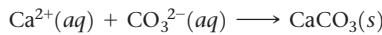
Exercises

- 18.24** Assume that a portable reverse-osmosis apparatus operates on seawater, whose concentrations of constituent ions are listed in Table 18.5, 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.)

- 18.25** (a) Explain why the concentration of dissolved oxygen in freshwater is an important indicator of the quality of the water. (b) Find graphical data in the text that show variations of gas solubility with temperature, and estimate to two significant figures the percent solubility of O_2 in water at 30 °C as compared with 20 °C. How do these data relate to the quality of natural waters?

- 18.26** Sewage causes removal of oxygen from the fresh water into which the sewage is discharged. For a town with a population of 100,000 people, this effluent causes a daily oxygen depletion of 50.0 g per person. How many liters of water at 8 ppm O_2 are 50% depleted of oxygen in a day by the population of this town?

- 18.27** In the lime soda process once used in large scale municipal water softening, calcium hydroxide prepared from lime and sodium carbonate are added to precipitate Ca^{2+} as $\text{CaCO}_3(s)$ and Mg^{2+} as $\text{Mg}(\text{OH})_2(s)$:



How many moles of $\text{Ca}(\text{OH})_2$ and Na_2CO_3 should be added to soften (remove the Ca^{2+} and Mg^{2+}) 1000 L of water in which

$$[\text{Ca}^{2+}] = 3.5 \times 10^{-4} M$$

$$[\text{Mg}^{2+}] = 7.5 \times 10^{-4} M$$

- 18.28** (a) Suppose that tests of a municipal water system reveal the presence of bromate ion, BrO_3^- . What are the likely origins of this ion? (b) Is bromate ion an oxidizing or reducing agent?

18.23 (b)

Answers to Self-Assessment Exercises



18.5 | 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 surroundings. 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 be released to the environment, that our needs be 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.

By the end of this section, you should be able to

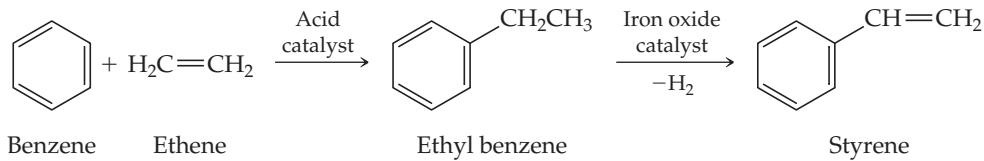
- The basic concepts underpinning green chemistry

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. Green chemistry rests on a set of 12 principles:

- 1. Prevention** It is better to prevent waste than to clean it up after it has been created.
- 2. Atom Economy** Methods to make chemical compounds should be designed to maximize the incorporation of all starting atoms into the final product.
- 3. Less Hazardous Chemical Syntheses** Wherever practical, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4. Design of Safer Chemicals** Chemical products should be designed to minimize toxicity and yet maintain their desired function.
- 5. Safer Solvents and Auxiliaries** Auxiliary substances (for example, solvents, separation agents, etc.) should be used as little as possible. Those that are used should be as nontoxic as possible.

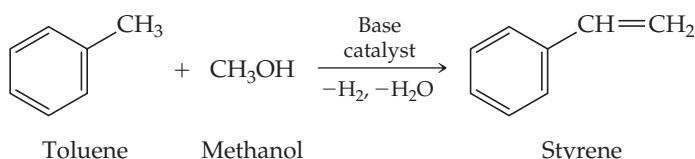
- 6. Design for Energy Efficiency** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, chemical reactions should be conducted at room temperature and pressure.
- 7. Use of Renewable Feedstocks** A raw material or feedstock should be renewable whenever technically and economically practical.
- 8. Reduction of Derivatives** Unnecessary derivatization (intermediate compound formation, temporary modification of physical/chemical processes) should be minimized or avoided if possible because such steps require additional reagents and can generate waste.
- 9. Catalysis** Catalytic reagents (as selective as possible) improve product yields within a given time and with a lower energy cost compared to noncatalytic processes and are, therefore, preferred to noncatalytic alternatives.
- 10. Design for Degradation** The end products of chemical processing should break down at the end of their useful lives into innocuous degradation products that do not persist in the environment.
- 11. Real-Time Analysis for Pollution Prevention** Analytical methods need to be developed that allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- 12. Inherently Safer Chemistry for Accident Prevention** Reagents and solvents used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.*

To illustrate how green chemistry works, consider the manufacture of styrene, an important building block for many polymers, including the expanded polystyrene packages used to pack eggs and restaurant takeout food. The global demand for styrene is more than 25 billion kg per year. For many years, styrene has been produced in a two-step process: Benzene and ethene react to form ethyl benzene, followed by the ethyl benzene being mixed with high-temperature steam and passed over an iron oxide catalyst to form styrene:



This process has several shortcomings. One is that both benzene, which is formed from crude oil, and ethene, formed from natural gas, are high-priced starting materials for a product that should be a low-priced commodity. Another is that benzene is a known carcinogen. In a recently developed 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:

*Adapted from P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*. New York: Oxford University Press 1998, p. 30. See also Mike Lancaster, *Green Chemistry: An Introductory Text*. Cambridge, UK: RSC Publishing, 2010, Second Edition, Chapter 1.



The one-step process saves money both because toluene and methanol are less expensive than benzene and ethene, and because the reaction requires less 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 is often key in discovering a new process.

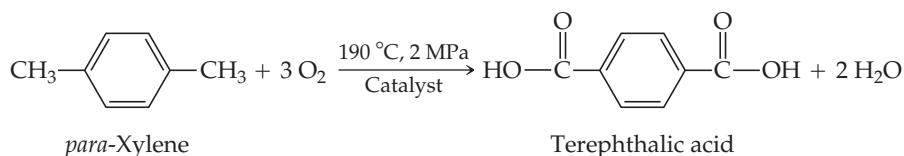
Let's consider some other examples in which green chemistry can operate to improve environmental quality.

Supercritical Solvents

A major area of concern in chemical processes is the use of volatile organic compounds as solvents. 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 represents a way to replace conventional solvents. Recall that a supercritical fluid is an unusual state of matter that has properties of both a gas and a liquid. 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 CO₂ in the production of polytetrafluoroethylene ($[CF_2CF_2]_n$, sold as Teflon®). Though CO₂ is a greenhouse gas, no new CO₂ need be manufactured for use as a supercritical fluid solvent.

