



**Pearson New International Edition**

Introduction to Environmental  
Engineering and Science  
Gilbert M. Masters   Wendell P. Ela  
Third Edition

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PEARSON

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# Table of Contents

|                                                                                             |            |
|---------------------------------------------------------------------------------------------|------------|
| <b>1. Mass and Energy Transfer</b><br>Gilbert M. Masters/Wendell P. Ela                     | <b>1</b>   |
| <b>2. Environmental Chemistry</b><br>Gilbert M. Masters/Wendell P. Ela                      | <b>47</b>  |
| <b>3. Mathematics of Growth</b><br>Gilbert M. Masters/Wendell P. Ela                        | <b>87</b>  |
| <b>4. Risk Assessment</b><br>Gilbert M. Masters/Wendell P. Ela                              | <b>127</b> |
| <b>5. Water Pollution</b><br>Gilbert M. Masters/Wendell P. Ela                              | <b>173</b> |
| <b>6. Water Quality Control</b><br>Gilbert M. Masters/Wendell P. Ela                        | <b>281</b> |
| <b>7. Air Pollution</b><br>Gilbert M. Masters/Wendell P. Ela                                | <b>367</b> |
| <b>8. Global Atmospheric Change</b><br>Gilbert M. Masters/Wendell P. Ela                    | <b>501</b> |
| <b>9. Solid Waste Management and Resource Recovery</b><br>Gilbert M. Masters/Wendell P. Ela | <b>601</b> |
| <b>Index</b>                                                                                | <b>687</b> |

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# Mass and Energy Transfer

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|   |                      |
|---|----------------------|
| 1 | Introduction         |
| 2 | Units of Measurement |
| 3 | Materials Balance    |
| 4 | Energy Fundamentals  |
|   | Problems             |

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When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science.

—William Thomson, Lord Kelvin (1891)

## 1 | Introduction

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This chapter begins with a section on units of measurement. Engineers need to be familiar with both the American units of feet, pounds, hours, and degrees Fahrenheit as well as the more recommended International System of units. Both are used in the practice of environmental engineering.

Next, two fundamental topics, which should be familiar from the study of elementary physics, are presented: the *law of conservation of mass* and the *law of conservation of energy*. These laws tell us that within any environmental system, we theoretically should be able to account for the flow of energy and materials into, and out of, that system. The law of conservation of mass, besides providing an important tool for quantitatively tracking pollutants as they disperse in the environment, reminds us that pollutants have to go somewhere, and that we should be wary of approaches that merely transport them from one medium to another.

In a similar way, the law of conservation of energy is also an essential accounting tool with special environmental implications. When coupled with other thermodynamic principles, it will be useful in a number of applications, including the study of global climate change, thermal pollution, and the dispersion of air pollutants.

## 2 Units of Measurement

In the United States, environmental quantities are measured and reported in both the *U.S. Customary System* (USCS) and the *International System of Units* (SI), so it is important to be familiar with both. Here, preference is given to SI units, although the U.S. system will be used in some circumstances. Table 1 lists conversion factors between the SI and USCS systems for some of the most basic units that will be encountered.

In the study of environmental engineering, it is common to encounter both extremely large quantities and extremely small ones. The concentration of some toxic substance may be measured in parts per billion (ppb), for example, whereas a country's rate of energy use may be measured in thousands of billions of watts (terawatts). To describe quantities that may take on such extreme values, it is useful to have a system of prefixes that accompany the units. Some of the most important prefixes are presented in Table 2.

Often, it is the concentration of some substance in air or water that is of interest. Using the metric system in either medium, concentrations may be based on mass (usually mg or g), volume (usually L or m<sup>3</sup>), or number (usually mol), which can lead to some confusion. It may be helpful to recall from chemistry that one mole of any substance has Avogadro's number of molecules in it ( $6.02 \times 10^{23}$  molecules/mol) and has a mass equal to its molecular weight.

### Liquids

Concentrations of substances dissolved in water are usually expressed in terms of mass or number per unit volume of mixture. Most often the units are milligrams (mg),

TABLE 1

| Some Basic Units and Conversion Factors |                             |                   |                   |                    |
|-----------------------------------------|-----------------------------|-------------------|-------------------|--------------------|
| Quantity                                | SI units                    | SI symbol         | Conversion factor | USCS units         |
| Length                                  | meter                       | m                 | 3.2808            | ft                 |
| Mass                                    | kilogram                    | kg                | 2.2046            | lb                 |
| Temperature                             | Celsius                     | °C                | $1.8 (°C) + 32$   | °F                 |
| Area                                    | square meter                | m <sup>2</sup>    | 10.7639           | ft <sup>2</sup>    |
| Volume                                  | cubic meter                 | m <sup>3</sup>    | 35.3147           | ft <sup>3</sup>    |
| Energy                                  | kilojoule                   | kJ                | 0.9478            | Btu                |
| Power                                   | watt                        | W                 | 3.4121            | Btu/hr             |
| Velocity                                | meter/sec                   | m/s               | 2.2369            | mi/hr              |
| Flow rate                               | meter <sup>3</sup> /sec     | m <sup>3</sup> /s | 35.3147           | ft <sup>3</sup> /s |
| Density                                 | kilogram/meter <sup>3</sup> | kg/m <sup>3</sup> | 0.06243           | lb/ft <sup>3</sup> |

TABLE 2

| Common Prefixes |        |        |
|-----------------|--------|--------|
| Quantity        | Prefix | Symbol |
| $10^{-15}$      | femto  | f      |
| $10^{-12}$      | pico   | p      |
| $10^{-9}$       | nano   | n      |
| $10^{-6}$       | micro  | $\mu$  |
| $10^{-3}$       | milli  | m      |
| $10^{-2}$       | centi  | c      |
| $10^{-1}$       | deci   | d      |
| 10              | deka   | da     |
| $10^2$          | hecto  | h      |
| $10^3$          | kilo   | k      |
| $10^6$          | mega   | M      |
| $10^9$          | giga   | G      |
| $10^{12}$       | tera   | T      |
| $10^{15}$       | peta   | P      |
| $10^{18}$       | exa    | E      |
| $10^{21}$       | zetta  | Z      |
| $10^{24}$       | yotta  | Y      |

micrograms ( $\mu\text{g}$ ), or moles (mol) of substance per liter (L) of mixture. At times, they may be expressed in grams per cubic meter ( $\text{g}/\text{m}^3$ ).