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

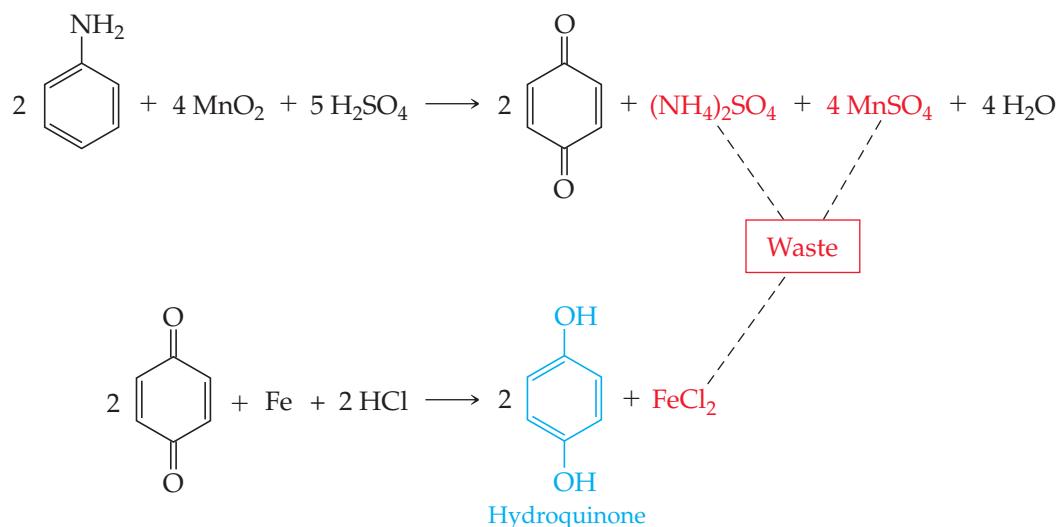


This commercial process requires pressurization and a relatively high temperature. Oxygen is the oxidizing agent, and acetic acid (CH_3COOH) is the solvent. An alternative route employs supercritical water as the solvent and hydrogen peroxide as the oxidant. This alternative process has several potential advantages, most particularly the elimination of acetic acid as solvent.

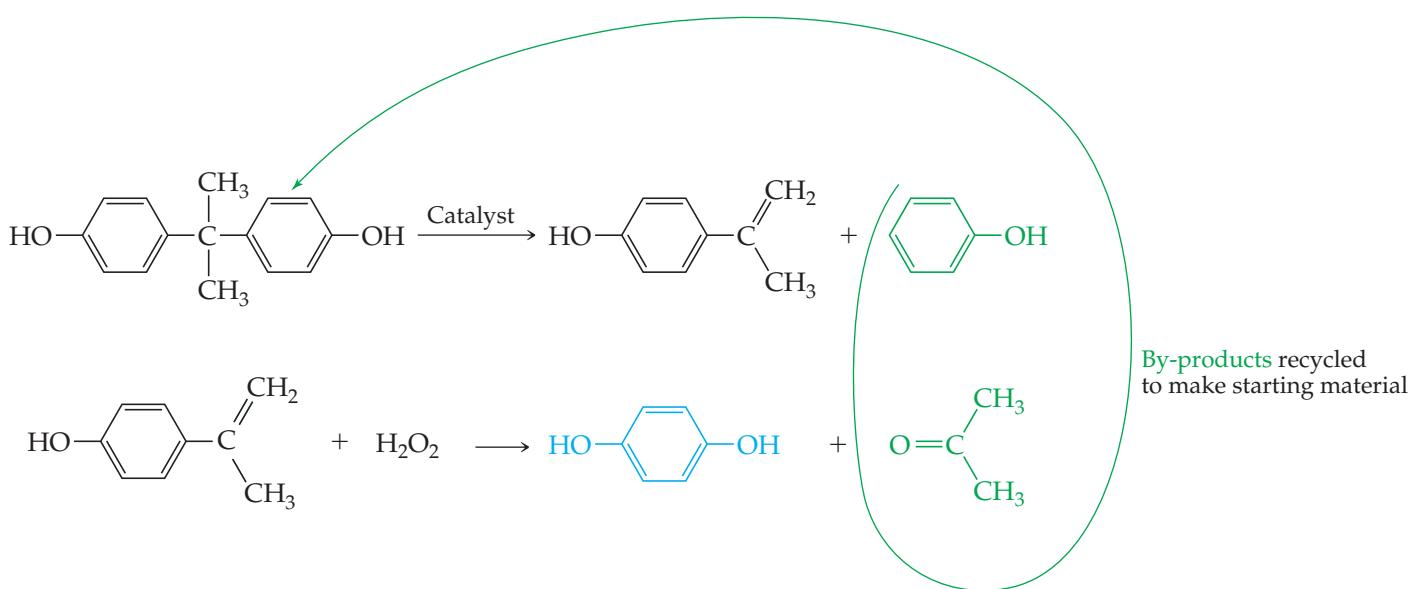
Greener Reagents and Processes

Let us examine two more examples of green chemistry in action.

Hydroquinone, $\text{HO}-\text{C}_6\text{H}_4-\text{OH}$, is a common intermediate used to make polymers. The standard industrial route to hydroquinone, used until recently, yields many by-products that are treated as waste:

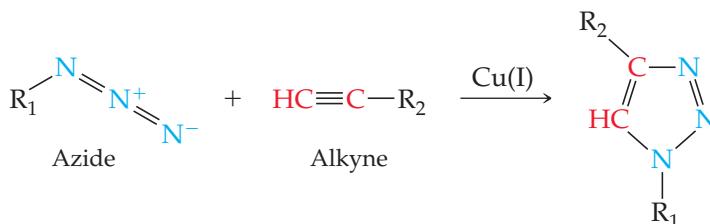


Using the principles of green chemistry, researchers have improved this process. The new process for hydroquinone production uses a new starting material. Two of the by-products of the new reaction (shown in green) can be isolated and used to make the new starting material.



The new process is an example of “atom economy,” a phrase that means that a high percentage of the atoms from the starting materials end up in the product.

Another example of atom economy is a reaction in which, at room temperature and in the presence of a copper(I) catalyst, an organic *azide* and an *alkyne* form one product molecule:



This reaction is informally called a *click reaction*. The yield—actual, not just theoretical—is close to 100%, and there are no by-products. Depending on the type of azide and type of alkyne we start with, this very efficient click reaction can be used to create any number of valuable product molecules.

Self-Assessment Exercise

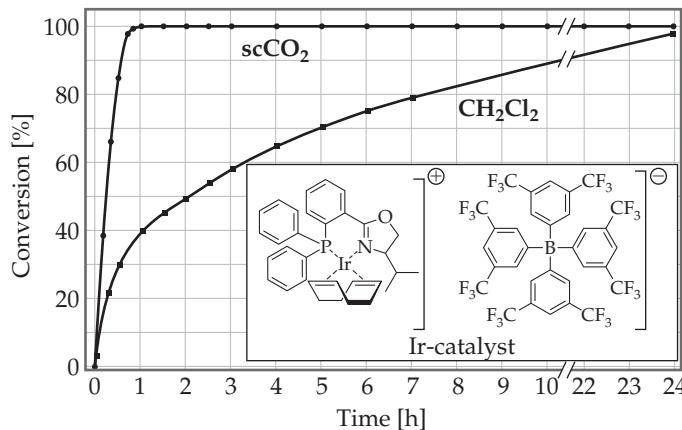
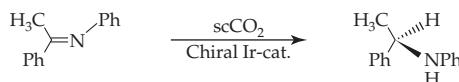
- 18.29** Assuming the by-products of the green manufacture of hydroquinone (these are: phenol and acetone) are recycled, what atoms, if any, used in this process do not end up in the final products?

- (a) All atoms are used
- (b) 3C and 5H remain
- (c) 1O and 2H remain

Exercises

- 18.30** Discuss how catalysts can make processes more energy efficient.
- 18.31** The hydrogenation reaction shown here was performed with an iridium catalyst, both in supercritical CO_2 (scCO_2) and in the chlorinated solvent CH_2Cl_2 . The kinetic data for the reaction in both solvents are plotted in the graph. In what respects is the use of scCO_2 a good example of a green chemical reaction?

- 18.32** In the following three instances, which choice is greener in a chemical process? Explain. (a) A reaction that can be run at 350 K for 12 h without a catalyst or one that can be run at 300 K for 1 h with a reusable catalyst. (b) A reagent for the reaction that can be obtained from corn husks or one that is obtained from petroleum. (c) A process that produces no by-products or one in which the by-products are recycled for another process.



18.29 (c)

Answers to Self-Assessment Exercise



Sample Integrative Exercise

Putting Concepts Together

- (a) Acid rain is no threat to lakes in areas where the rock is limestone (calcium carbonate), which can neutralize the acid. Where the rock is granite, however, no neutralization occurs. How does limestone neutralize 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 ($V = 4 \times 10^9 \text{ L}$) 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, a reaction that evidently does not happen with acid and granite. For (b), we need to think about what reaction between an acid and CaO is possible 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 is needed.

Solve

(a) The carbonate ion, which is the anion of a weak acid, is basic and so reacts with $\text{H}^+(aq)$. If the concentration of $\text{H}^+(aq)$ is low, the major product is the bicarbonate ion, HCO_3^- . If the concentration of $\text{H}^+(aq)$ is high, H_2CO_3 forms and decomposes to CO_2 and H_2O .

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

$$[\text{H}^+]_{\text{initial}} = 10^{-5.0} = 1 \times 10^{-5} \text{ M}$$

$$[\text{H}^+]_{\text{final}} = 10^{-6.5} = 3 \times 10^{-7} \text{ M}$$

Using the lake volume, we can calculate the number of moles of $\text{H}^+(aq)$ 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 $\text{H}^+(aq)$ 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 $\text{H}^+(aq)$ contributing to the pH needs to be neutralized. We need to neutralize at least that much acid, although there may be a great deal more than that amount in the lake.

The oxide ion of CaO is very basic. In the neutralization reaction, 1 mol of CaO reacts with 2 mol of H^+ to form H_2O and Ca^{2+} ions. Thus, $4 \times 10^4 \text{ mol}$ of H^+ requires

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

A tonne of CaO costs about \$100 when purchased in large quantities, so it relatively inexpensive. This amount of CaO is the minimum amount needed, however, because there are likely to be weak acids in the water that must also be neutralized.

This liming procedure has been used to bring the pH of some small lakes into the range necessary for fish to live. The lake in our example would be about a kilometer long and a kilometer wide and have an average depth of 6 m.

Chapter Summary and Key Terms

EARTH'S ATMOSPHERE (SECTION 18.1) In this section 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**.

HUMAN ACTIVITIES AND EARTH'S ATMOSPHERE (SECTION 18.2) 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 harmful ultraviolet light that are not removed by any other atmospheric component. 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 it with CaO to form calcium sulfite CaSO_3 .

Photochemical smog is a complex mixture 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 surface temperature. The concentrations of CO_2 and other so-called **greenhouse gases** in the atmosphere are thus important in determining global 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, which in turn appears to be contributing to an increase in the average temperature of the Earth.

EARTH'S WATER (SECTION 18.3) Earth's water is largely in the oceans and seas; only a small fraction is freshwater. Seawater contains about 3.5% by mass of dissolved salts and is described as having a **salinity** (grams of dry salts per 1 kg seawater) of 35. Seawater's density and salinity vary with depth. Because most of the world's water is in the oceans, humans may eventually need to recover freshwater from seawater. The global water cycle involves continuous phase changes of water.

HUMAN ACTIVITIES AND WATER QUALITY (SECTION 18.4) 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. **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**.

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, and sterilization.

GREEN CHEMISTRY (SECTION 18.5) 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.