Alternatively, concentrations in liquids are expressed as mass of substance per mass of mixture, with the most common units being parts per million (ppm) or parts per billion (ppb). To help put these units in perspective, 1 ppm is about the same as 1 drop of vermouth added to 15 gallons of gin, whereas 1 ppb is about the same as one drop of pollutant in a fairly large ( $70 \text{ m}^3$ ) back-yard swimming pool. Since most concentrations of pollutants are very small, 1 liter of mixture has a mass that is essentially 1,000 g, so for all practical purposes, we can write

$$1 \text{ mg/L} = 1 \text{ g}/\text{m}^3 = 1 \text{ ppm (by weight)} \quad (1)$$

$$1 \mu\text{g/L} = 1 \text{ mg}/\text{m}^3 = 1 \text{ ppb (by weight)} \quad (2)$$

In unusual circumstances, the concentration of liquid wastes may be so high that the specific gravity of the mixture is affected, in which case a correction to (1) and (2) may be required:

$$\text{mg/L} = \text{ppm (by weight)} \times \text{specific gravity of mixture} \quad (3)$$

### EXAMPLE 1 Fluoridation of Water

The fluoride concentration in drinking water may be increased to help prevent tooth decay by adding sodium fluoride; however, if too much fluoride is added, it can cause discoloring (mottling) of the teeth. The optimum dose of fluoride in drinking water is about 0.053 mM (millimole/liter). If sodium fluoride (NaF) is purchased in 25 kg bags, how many gallons of drinking water would a bag treat? (Assume there is no fluoride already in the water.)



**Solution** Note that the mass in the 25 kg bag is the sum of the mass of the sodium and the mass of the fluoride in the compound. The atomic weight of sodium is 23.0, and fluoride is 19.0, so the molecular weight of NaF is 42.0. The ratio of sodium to fluoride atoms in NaF is 1:1. Therefore, the mass of fluoride in the bag is

$$\text{mass F} = 25 \text{ kg} \times \frac{19.0 \text{ g/mol}}{42.0 \text{ g/mol}} = 11.31 \text{ kg}$$

Converting the molar concentration to a mass concentration, the optimum concentration of fluoride in water is

$$F = \frac{0.053 \text{ mmol/L} \times 19.0 \text{ g/mol} \times 1,000 \text{ mg/g}}{1,000 \text{ mmol/mol}} = 1.01 \text{ mg/L}$$

The mass concentration of a substance in a fluid is generically

$$C = \frac{m}{V} \quad (4)$$

where  $m$  is the mass of the substance and  $V$  is the volume of the fluid. Using (4) and the results of the two calculations above, the volume of water that can be treated is

$$V = \frac{11.31 \text{ kg} \times 10^6 \text{ mg/kg}}{1.01 \text{ mg/L} \times 3.785 \text{ L/gal}} = 2.97 \times 10^6 \text{ gal}$$

The bag would treat a day's supply of drinking water for about 20,000 people in the United States!

## Gases

For most air pollution work, it is customary to express pollutant concentrations in volumetric terms. For example, the concentration of a gaseous pollutant in parts per million (ppm) is the volume of pollutant per million volumes of the air mixture:

$$\frac{1 \text{ volume of gaseous pollutant}}{10^6 \text{ volumes of air}} = 1 \text{ ppm (by volume)} = 1 \text{ ppmv} \quad (5)$$

To help remind us that this fraction is based on volume, it is common to add a "v" to the ppm, giving ppmv, as suggested in (5).

At times, concentrations are expressed as mass per unit volume, such as  $\mu\text{g}/\text{m}^3$  or  $\text{mg}/\text{m}^3$ . The relationship between ppmv and  $\text{mg}/\text{m}^3$  depends on the pressure, temperature, and molecular weight of the pollutant. The ideal gas law helps us establish that relationship:

$$P V = n R T \quad (6)$$

where

$P$  = absolute pressure (atm)

$V$  = volume ( $\text{m}^3$ )

$n$  = mass (mol)

## Mass and Energy Transfer

$$R = \text{ideal gas constant} = 0.082056 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T = \text{absolute temperature (K)}$$

The mass in (6) is expressed as moles of gas. Also note the temperature is expressed in kelvins (K), where

$$K = ^\circ\text{C} + 273.15 \quad (7)$$

There are a number of ways to express pressure; in (6), we have used atmospheres. One atmosphere of pressure equals 101.325 kPa (Pa is the abbreviation for Pascals). One atmosphere is also equal to 14.7 pounds per square inch (psi), so 1 psi = 6.89 kPa. Finally, 100 kPa is called a bar, and 100 Pa is a millibar, which is the unit of pressure often used in meteorology.

### EXAMPLE 2 Volume of an Ideal Gas

Find the volume that 1 mole of an ideal gas would occupy at standard temperature and pressure (STP) conditions of 1 atmosphere of pressure and 0°C temperature. Repeat the calculation for 1 atm and 25°C.

**Solution** Using (6) at a temperature of 0°C (273.15 K) gives

$$V = \frac{1 \text{ mol} \times 0.082056 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273.15 \text{ K}}{1 \text{ atm}} = 22.414 \text{ L}$$

and at 25°C (298.15 K)

$$V = \frac{1 \text{ mol} \times 0.082056 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298.15 \text{ K}}{1 \text{ atm}} = 22.465 \text{ L}$$

From Example 2, 1 mole of an ideal gas at 0°C and 1 atm occupies a volume of 22.414 L ( $22.414 \times 10^{-3} \text{ m}^3$ ). Thus we can write

$$\text{mg/m}^3 = \text{ppmv} \times \frac{1 \text{ m}^3 \text{ pollutant}/10^6 \text{ m}^3 \text{ air}}{\text{ppmv}} \times \frac{\text{mol wt (g/mol)}}{22.414 \times 10^{-3} \text{ m}^3/\text{mol}} \times 10^3 \text{ mg/g}$$

or, more simply,

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{mol wt}}{22.414} \quad (\text{at } 0^\circ\text{C and } 1 \text{ atm}) \quad (8)$$

Similarly, at 25°C and 1 atm, which are the conditions that are assumed when air quality standards are specified in the United States,

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{mol wt}}{24.465} \quad (\text{at } 25^\circ\text{C and } 1 \text{ atm}) \quad (9)$$

In general, the conversion from ppm to  $\text{mg/m}^3$  is given by

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{mol wt}}{22.414} \times \frac{273.15 \text{ K}}{T \text{ (K)}} \times \frac{P \text{ (atm)}}{1 \text{ atm}} \quad (10)$$

**EXAMPLE 3** Converting ppmv to  $\text{mg}/\text{m}^3$ 

The U.S. Air Quality Standard for carbon monoxide (based on an 8-hour measurement) is 9.0 ppmv. Express this standard as a percent by volume as well as in  $\text{mg}/\text{m}^3$  at 1 atm and  $25^\circ\text{C}$ .

**Solution** Within a million volumes of this air there are 9.0 volumes of CO, no matter what the temperature or pressure (this is the advantage of the ppmv units). Hence, the percentage by volume is simply

$$\text{percent CO} = \frac{9.0}{1 \times 10^6} \times 100 = 0.0009\%$$

To find the concentration in  $\text{mg}/\text{m}^3$ , we need the molecular weight of CO, which is 28 (the atomic weights of C and O are 12 and 16, respectively). Using (9) gives

$$\text{CO} = \frac{9.0 \times 28}{24.465} = 10.3 \text{ mg}/\text{m}^3$$

Actually, the standard for CO is usually rounded and listed as  $10 \text{ mg}/\text{m}^3$ .

The fact that 1 mole of every ideal gas occupies the same volume (under the same temperature and pressure condition) provides several other interpretations of volumetric concentrations expressed as ppmv. For example, 1 ppmv is 1 volume of pollutant per million volumes of air, which is equivalent to saying 1 mole of pollutant per million moles of air. Similarly, since each mole contains the same number of molecules, 1 ppmv also corresponds to 1 molecule of pollutant per million molecules of air.