Learning Outcomes After studying this chapter, you should be able to:

- Describe the regions of Earth's atmosphere in terms of how temperature varies with altitude. (Section 18.1)
Related exercises 18.4, 18.43
- Describe the composition of the atmosphere in terms of the major components in dry air at sea level. (Section 18.1)
Related exercises 18.6, 18.44
- Calculate concentrations of gases in parts per million (ppm). (Section 18.1) *Related exercises 18.5, 18.45*
- Describe the processes of photodissociation and photoionization and their role in the upper atmosphere. (Section 18.1)
Related exercises 18.8, 18.47
- Calculate the minimum frequency or maximum wavelength needed to cause photodissociation or photoionization. (Section 18.1) *Related exercises 18.7, 18.46, 18.48*
- Explain how ozone in the upper atmosphere functions to filter short wavelength solar radiation, and how chlorofluorcarbons (CFCs) cause depletion of the ozone layer. (Sections 18.1 and 18.2) *Related exercises 18.9, 18.13, 18.14, 18.51*
- Describe the origins and behavior of sulfur oxides and nitrogen oxides as air pollutants, including the generation of acid rain and photochemical smog. (Section 18.2)
Related exercises 18.15, 18.17, 18.52, 18.54
- Describe how water and carbon dioxide cause an increase in atmospheric temperature near Earth's surface. (Section 18.2)
Related exercises 18.18, 18.55
- Describe the global water cycle. (Section 18.3)
Related exercises 18.21, 18.57
- Explain what is meant by the salinity of water and describe the process of reverse osmosis as a means of desalination. (Section 18.4) *Related Exercises 18.24, 18.60*
- List the major cations, anions, and gases present in natural waters and describe the relationship between dissolved oxygen and water quality. (Section 18.4)
Related exercises 18.25, 18.26, 18.59, 18.62
- List the main steps involved in treating water for domestic uses. (Section 18.4) *Related exercises 18.27, 18.28, 18.63, 18.64*
- Describe the main goals of green chemistry. (Section 18.5)
Related exercises 18.30, 18.65
- Compare reactions and decide which reaction is greener. (Section 18.5) *Related exercises 18.31, 18.32, 18.67*

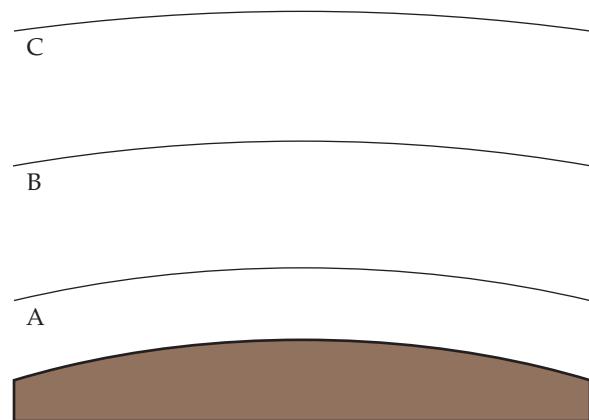
Exercises

Visualizing Concepts

- 18.33** At 273 K and 101.3 kPa, 1 mol of an ideal gas occupies 22.4 L. (Section 10.4) (a) Looking at Figure 18.1, predict whether a 1 mol sample of the atmosphere in the middle of the stratosphere would occupy a greater or smaller volume than 22.4 L (b) Looking at Figure 18.1, 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. (c) In which parts of the atmosphere would you expect gases to behave most ideally (ignoring any photochemical reactions)? [Section 18.1]
- 18.34** Molecules in the upper atmosphere tend to contain double and triple bonds rather than single bonds. Suggest an explanation. [Section 18.1]

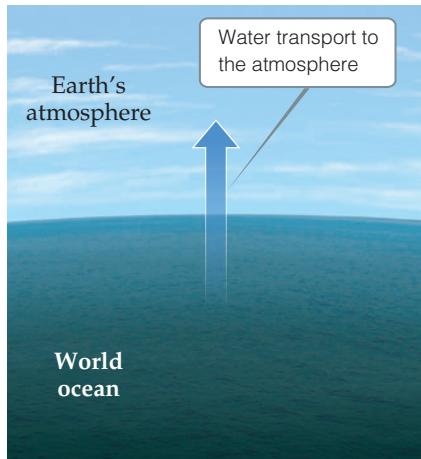
- 18.35** The figure shows the three lowest regions of Earth's atmosphere. (a) Name each and indicate the approximate elevations at which the boundaries occur. (b) In which region is ozone a pollutant? In which region does it filter UV solar radiation? (c) In which region is infrared radiation from Earth's surface most strongly reflected back? (d) An aurora borealis is due to excitation of atoms and molecules in

the atmosphere 55–95 km above Earth's surface. Which regions in the figure are involved in an aurora borealis? (e) Compare the changes in relative concentrations of water vapor and carbon dioxide with increasing elevation in these three regions [Section 18.1].



18.36 You are working with an artist who has been commissioned to make a sculpture for a big city. The artist is wondering what material to use to make her sculpture because she has heard that acid rain 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 are 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 18.2]

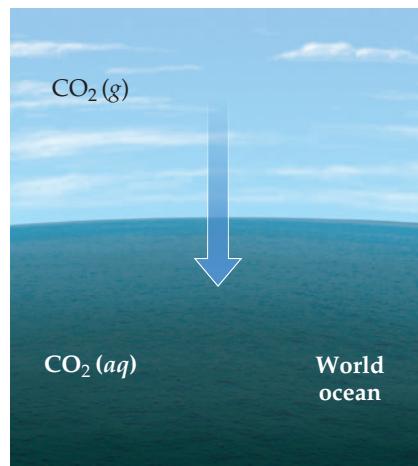
18.37 Where does the energy come from to evaporate the estimated $425,000 \text{ km}^3$ of water that annually leaves the oceans, as illustrated here? [Section 18.3]