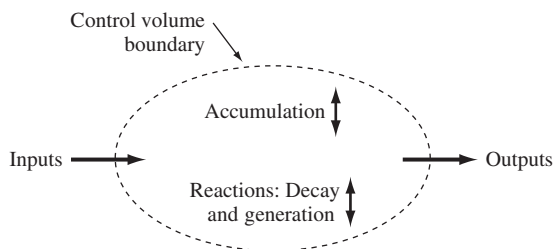
$$1 \text{ ppmv} = \frac{1 \text{ mol of pollutant}}{10^6 \text{ mol of air}} = \frac{1 \text{ molecule of pollutant}}{10^6 \text{ molecules of air}} \quad (11)$$

### 3 | Materials Balance

*Everything has to go somewhere* is a simple way to express one of the most fundamental engineering principles. More precisely, the *law of conservation of mass* says that when chemical reactions take place, matter is neither created nor destroyed (though in nuclear reactions, mass can be converted to energy). What this concept allows us to do is track materials, for example pollutants, from one place to another with *mass balance* equations. This is one of the most widely used tools in analyzing pollutants in the environment.

The first step in a mass balance analysis is to define the particular region in space that is to be analyzed. This is often called the control volume. As examples, the control volume might include anything from a glass of water or simple chemical mixing tank, to an entire coal-fired power plant, a lake, a stretch of stream, an air basin above a city, or the globe itself. By picturing an imaginary boundary around

## Mass and Energy Transfer



**FIGURE 1** A materials balance diagram.

the region, as is suggested in Figure 1, we can then begin to quantify the flow of materials across the boundary as well as the accumulation and reaction of materials within the region.

A substance that enters the control volume has four possible fates. Some of it may leave the region unchanged, some of it may accumulate within the boundary, and some of it may be converted to some other substance (*e.g.*, entering CO may be oxidized to CO<sub>2</sub> within the region). There is also the possibility that more substance may be produced (*e.g.*, CO may be produced by cigarette smoking within the control volume of a room). Often, the conversion and production processes that may occur are lumped into a single category termed *reactions*. Thus, using Figure 1 as a guide, the following materials balance equation can be written for each substance of interest:

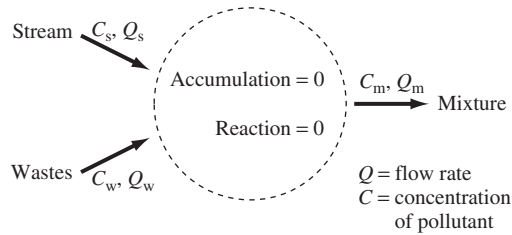
$$\left( \frac{\text{Accumulation}}{\text{rate}} \right) = \left( \frac{\text{Input}}{\text{rate}} \right) - \left( \frac{\text{Output}}{\text{rate}} \right) + \left( \frac{\text{Reaction}}{\text{rate}} \right) \quad (12)$$

The reaction rate may be positive if generation of the substance is faster than its decay, or negative if it is decaying faster than it is being produced. Likewise, the accumulation rate may be positive or negative. The *reaction* term in (12) does not imply a violation of the law of conservation of mass. Atoms are conserved, but there is no similar constraint on the chemical compounds, which may chemically change from one substance into another. It is also important to notice that each term in (12) quantifies a mass rate of change (*e.g.*, mg/s, lb/hr) and not a mass. Strictly, then, it is a mass rate balance rather than a mass balance, and (12) denotes that the rate of mass accumulation is equal to the difference between the rate the mass enters and leaves plus the net rate that the mass reacts within the defined control volume.

Frequently, (12) can be simplified. The most common simplification results when *steady state* or *equilibrium* conditions can be assumed. Equilibrium simply means that there is no accumulation of mass with time; the system has had its inputs held constant for a long enough time that any transients have had a chance to die out. Pollutant concentrations are constant. Hence the *accumulation rate* term in (12) is set equal to zero, and problems can usually be solved using just simple algebra.

A second simplification to (12) results when a substance is *conserved* within the region in question, meaning there is no reaction occurring—no radioactive decay, bacterial decomposition, or chemical decay or generation. For such conservative substances, the reaction rate in (12) is 0. Examples of substances that are typically modeled as conservative include total dissolved solids in a body of water, heavy metals in soils, and carbon dioxide in air. Radioactive radon gas in a home or

## Mass and Energy Transfer



**FIGURE 2** A steady-state conservative system. Pollutants enter and leave the region at the same rate.

decomposing organic wastes in a lake are examples of nonconservative substances. Often problems involving nonconservative substances can be simplified when the reaction rate is small enough to be ignored.

### Steady-State Conservative Systems

The simplest systems to analyze are those in which steady state can be assumed (so the accumulation rate equals 0), and the substance in question is conservative (so the reaction rate equals 0). In these cases, (12) simplifies to the following:

$$\text{Input rate} = \text{Output rate} \quad (13)$$

Consider the steady-state conservative system shown in Figure 2. The system contained within the boundaries might be a lake, a section of a free flowing stream, or the mass of air above a city. One input to the system is a stream (of water or air, for instance) with a flow rate  $Q_s$  (volume/time) and pollutant concentration  $C_s$  (mass/volume). The other input is assumed to be a waste stream with flow rate  $Q_w$  and pollutant concentration  $C_w$ . The output is a mixture with flow rate  $Q_m$  and pollutant concentration  $C_m$ . If the pollutant is conservative, and if we assume steady state conditions, then a mass balance based on (13) allows us to write the following:

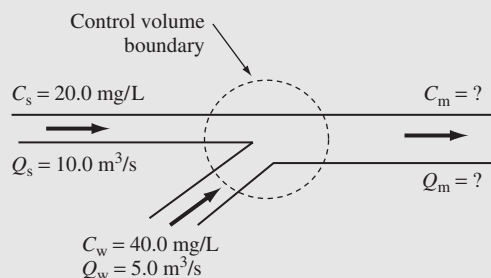
$$C_s Q_s + C_w Q_w = C_m Q_m \quad (14)$$

The following example illustrates the use of this equation. More importantly, it also provides a general algorithm for doing mass balance problems.

#### EXAMPLE 4 Two Polluted Streams

A stream flowing at  $10.0 \text{ m}^3/\text{s}$  has a tributary feeding into it with a flow of  $5.0 \text{ m}^3/\text{s}$ . The stream's concentration of chloride upstream of the junction is  $20.0 \text{ mg/L}$ , and the tributary chloride concentration is  $40.0 \text{ mg/L}$ . Treating chloride as a conservative substance and assuming complete mixing of the two streams, find the downstream chloride concentration.

**Solution** The first step in solving a mass balance problem is to sketch the problem, identify the “region” or control volume that we want to analyze, and label the variables as has been done in Figure 3 for this problem.



**FIGURE 3** Sketch of system, variables, and quantities for a stream and tributary mixing example.

Next the mass balance equation (12) is written and simplified to match the problem's conditions

$$\cancel{\left( \begin{array}{c} \text{Accumulation} \\ \text{rate} \end{array} \right)} = \left( \begin{array}{c} \text{Input} \\ \text{rate} \end{array} \right) - \left( \begin{array}{c} \text{Output} \\ \text{rate} \end{array} \right) + \cancel{\left( \begin{array}{c} \text{Reaction} \\ \text{rate} \end{array} \right)}$$

The simplified (12) is then written in terms of the variables in the sketch

$$0 = C_s Q_s + C_w Q_w - C_m Q_m$$

The next step is to rearrange the expression to solve for the variable of interest—in this case, the chloride concentration downstream of the junction,  $C_m$ . Note that since the mixture's flow is the sum of the two stream flows,  $Q_s + Q_w$  can be substituted for  $Q_m$  in this expression.

$$C_m = \frac{C_s Q_s + C_w Q_w}{Q_m} = \frac{C_s Q_s + C_w Q_w}{Q_s + Q_w}$$

The final step is to substitute the appropriate values for the known quantities into the expression, which brings us to a question of units. The units given for  $C$  are mg/L, and the units for  $Q$  are  $\text{m}^3/\text{s}$ . Taking the product of concentrations and flow rates yields mixed units of  $\text{mg/L} \cdot \text{m}^3/\text{s}$ , which we could simplify by applying the conversion factor of  $10^3 \text{ L} = 1 \text{ m}^3$ . However, if we did so, we should have to reapply that same conversion factor to get the mixture concentration back into the desired units of mg/L. In problems of this sort, it is much easier to simply leave the mixed units in the expression, even though they may look awkward at first, and let them work themselves out in the calculation. The downstream concentration of chloride is thus

$$C_m = \frac{(20.0 \times 10.0 + 40.0 \times 5.0) \text{ mg/L} \cdot \text{m}^3/\text{s}}{(10.0 + 5.0) \text{ m}^3/\text{s}} = 26.7 \text{ mg/L}$$

This stream mixing problem is relatively simple, whatever the approach used. Drawing the system, labeling the variables and parameters, writing and simplifying the mass balance equation, and then solving it for the variable of interest is the same approach that will be used to solve much more complex mass balance problems later in this chapter.

## Batch Systems with Nonconservative Pollutants

The simplest system with a nonconservative pollutant is a *batch system*. By definition, there is no contaminant flow into or out of a batch system, yet the contaminants in the system undergo chemical, biological, or nuclear reactions fast enough that they must be treated as nonconservative substances. A batch system (reactor) assumes that its contents are homogeneously distributed and is often referred to as a *completely mixed batch reactor* (CMBR). The bacterial concentration in a closed water storage tank may be considered a nonconservative pollutant in a batch reactor because it will change with time even though no water is fed into or withdrawn from the tank. Similarly, the concentration of carbon dioxide in a poorly ventilated room can be modeled as a nonconservative batch system because the concentration of carbon dioxide increases as people in the room breathe. For a batch reactor, (12) simplifies to

$$\text{Accumulation rate} = \text{Reaction rate} \quad (15)$$

As discussed before, the *reaction rate* is the sum of the *rates of decay*, which are negative, and the *rates of generation*, which are positive. Although the rates of reaction can exhibit many dependencies and complex relationships, most nuclear, chemical, and biochemical reaction rates can be approximated as either *zero-, first-, or second-order reaction rates*. In a zero-order reaction, the rate of reaction,  $r(C)$ , of the substance is not dependent on the amount of the substance present and can be expressed as

$$r(C) = k \text{ (generation)} \quad \text{or} \quad r(C) = -k \text{ (decay)} \quad (16)$$

where  $k$  is a reaction rate coefficient, which has the units of  $\text{mass} \cdot \text{volume}^{-1} \cdot \text{time}^{-1}$  (e.g.,  $\text{mg} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ ). The rate of evaporation of water from a bucket is a zero-order reaction because the rate of loss of the water is not dependent on the amount of water in the bucket but is only dependent on the nearly constant surface area of the water exposed to the air.

Using (15) and (16), the mass balance for the zero-order reaction of a substance in a batch reactor is

$$V \frac{dC}{dt} = -Vk$$

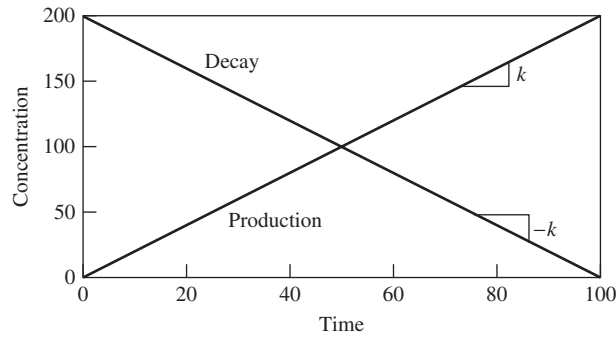
The equation is written as a zero-order decay, denoted by the negative sign on the right-hand side of the equation. So that each term in the mass balance has the correct units of mass/time, both the accumulation and reaction terms are multiplied by the volume of the batch reactor. Although in a batch system, the volume coefficient disappears by dividing both sides by  $V$ , it is worth remembering its presence in the initial balance equation because in other systems it may not cancel out. To solve the differential equation, the variables are separated and integrated as

$$\int_{C_0}^C dC = -k \int_0^t dt \quad (17)$$

which yields

$$C - C_0 = -kt$$

## Mass and Energy Transfer



**FIGURE 4** Concentration of a substance reacting in a batch system with zero-order kinetics.

Solving for concentration gives us

$$C = C_0 - kt \quad (18)$$

where  $C_0$  is the initial concentration. Using (18) and its analog for a zero-order generation reaction, Figure 4 shows how the concentration of a substance will change with time, if it is reacting (either being generated or destroyed) with zero-order kinetics.

For all nonconservative pollutants undergoing a reaction other than zero-order, the rate of the reaction is dependent on the concentration of the pollutant present. Although decay and generation rates may be any order, the most commonly encountered reaction rate for generation is zero-order, whereas for decay it is first-order. The first-order reaction rate is

$$r(C) = kC \text{ (generation)} \quad \text{or} \quad r(C) = -kC \text{ (decay)} \quad (19)$$

where  $k$  is still a reaction rate constant, but now has the units of reciprocal time ( $\text{time}^{-1}$ ). Radioactive decay of radon gas follows first-order decay—the mass that decays per given time is directly proportional to the mass that is originally present. Using (15) and (19), the mass balance for a pollutant undergoing first-order decay in a batch reactor is

$$V \frac{dC}{dt} = -VkC$$

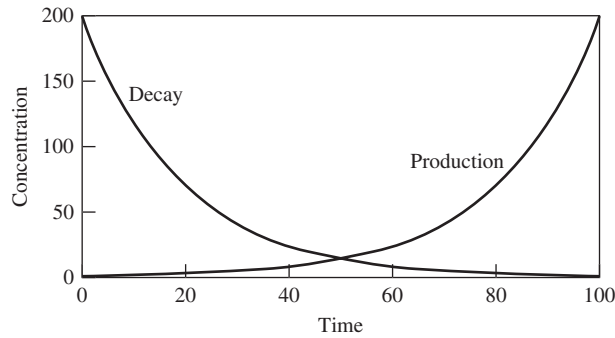
This equation can be integrated by separation of variables and solved similarly to (17). When solved for concentration, it yields

$$C = C_0 e^{-kt} \quad (20)$$

That is, assuming a first-order reaction, the concentration of the substance in question decays exponentially. The first-order time dependence of a nonconservative pollutant's concentration in a batch system can be seen in Figure 5.