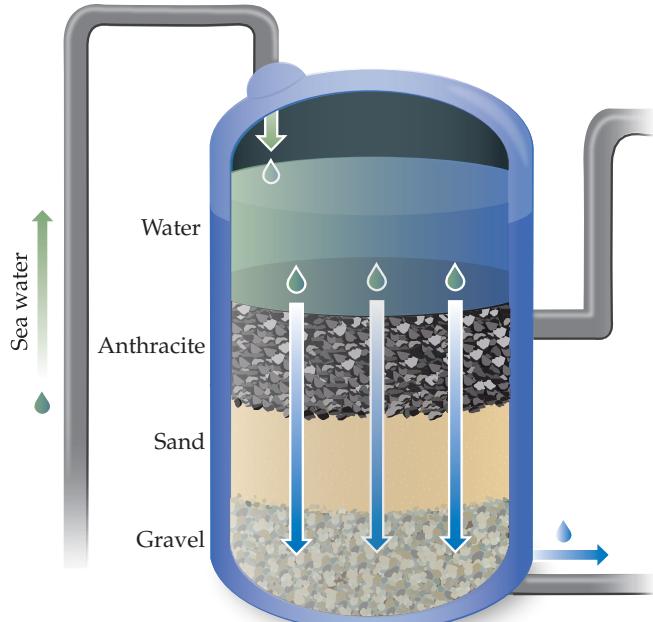
18.40 The first stage of treatment at a reverse osmosis plant is to flow the water through rock, sand, and gravel as shown

18.38 The Earth's oceans have a salinity of 35. What is the concentration of dissolved salts in seawater when expressed in ppm? What percentage of salts must be removed from seawater before it can be considered freshwater (dissolved salts $< 500 \text{ ppm}$)? [Section 18.3]

18.39 Describe what changes occur when atmospheric CO_2 interacts with the world ocean as illustrated here. [Section 18.3]



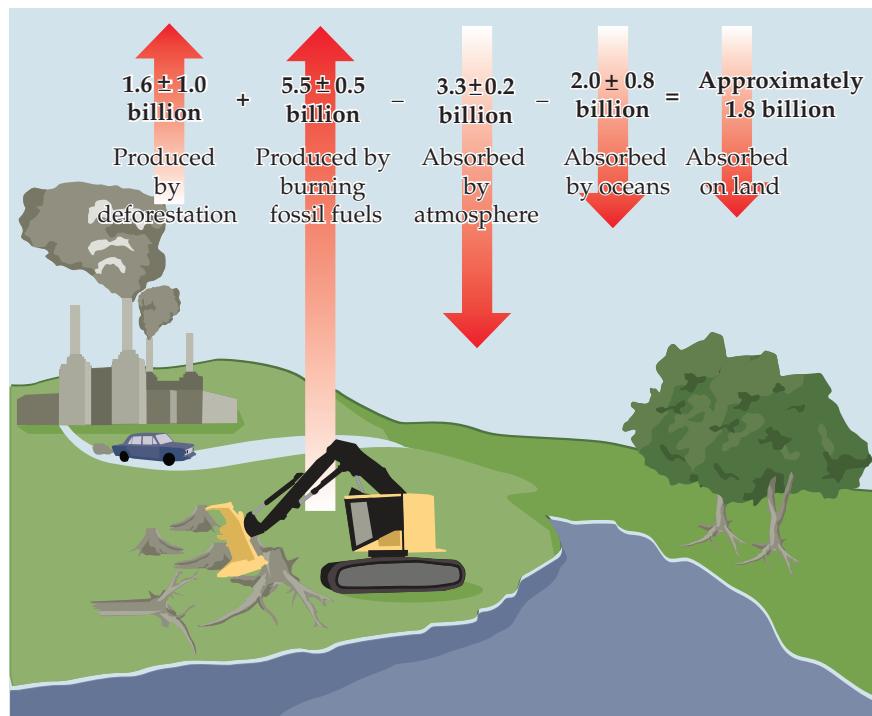
here. Would this step remove particulate matter? Would this step remove dissolved salts? [Section 18.4]



- 18.41** From study of Figure 18.21, describe the various ways in which operation of a fracking well site could lead to environmental contamination.

- 18.42** One mystery in environmental science is the imbalance in the “carbon dioxide budget.” Considering only human activities, scientists have estimated that 1.6 billion tonne tons of CO₂ is added to the atmosphere every year because of deforestation (plants use CO₂, and fewer plants will leave more CO₂ in the atmosphere). Another 5.5 billion tonne 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 tonne of this CO₂ per year, while the oceans take up 2 billion tonne per year, leaving about 1.8 billion tonne of CO₂ per year unaccounted for. Describe a mechanism by which CO₂ is removed from the atmosphere and ultimately ends up below the surface (*Hint:* What is the source of the fossil fuels?). [Sections 18.1–18.3]



Earth's Atmosphere (Section 18.1)

- 18.43** (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.

- 18.44** From the data in Table 18.1, calculate the partial pressures of neon and helium when the total atmospheric pressure is 102.3 kPa.

- 18.45** The average concentration of carbon monoxide in air in a city in 2007 was 3.0 ppm. Calculate the number of CO molecules in 1.0 L of this air at a pressure of 100 kPa and a temperature of 25 °C.

- 18.46** The dissociation energy of a carbon–iodine bond is typically about 240 kJ/mol. (a) What is the maximum wavelength of photons that can cause C—I bond dissociation? (b) Which kind of electromagnetic radiation—ultraviolet, visible, or infrared—does the wavelength you calculated in part (a) correspond to?

- 18.47** (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.

- 18.48** The dissociation energy of N₂ is very high, 941 kJ/mol. (a) Calculate the wavelength of the photons that possess sufficient energy to dissociate N₂. (b) In which region of the electromagnetic spectrum does this light fall? Does this light have enough energy to photoionize N₂?

Human Activities and Earth's Atmosphere (Section 18.2)

- 18.49** Do the reactions involved in ozone depletion involve changes in oxidation state of the O atoms? Explain.

- 18.50** Draw the Lewis structure for the chlorofluorocarbon CFC-11, CFCl₃. What chemical characteristics of this substance allow it to effectively deplete stratospheric ozone?

- 18.51** The average bond enthalpies of the C—C and C—H bonds are 348 kJ/mol and 413 kJ/mol, respectively. (a) What is the maximum wavelength that a photon can possess and still have sufficient energy to break the C—H and C—C bonds, respectively? (b) Given the fact that O₂, N₂, and O in the upper atmosphere absorb most of the light with wavelengths shorter than 240 nm, would you expect the photo-dissociation of C—C and C—H bonds to be significant in the lower atmosphere?

- 18.52** Nitrogen oxides like NO₂ and NO are a significant source of acid rain. For each of these molecules write an equation that shows how an acid is formed from the reaction with water.