Although not nearly as common as first-order processes, sometimes a substance will decay or be generated by a second-order process. For instance, hydroxyl





**FIGURE 5** Concentration of a substance reacting in a batch system with first-order kinetics.

radical reactions with volatile organic pollutants is a key step in smog generation. However, if two hydroxyl radicals collide and react, they form a much less potent hydrogen peroxide molecule. This is a second-order reaction, since two hydroxyl radicals are consumed for each hydrogen peroxide produced. The second-order reaction rate is

$$r(C) = kC^2 \text{ (generation) or } r(C) = -kC^2 \text{ (decay)} \quad (21)$$

where  $k$  is now a reaction rate constant with units of  $(\text{volume} \cdot \text{mass}^{-1} \cdot \text{time}^{-1})$ . Again substituting (21) into (15), we have the differential equation for the second-order decay of a nonconservative substance in a batch reactor

$$V \frac{dC}{dt} = -V k C^2$$

which can be integrated and then solved for the concentration to yield

$$C = \frac{C_0}{1 + C_0 k t} \quad (22)$$

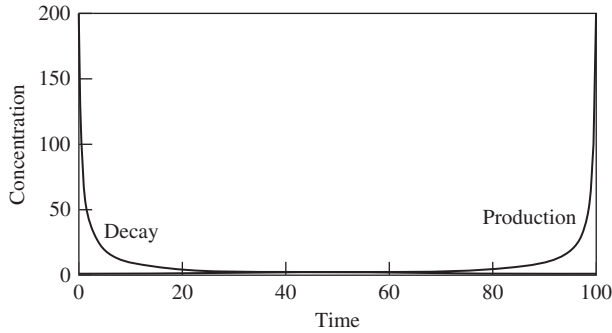
Figure 6 shows how the concentration of a substance changes with time if it decays or is produced by a second-order reaction in a batch reactor.

### Steady-State Systems with Nonconservative Pollutants

If we assume that steady-state conditions prevail and treat the pollutants as nonconservative, then (12) becomes

$$0 = \text{Input rate} - \text{Output rate} + \text{Reaction rate} \quad (23)$$

The batch reactor, which has just been discussed, can't describe a steady-state system with a nonconservative substance because now there is input and output. Although there are an infinite number of other possible types of reactors, simply employing two other types of ideal reactors allows us to model a great number of environmental processes. The type of mixing in the system distinguishes between the



**FIGURE 6** Concentration of a substance reacting in a batch system with second-order kinetics.

two other ideal reactors. In the first, the substances within the system are still homogeneously mixed as in a batch reactor. Such a system is variously termed a *continuously stirred tank reactor* (CSTR), a perfectly mixed flow reactor, and a complete mix box model. The water in a shallow pond with an inlet and outlet is typically modeled as a CSTR as is the air within a well-ventilated room. The key concept is that the concentration,  $C$ , within the CSTR container is uniform throughout. We'll give examples of CSTR behavior first and later discuss the other ideal reactor model that is often used, the *plug flow reactor* (PFR).

The reaction rate term in the right-hand side of (23) can denote either a substance's decay or generation (by making it positive or negative) and, for most environmental purposes, its rate can be approximated as either zero-, first-, or second-order. Just as for the batch reactor, for a CSTR, we assume the substance is uniformly distributed throughout a volume  $V$ , so the total amount of substance is  $CV$ . The total rate of reaction of the amount of a nonconservative substance is thus  $d(CV)/dt = V dC/dt = Vr(C)$ . So summarizing (16), (19), and (21), we can write the reaction rate expressions for a nonconservative substance:

$$\text{Zero-order, decay rate} = -Vk \quad (24)$$

$$\text{Zero-order, generation rate} = Vk \quad (25)$$

$$\text{First-order, decay rate} = -VkC \quad (26)$$

$$\text{First-order, generation rate} = VkC \quad (27)$$

$$\text{Second-order, decay rate} = -VkC^2 \quad (28)$$

$$\text{Second-order, generation rate} = VkC^2 \quad (29)$$

Thus, for example, to model a CSTR containing a substance that is decaying with a second-order rate, we combine (23) with (28) to get a final, simple, and useful expression for the mass balance involving a nonconservative pollutant in a steady-state, CSTR system:

$$\text{Input rate} = \text{Output rate} + kC^2V \quad (30)$$

### EXAMPLE 5 A Polluted Lake

Consider a  $10 \times 10^6 \text{ m}^3$  lake fed by a polluted stream having a flow rate of  $5.0 \text{ m}^3/\text{s}$  and pollutant concentration equal to  $10.0 \text{ mg/L}$  (Figure 7). There is also a sewage outfall that discharges  $0.5 \text{ m}^3/\text{s}$  of wastewater having a pollutant concentration of  $100 \text{ mg/L}$ . The stream and sewage wastes have a decay rate coefficient of  $0.20/\text{day}$ . Assuming the pollutant is completely mixed in the lake and assuming no evaporation or other water losses or gains, find the steady-state pollutant concentration in the lake.

**Solution** We can conveniently use the lake in Figure 7 as our control volume. Assuming that complete and instantaneous mixing occurs in the lake—it acts as a CSTR—implies that the concentration in the lake,  $C$ , is the same as the concentration of the mix leaving the lake,  $C_m$ . The units ( $\text{day}^{-1}$ ) of the reaction rate constant indicate this is a first-order reaction. Using (23) and (26):

$$\text{Input rate} = \text{Output rate} + kCV \quad (31)$$

We can find each term as follows:

There are two input sources, so the total input rate is

$$\text{Input rate} = Q_s C_s + Q_w C_w$$

The output rate is

$$\text{Output rate} = Q_m C_m = (Q_s + Q_w)C$$

(31) then becomes

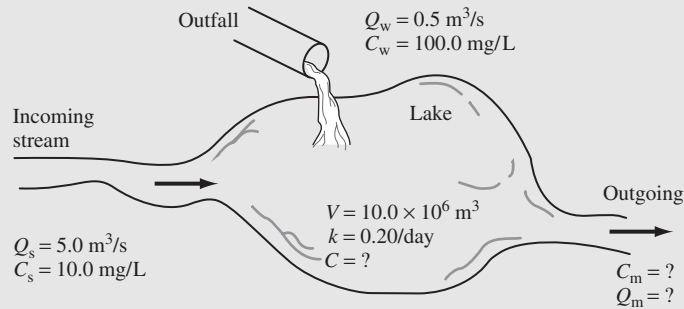
$$Q_s C_s + Q_w C_w = (Q_s + Q_w)C + kCV$$

And rearranging to solve for  $C$ ,

$$\begin{aligned} C &= \frac{Q_s C_s + Q_w C_w}{Q_s + Q_w + kV} \\ &= \frac{5.0 \text{ m}^3/\text{s} \times 10.0 \text{ mg/L} + 0.5 \text{ m}^3/\text{s} \times 100.0 \text{ mg/L}}{(5.0 + 0.5) \text{ m}^3/\text{s} + \frac{0.20/\text{d} \times 10.0 \times 10^6 \text{ m}^3}{24 \text{ hr/d} \times 3600 \text{ s/hr}}} \end{aligned}$$

So,

$$C = \frac{100}{28.65} = 3.5 \text{ mg/L}$$



**FIGURE 7** A lake with a nonconservative pollutant.

Idealized models involving nonconservative pollutants in completely mixed, steady-state systems are used to analyze a variety of commonly encountered water pollution problems such as the one shown in the previous example. The same simple models can be applied to certain problems involving air quality, as the following example demonstrates.

### EXAMPLE 6 A Smoky Bar

A bar with volume  $500 \text{ m}^3$  has 50 smokers in it, each smoking 2 cigarettes per hour (see Figure 8). An individual cigarette emits, among other things, about  $1.4 \text{ mg}$  of formaldehyde ( $\text{HCHO}$ ). Formaldehyde converts to carbon dioxide with a reaction rate coefficient  $k = 0.40/\text{hr}$ . Fresh air enters the bar at the rate of  $1,000 \text{ m}^3/\text{hr}$ , and stale air leaves at the same rate. Assuming complete mixing, estimate the steady-state concentration of formaldehyde in the air. At  $25^\circ\text{C}$  and  $1 \text{ atm}$  of pressure, how does the result compare with the threshold for eye irritation of  $0.05 \text{ ppm}$ ?

**Solution** The bar's building acts as a CSTR reactor, and the complete mixing inside means the concentration of formaldehyde  $C$  in the bar is the same as the concentration in the air leaving the bar. Since the formaldehyde concentration in fresh air can be considered 0, the input rate in (23) is also 0. Our mass balance equation is then

$$\text{Output rate} = \text{Reaction rate} \quad (32)$$

However, both a generation term (the cigarette smoking) and a decay term (the conversion of formaldehyde to carbon dioxide) are contributing to the reaction rate. If we call the generation rate,  $G$ , we can write

$$G = 50 \text{ smokers} \times 2 \text{ cigs/hr} \times 1.4 \text{ mg/cig} = 140 \text{ mg/hr}$$

We can then express (32) in terms of the problem's variables and (26) as

$$QC = G - kCV$$

so

$$C = \frac{G}{Q + kV} = \frac{140 \text{ mg/hr}}{1,000 \text{ m}^3/\text{hr} + (0.40/\text{hr}) \times 500 \text{ m}^3} = 0.117 \text{ mg/m}^3$$

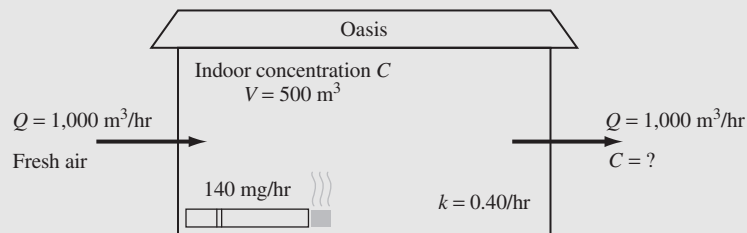


FIGURE 8 Tobacco smoke in a bar.

We will use (9) to convert  $\text{mg/m}^3$  to ppm. The molecular weight of formaldehyde is 30, so

$$\text{HCHO} = \frac{C (\text{mg/m}^3) \times 24.465}{\text{mol wt}} = \frac{0.117 \times 24.465}{30} = 0.095 \text{ ppm}$$

This is nearly double the 0.05 ppm threshold for eye irritation.

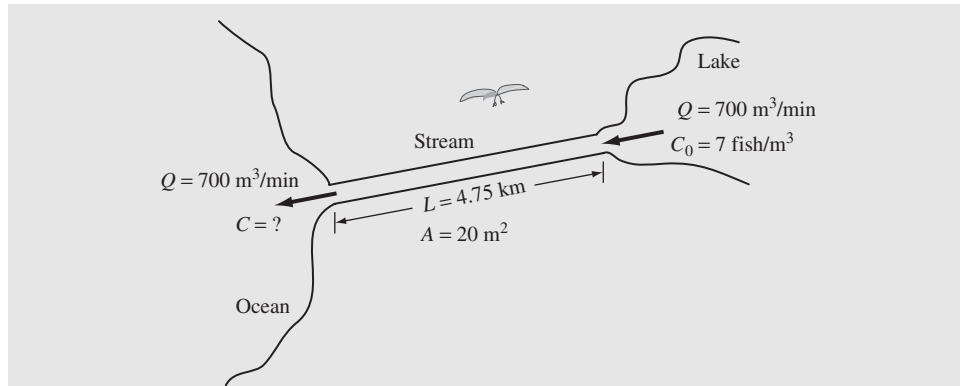
Besides a CSTR, the other type of ideal reactor that is often useful to model pollutants as they flow through a system is a *plug flow reactor* (PFR). A PFR can be visualized as a long pipe or channel in which there is no mixing of the pollutant along its length between the inlet and outlet. A PFR could also be seen as a conveyor belt carrying a single-file line of bottles in which reactions can happen within each bottle, but there is no mixing of the contents of one bottle with another. The behavior of a pollutant being carried in a river or in the jet stream in the Earth's upper atmosphere could be usefully represented as a PFR system. The key difference between a PFR and CSTR is that in a PFR, there is no mixing of one parcel of fluid with other parcels in front or in back of it in the control volume, whereas in a CSTR, all of the fluid in the container is continuously and completely mixed. (23) applies to both a CSTR and PFR at steady state, but for a PFR, we cannot make the simplification that the concentration everywhere in the control volume and in the fluid leaving the region is the same, as we did in the CSTR examples. The pollutant concentration in a parcel of fluid changes as the parcel progresses through the PFR. Intuitively, it can then be seen that a PFR acts like a conveyor belt of differentially thin batch reactors translating through the control volume. When the pollutant enters the PFR at concentration,  $C_0$ , then it will take a given time,  $t$ , to move the length of the control volume and will leave the PFR with a concentration just as it would if it had been in a batch reactor for that period of time. Thus, a substance decaying with a zero-, first-, or second-order rate will leave a PFR with a concentration given by (18), (20), and (22), respectively, with the understanding that  $t$  in each equation is the residence time of the fluid in the control volume and is given by

$$t = l/v = V/Q \quad (33)$$

where  $l$  is the length of the PFR,  $v$  is the fluid velocity,  $V$  is the PFR control volume, and  $Q$  is the fluid flowrate.

### EXAMPLE 7 Young Salmon Migration

Every year, herons, seagulls, eagles, and other birds mass along a 4.75 km stretch of stream connecting a lake to the ocean to catch the fingerling salmon as they migrate downstream to the sea. The birds are efficient fishermen and will consume 10,000 fingerlings per kilometer of stream each hour regardless of the number of the salmon in the stream. In other words, there are enough salmon; the birds are only limited by how fast they can catch and eat the fish. The stream's average cross-sectional area is  $20 \text{ m}^2$ , and the salmon move downstream with the stream's flow rate of  $700 \text{ m}^3/\text{min}$ . If there are 7 fingerlings per  $\text{m}^3$  in the water entering the stream, what is the concentration of salmon that reach the ocean when the birds are feeding?