- 18.53** (a) It has been reported, that acid rain with a pH of 3.5 could corrode mild steel. Write a chemical equation that describes the attack of acid rain on an iron (Fe) material. (b) If the iron material were covered with a surface layer of copper, would this help to stop the effects of acid rain? Explain.

- 18.54** Alcohol-based fuels for cars lead to the production of formaldehyde (CH_2O) in exhaust gases. Formaldehyde undergoes photodissociation, which contributes to photochemical smog:



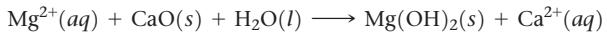
The maximum wavelength of light that can cause this reaction is 335 nm. (a) In what part of the electromagnetic spectrum is light with this wavelength found? (b) What is the maximum strength of a bond, in kJ/mol, that can be broken by absorption of a photon of 335 nm light? (c) Compare your answer from part (b) to the appropriate value from Table 8.3. What do you conclude about C—H bond energy in formaldehyde? (d) Write out the formaldehyde photodissociation reaction, showing Lewis-dot structures.

- 18.55** Consider the Earth's energy balance shown in Figure 18.10. (a) How many different sources transfer energy to the atmosphere? Which makes the largest contribution? What is the total amount of energy transferred into the atmosphere in W/m²? (b) To maintain a balance the atmosphere must lose an equal amount of energy by emitting radiation, either into space or back toward the surface. What fraction is radiated back to the surface?

Earth's Water (Section 18.3)

- 18.56** What is the molarity of Na^+ in a solution of NaCl whose salinity is 25.0 if the solution has a density of 1.04 g/mL?
- 18.57** The enthalpy of evaporation of water is 40.67 kJ/mol. Sunlight striking Earth's surface supplies 168 W per square meter (1 W = 1 watt = 1 J/s). (a) Assuming that evaporation of water is due only to energy input from the Sun, calculate how many grams of water could be evaporated from a 1.00 square meter patch of ocean over a 12 h day. (b) The specific heat capacity of liquid water is 4.184 J/g °C. If the initial surface temperature of a 1.00 square meter patch of ocean is 26 °C, what is its final temperature after being in sunlight for 12 h, assuming no phase changes and assuming that sunlight penetrates uniformly to depth of 10.0 cm?

- 18.58** A first-stage recovery of magnesium from seawater is precipitation of $\text{Mg}(\text{OH})_2$ with CaO:



What mass of CaO, in grams, is needed to precipitate 1000 kg of $\text{Mg}(\text{OH})_2$?

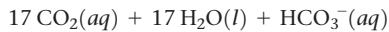
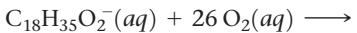
- 18.59** Although there are many ions in seawater, the overall charges of the dissolved cations and anions must maintain charge neutrality. Consider only the six most abundant ions in seawater, as listed in Table 18.5 (Cl^- , Na^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , and K^+), calculate the total charge in Coulombs of the cations in 1.0 L of seawater. Calculate the total charge in Coulombs of the anions in 1.0 L of seawater. To how many significant figures are the two numbers equal?

Human Activities and Water Quality (Section 18.4)

- 18.60** Suppose that one wishes to use reverse osmosis to reduce the salt content of brackish water containing 0.265 M total salt concentration to a value of 0.015 M, thus rendering it usable for human consumption. What is the minimum pressure that needs to be applied in the permeators (Figure 18.18) to achieve this goal, assuming that the operation occurs at 15 °C? (Hint: Refer to Section 13.5.)

- 18.61** 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.

- 18.62** Sodium stearate ($\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}$) is the most common soap. Assume that the stearate anion undergoes aerobic decomposition in the following manner:



What is the total mass of O_2 required to biodegrade 3.0 g of this substance?

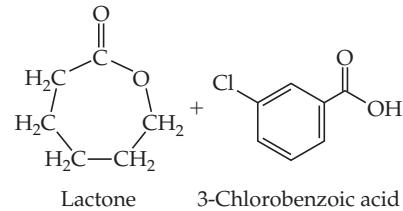
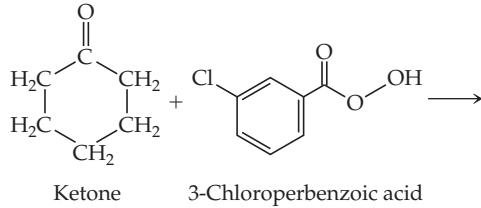
- 18.63** Hydrogen phosphate (HPO_4^{2-}) can be removed in water treatment by the addition of slaked lime, $\text{Ca}(\text{OH})_2$. Write a balanced chemical equation for the reaction (using ions as reactant), in which $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ forms as a precipitate.

- 18.64** (a) What are trihalomethanes (THMs)? (b) Draw the Lewis structures of two example THMs.

Green Chemistry (Section 18.5)

- 18.65** One of the principles of green chemistry is that it is better to use as few steps as possible in making new chemicals. In what ways does following this rule advance the goals of green chemistry? How does this principle relate to energy efficiency?

- 18.66** A reaction for converting ketones to lactones, called the Baeyer–Villiger reaction,

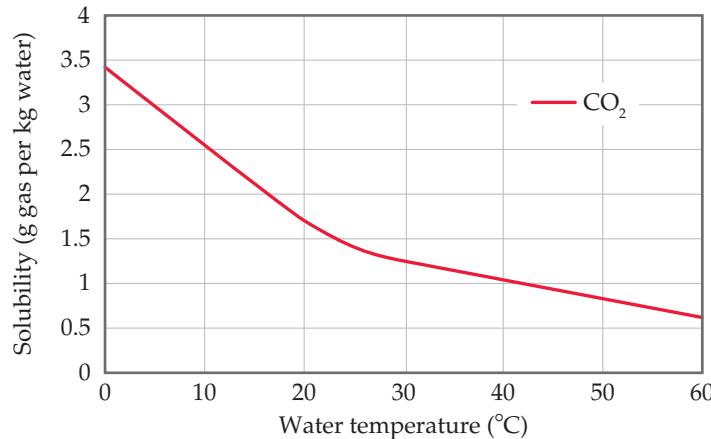


is used in the manufacture of plastics and pharmaceuticals. 3-Chloroperbenzoic acid is shock-sensitive, however, and prone to explode. Also, 3-chlorobenzoic acid is a waste product. An alternative process being developed uses hydrogen peroxide and a catalyst consisting of tin deposited within a solid 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?