**FIGURE 9** Birds fishing along a salmon stream.

**Solution** First we draw a figure depicting the stream as the control volume and the variables (Figure 9).

Since the birds eat the salmon at a steady rate that is not dependent on the concentration of salmon in the stream, the rate of salmon consumption is zero-order. So,

$$k = \frac{10,000 \text{ fish} \cdot \text{km}^{-1} \cdot \text{hr}^{-1}}{20 \text{ m}^2 \times 1,000 \text{ m/km}} = 0.50 \text{ fish} \cdot \text{m}^{-3} \cdot \text{hr}^{-1}$$

For a steady-state PFR, (23) becomes (18),

$$C = C_0 - kt$$

The residence time,  $t$ , of the stream can be calculated using (33) as

$$t = \frac{V}{Q} = \frac{4.75 \text{ km} \times 20 \text{ m}^2 \times 1,000 \text{ m/km}}{700 \text{ m}^3/\text{min} \times 60 \text{ min/hr}} = 2.26 \text{ hr}$$

and the concentration of fish reaching the ocean is

$$C = 7 \text{ fish/m}^3 - 0.50 \text{ fish} \cdot \text{m}^{-3} \cdot \text{hr}^{-1} \times 2.26 \text{ hr} = 5.9 \text{ fish/m}^3$$

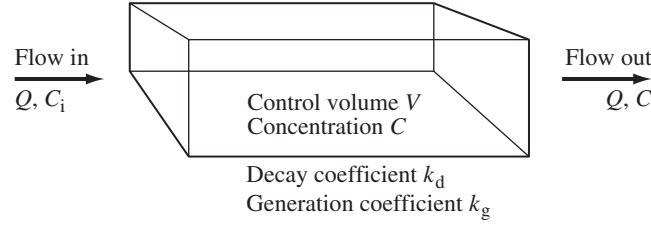
## Step Function Response

So far, we have computed steady-state concentrations in environmental systems that are contaminated with either conservative or nonconservative pollutants. Let us now extend the analysis to include conditions that are not steady state. Quite often, we will be interested in how the concentration will change with time when there is a sudden change in the amount of pollution entering the system. This is known as the *step function response* of the system.

In Figure 10, the environmental system to be modeled has been drawn as if it were a box of volume  $V$  that has flow rate  $Q$  in and out of the box.

Let us assume the contents of the box are at all times completely mixed (a CSTR model) so that the pollutant concentration  $C$  in the box is the same as the concentration leaving the box. The total mass of pollutant in the box is therefore

## Mass and Energy Transfer



**FIGURE 10** A box model for a transient analysis.

$VC$ , and the rate of accumulation of pollutant in the box is  $VdC/dt$ . Let us designate the concentration of pollutant entering the box as  $C_i$ . We'll also assume there are both production and decay components of the reaction rate and designate the decay coefficient  $k_d$  and the generation coefficient  $k_g$ . However, as is most common, the decay will be first-order, so  $k_d$ 's units are  $\text{time}^{-1}$ , whereas the generation is zero-order, so  $k_g$ 's units are  $\text{mass} \cdot \text{volume}^{-1} \cdot \text{time}^{-1}$ . From (12), we can write

$$\left( \begin{array}{c} \text{Accumulation} \\ \text{rate} \end{array} \right) = \left( \begin{array}{c} \text{Input} \\ \text{rate} \end{array} \right) - \left( \begin{array}{c} \text{Output} \\ \text{rate} \end{array} \right) + \left( \begin{array}{c} \text{Reaction} \\ \text{rate} \end{array} \right)$$

$$V \frac{dC}{dt} = QC_i - QC - Vk_dC + k_gV \quad (34)$$

where

- $V$  = box volume ( $\text{m}^3$ )
- $C$  = concentration in the box and exiting waste stream ( $\text{g}/\text{m}^3$ )
- $C_i$  = concentration of pollutants entering the box ( $\text{g}/\text{m}^3$ )
- $Q$  = the total flow rate in and out of the box ( $\text{m}^3/\text{hr}$ )
- $k_d$  = decay rate coefficient ( $\text{hr}^{-1}$ )
- $k_g$  = production rate coefficient ( $\text{g} \cdot \text{m} \cdot \text{hr}^{-1}$ )

The units given in the preceding list are representative of those that might be encountered; any consistent set will do.

An easy way to find the steady-state solution to (34) is simply to set  $dC/dt = 0$ , which yields

$$C_\infty = \frac{QC_i + k_gV}{Q + k_dV} \quad (35)$$

where  $C_\infty$  is the concentration in the box at time  $t = \infty$ . Our concern now, though, is with the concentration before it reaches steady state, so we must solve (34). Rearranging (34) gives

$$\frac{dC}{dt} = -\left(\frac{Q}{V} + k_d\right) \cdot \left(C - \frac{QC_i + k_gV}{Q + k_dV}\right) \quad (36)$$

which, using (35), can be rewritten as

$$\frac{dC}{dt} = -\left(\frac{Q}{V} + k_d\right) \cdot (C - C_\infty) \quad (37)$$

One way to solve this differential equation is to make a change of variable. If we let

$$y = C - C_\infty \quad (38)$$

then

$$\frac{dy}{dt} = \frac{dC}{dt} \quad (39)$$

so (37) becomes

$$\frac{dy}{dt} = -\left(\frac{Q}{V} + k_d\right)y \quad (40)$$

This is a differential equation, which we can solve by separating the variables to give

$$\int_{y_0}^y dy = -\left(\frac{Q}{V} + k_d\right) \int_0^t dt \quad (41)$$

where  $y_0$  is the value of  $y$  at  $t = 0$ . Integrating gives

$$y = y_0 e^{-(k_d + \frac{Q}{V})t} \quad (42)$$

If  $C_0$  is the concentration in the box at time  $t = 0$ , then from (38) we get

$$y_0 = C_0 - C_\infty \quad (43)$$

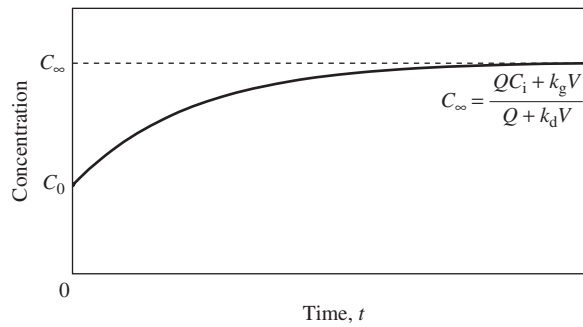
Substituting (38) and (43) into (42) yields

$$C - C_\infty = (C_0 - C_\infty) e^{-(k_d + \frac{Q}{V})t} \quad (44)$$

Solving for the concentration in the box, writing it as a function of time  $C(t)$ , and expressing the exponential as  $\exp(\ )$  gives

$$C(t) = C_\infty + (C_0 - C_\infty) \exp\left[-\left(k_d + \frac{Q}{V}\right)t\right] \quad (45)$$

Equation (45) should make some sense. At time  $t = 0$ , the exponential function equals 1 and  $C = C_0$ . At  $t = \infty$ , the exponential term equals 0, and  $C = C_\infty$ . Equation (45) is plotted in Figure 11.