- 18.67** In the following three instances, which choice is greener in each situation? Explain. (a) Petroleum as a raw material or vegetable oil as a raw material. (b) Toluene as a solvent or water as a solvent. (c) Catalyzed reaction at 600 K or uncatalyzed reaction at 800 K.

Additional Exercises

- 18.68** 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.
- 18.69** Suppose that on another planet the atmosphere consists of 10% Kr, 40% CH_4 , and 50% O_2 . What is the average molar mass at the surface? What is the average molar mass at an altitude at which all the O_2 is photodissociated?
- 18.70** If an average O_3 molecule “lives” only 100–200 seconds in the stratosphere before undergoing dissociation, how can O_3 offer any protection from ultraviolet radiation?
- 18.71** Show how Equations 18.7 and 18.9 can be added to give Equation 18.10.
- 18.72** What properties of CFCs make them ideal for various commercial applications but also make them a long-term problem in the stratosphere?
- 18.73** Halons are fluorocarbons that contain bromine, such as 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 8.3, 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.
- 18.74** (a) What is the difference between a CFC and an HFC? (b) It is estimated that the lifetime for HFCs in the stratosphere is 2–7 years. Why is this number significant? (c) Why have HFCs been used to replace CFCs? (d) What is the major disadvantage of HFCs as replacements for CFCs?
- 18.75** Explain, using Le Châtelier’s principle, why the equilibrium constant for the formation of NO from N_2 and O_2 increases with increasing temperature, whereas the equilibrium constant for the formation of NO_2 from NO and O_2 decreases with increasing temperature.
- 18.76** Liquefied petroleum gas (LPG) consists primarily of propane, $\text{C}_3\text{H}_8(l)$ or butane $\text{C}_4\text{H}_{10}(l)$. (a) Write a balanced chemical equation for the complete combustion of propane to produce $\text{CO}_2(g)$ as the only carbon-containing product. (b) Write a balanced chemical equation for the incomplete combustion of propane to produce $\text{CO}(g)$ as the only carbon-containing product. (c) At 25 °C and 101.3 kPa pressure, what is the minimum quantity of dry air needed to combust 10.0 mL of $\text{C}_3\text{H}_8(l)$ completely to $\text{CO}_2(g)$? The density of the LPG is 0.50 g/mL.
- 18.77** It was estimated that the eruption of the Mount Pinatubo volcano resulted in the injection of 20 million metric tons of SO_2 into the atmosphere. Most of this SO_2 underwent oxidation to SO_3 , which reacts with atmospheric water to form an aerosol. (a) Write chemical equations for the processes leading to formation of the aerosol. (b) The aerosols caused a 0.5–0.6 °C drop in surface temperature in the northern hemisphere. What is the mechanism by which this occurs? (c) The sulfate aerosols, as they are called, also cause loss of ozone from the stratosphere. How might this occur?
- 18.78** One of the possible consequences of climate change 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) The accompanying figure shows the solubility of CO_2 in water as a function of temperature. Does CO_2 behave more or less similarly to other gases in this respect?
- (b) What are the implications of this figure for the problem of climate change?
- 18.79** The rate of solar energy striking Earth averages 168 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?
- 18.80** In 2008, the global average electricity consumption per head was 3.0 MWh. The solar power striking Earth every day averages 168 watts per square meter. Considering that present technology for solar energy conversion is about 10% efficient, from how many square meters of land must sunlight be collected in order to provide this power?
- 18.81** Write balanced chemical equations for each of the following reactions: (a) The carbon dioxide molecule undergoes photodissociation in the upper atmosphere. (b) The carbon dioxide molecule undergoes photoionization in the upper atmosphere. (c) Carbon monoxide undergoes oxidation by ozone in the stratosphere. (d) Carbon dioxide dissolves in water to form hydrogen carbonate.
- 18.82** (a) When sufficient Na_2CO_3 is added to a solution containing Mg^{2+} , $\text{Mg}(\text{OH})_2$ will precipitate. Explain by writing balanced equations of the reactions. (b) Will $\text{Mg}(\text{OH})_2$ precipitate when 2.0 g of Na_2CO_3 is added to 1.00 L of a solution containing 25 ppm of Mg^{2+} ?
- 18.83** The CDC (Centers for Disease Control and Prevention) published a reference blood lead level (BLL), which is based on the BLL distribution among children. It is currently 5 $\mu\text{g}/\text{dL}$. (a) What is the molarity of an aqueous solution with this concentration? (b) Express this concentration in ppb.

Integrative Exercises

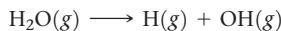
18.84 The estimated average concentration of NO_2 in air in an urbanized country in 2015 was 0.010 ppm. (a) Calculate the partial pressure of the NO_2 in a sample of this air when the atmospheric pressure is 101 kPa. (b) How many molecules of NO_2 are present under these conditions at 25°C in a room that measures 10 m × 8 m × 2.50 m?

18.85 A 500 megawatt electrical power plant typically burned 1,430,000 tonne of coal in a year. (a) Assuming that the coal was 80% carbon and 3% sulfur and that combustion was complete, calculate the number of tonne of carbon dioxide and sulfur dioxide produced by the plant during the year. (b) If 50% of the SO_2 could be removed by reaction with powdered CaO to form CaSO_3 , how many tonne of CaSO_3 would be produced?

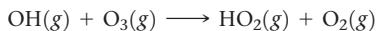
18.86 Figure 14.4 shows the visible spectra of iodine (I_2) solutions at different concentrations (1 mg/L 100 mg/L). The absorption maximum is at 450 nm. (a) What color corresponds to a wavelength of 450 nm? (b) Calculate the extinction coefficient ϵ of iodine in this solution at 450 nm. Assume a common spectrometer path length of $b = 1.0 \text{ cm}$.

18.87 Common lab spectrometers can detect absorbance down to 0.0002 with good reliability. Consider a dissolved harmful organic substance with a molar mass of 120.5 g/mol, which can be detected in this spectrometer. It shows an extinction coefficient of $\epsilon = 1.43 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 320 nm, its absorption maximum (A Closer Look, p. 667). (a) Calculate the minimum concentration of the organic substance detectable by this spectrometer (path length 1 cm). (b) Convert the minimum observable molarity to ppb.

18.88 The concentration of H_2O in the stratosphere is about 5 ppm. It undergoes photodissociation according to:



- (a) Write out the Lewis-dot structures for both products and reactant.
- (b) Using Table 8.3, calculate the wavelength required to cause this dissociation.
- (c) The hydroxyl radical, OH , can react with ozone, giving the following reactions:



What overall reaction results from these two elementary reactions? What is the catalyst in the overall reaction? Explain.

18.89 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 $2 \times 10^{-6} \text{ s}^{-1}$. At that rate, how many days would it take for the hydrocarbons to decrease to 10% of their initial value?

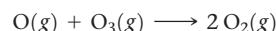
18.90 The standard enthalpies of formation of ClO and ClO_2 are 101 and 102 kJ/mol, respectively. Using these data and the thermodynamic data in Appendix C, calculate the overall enthalpy change for each step in the following catalytic cycle:



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

18.91 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 L of water beginning with water at 25°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 \$0.49 per L, what percentage of the sales price is represented by the cost of the energy?

18.92 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) Use ΔH_f° values from Appendix C to estimate the enthalpy change for this reaction. Would this reaction raise or lower the temperature of the stratosphere?

18.93 The following data were collected for the decomposition of O_3 by ($\text{O}_3 + \text{H} \longrightarrow \text{O}_2 + \text{OH}$) at very low concentrations:

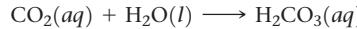
Trial	$[\text{O}_3] (\text{M})$	$[\text{H}] (\text{M})$	Initial Rate (M/s)
1	3.25×10^{-33}	2.25×10^{-26}	8.10×10^{-15}
2	6.50×10^{-33}	4.50×10^{-26}	3.25×10^{-14}
3	6.48×10^{-33}	2.23×10^{-26}	1.62×10^{-14}

(a) Write the rate law for the reaction.

(b) Calculate the rate constant.

18.94 The degradation of $\text{CF}_3\text{CH}_2\text{F}$ (an HFC) by OH radicals in the troposphere is first order in each reactant and has a rate constant of $k = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 10°C. If the tropospheric concentrations of OH and $\text{CF}_3\text{CH}_2\text{F}$ are 1.0×10^{12} and 7.5×10^{14} molecules/m³, respectively, what is the rate of reaction at this temperature in M/s?

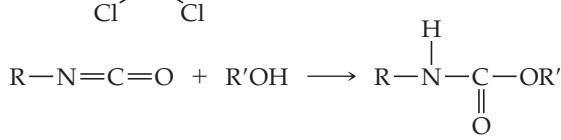
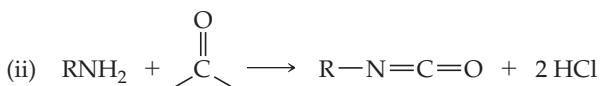
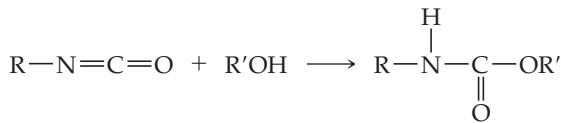
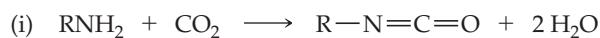
18.95 The Henry's law constant for CO_2 in water at 25°C is $3.4 \times 10^{-4} \text{ mol/m}^3\text{-Pa}$ (a) What is the solubility of CO_2 in water at this temperature if the solution is in contact with air at normal atmospheric pressure? (b) Assume that all of this CO_2 is in the form of H_2CO_3 produced by the reaction between CO_2 and H_2O :



What is the pH of this solution?

18.96 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 kg of $\text{Al}_2(\text{SO}_4)_3$ is added to 10,000 L of water. (b) Approximately how many pounds of CaO must be added to the water to achieve this pH?

18.97 The valuable polymer polyurethane is made by a condensation reaction of alcohols (ROH) with compounds that contain an isocyanate group (RNCO). Two reactions that can generate a urethane monomer are shown here:



- (a) Which process, i or ii, is greener? Explain.
- (b) What are the hybridization and geometry of the carbon atoms in each C-containing compound in each reaction?
- (c) If you wanted to promote the formation of the isocyanate intermediate in each reaction, what could you do, using Le Châtelier's principle?

- 18.98** The pH of a particular raindrop is 5.6. (a) Assuming the major species in the raindrop are $\text{H}_2\text{CO}_3(aq)$, $\text{HCO}_3^-(aq)$, and $\text{CO}_3^{2-}(aq)$, calculate the concentrations of these species in the raindrop, assuming the total carbonate concentration is $1.0 \times 10^{-5}\text{ M}$. The appropriate K_a values are given in Table 16.3. (b) What experiments could you do to test the hypothesis that the rain also contains sulfur-containing species that contribute to its pH? Assume you have a large sample of rain to test.

Design an Experiment

Considerable fracking of petroleum/gas wells (see Closer Look box in Section 18.4) has occurred in recent years in a particular rural area. The residents have complained that the water in the residential wells serving their domestic water needs has become contaminated with chemicals associated with the fracking operations. The well operators respond that the chemicals about which complaints are lodged occur naturally, and are not the result of well-drilling activities.

Describe experiments that you could conduct on the waters from residential wells to help determine whether and to what extent well contaminants are due to fracking operations. Among the

chemicals that might be expected to be employed in fracking operations are hydrochloric acid, sodium chloride, ethylene glycol, borate salts, water-soluble gelling agents such as guar gum, citric acid, methanol, and other alcohols such as isopropanol, and methane. Assume that you have available the techniques to make measurements of the concentrations of these substances in the residential wells. What experiments would you conduct, and what analyses of the results would you carry out in an attempt to settle the question of whether fracking operations have led to contamination of the well water? Would simply measuring the concentrations of some or all of these substances in the well waters be sufficient to settle the issue?