**FIGURE 11** Step function response for the CSTR box model.



**EXAMPLE 8 The Smoky Bar Revisited**

The bar in Example 6 had volume  $500 \text{ m}^3$  with fresh air entering at the rate of  $1,000 \text{ m}^3/\text{hr}$ . Suppose when the bar opens at 5 P.M., the air is clean. If formaldehyde, with decay rate  $k_d = 0.40/\text{hr}$ , is emitted from cigarette smoke at the constant rate of  $140 \text{ mg/hr}$  starting at 5 P.M., what would the concentration be at 6 P.M.?

**Solution** In this case,  $Q = 1,000 \text{ m}^3/\text{hr}$ ,  $V = 500 \text{ m}^3$ ,  $G = k_g V = 140 \text{ mg/hr}$ ,  $C_i = 0$ , and  $k_d = 0.40/\text{hr}$ . The steady-state concentration is found using (35):

$$\begin{aligned} C_\infty &= \frac{QC_i + k_g V}{Q + k_d V} = \frac{G}{Q + k_d V} = \frac{140 \text{ mg/hr}}{1,000 \text{ m}^3/\text{hr} + 0.40/\text{hr} \times 500 \text{ m}^3} \\ &= 0.117 \text{ mg/m}^3 \end{aligned}$$

This agrees with the result obtained in Example 6. To find the concentration at any time after 5 P.M., we can apply (45) with  $C_0 = 0$ .

$$\begin{aligned} C(t) &= C_\infty \left\{ 1 - \exp \left[ - \left( k_d + \frac{Q}{V} \right) t \right] \right\} \\ &= 0.117 [1 - \exp[-(0.40 + 1,000/500)t]] \end{aligned}$$

at 6 P.M.,  $t = 1 \text{ hr}$ , so

$$C(1 \text{ hr}) = 0.117 [1 - \exp(-2.4 \times 1)] = 0.106 \text{ mg/m}^3$$

To further demonstrate the use of (45), let us reconsider the lake analyzed in Example 5. This time we will assume that the outfall suddenly stops draining into the lake, so its contribution to the lake's pollution stops.

**EXAMPLE 9 A Sudden Decrease in Pollutants Discharged into a Lake**

Consider the  $10 \times 10^6 \text{ m}^3$  lake analyzed in Example 5 which, under a conditions given, was found to have a steady-state pollution concentration of  $3.5 \text{ mg/L}$ . The pollution is nonconservative with reaction-rate constant  $k_d = 0.20/\text{day}$ . Suppose the condition of the lake is deemed unacceptable. To solve the problem, it is decided to completely divert the sewage outfall from the lake, eliminating it as a source of pollution. The incoming stream still has flow  $Q_s = 5.0 \text{ m}^3/\text{s}$  and concentration  $C_s = 10.0 \text{ mg/L}$ . With the sewage outfall removed, the outgoing flow  $Q$  is also  $5.0 \text{ m}^3/\text{s}$ . Assuming complete-mix conditions, find the concentration of pollutant in the lake one week after the diversion, and find the new final steady-state concentration.

**Solution** For this situation,

$$C_0 = 3.5 \text{ mg/L}$$

$$V = 10 \times 10^6 \text{ m}^3$$

$$Q = Q_s = 5.0 \text{ m}^3/\text{s} \times 3,600 \text{ s/hr} \times 24 \text{ hr/day} = 43.2 \times 10^4 \text{ m}^3/\text{day}$$

$$C_s = 10.0 \text{ mg/L} = 10.0 \times 10^3 \text{ mg/m}^3$$

$$k_d = 0.20/\text{day}$$

The total rate at which pollution is entering the lake from the incoming stream is

$$Q_s C_s = 43.2 \times 10^4 \text{ m}^3/\text{day} \times 10.0 \times 10^3 \text{ mg/m}^3 = 43.2 \times 10^8 \text{ mg/day}$$

The steady-state concentration can be obtained from (35)

$$C_\infty = \frac{Q C_s}{Q + k_d V} = \frac{43.2 \times 10^8 \text{ mg/day}}{43.2 \times 10^4 \text{ m}^3/\text{day} + 0.20/\text{day} \times 10^7 \text{ m}^3}$$

$$= 1.8 \times 10^3 \text{ mg/m}^3 = 1.8 \text{ mg/L}$$

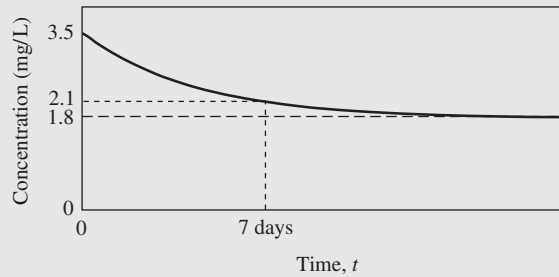
Using (45), we can find the concentration in the lake one week after the drop in pollution from the outfall:

$$C(t) = C_\infty + (C_0 - C_\infty) \exp \left[ - \left( k_d + \frac{Q}{V} \right) t \right]$$

$$C(7 \text{ days}) = 1.8 + (3.5 - 1.8) \exp \left[ - \left( 0.2/\text{day} + \frac{43.2 \times 10^4 \text{ m}^3/\text{day}}{10 \times 10^6 \text{ m}^3} \right) \times 7 \text{ days} \right]$$

$$C(7 \text{ days}) = 2.1 \text{ mg/L}$$

Figure 12 shows the decrease in contaminant concentration for this example.



**FIGURE 12** The contaminant concentration profile for Example 9.

## 4 Energy Fundamentals

Just as we are able to use the law of conservation of mass to write mass balance equations that are fundamental to understanding and analyzing the flow of materials, we can use the *first law of thermodynamics* to write energy balance equations that will help us analyze energy flows.

One definition of *energy* is that it is the capacity for doing work, where *work* can be described by the product of force and the displacement of an object caused by that force. A simple interpretation of the *second law of thermodynamics* suggests that when work is done, there will always be some inefficiency, that is, some portion of the energy put into the process will end up as waste heat. How that waste heat

affects the environment is an important consideration in the study of environmental engineering and science.

Another important term to be familiar with is *power*. Power is the *rate* of doing work. It has units of energy per unit of time. In SI units, power is given in joules per second (J/s) or kilojoules per second (kJ/s). To honor the Scottish engineer James Watt, who developed the reciprocating steam engine, the joule per second has been named the watt ( $1 \text{ J/s} = 1 \text{ W} = 3.412 \text{ Btu/hr}$ ).

## The First Law of Thermodynamics

The first law of thermodynamics says, simply, that energy can neither be created nor destroyed. Energy may change forms in any given process, as when chemical energy in a fuel is converted to heat and electricity in a power plant or when the potential energy of water behind a dam is converted to mechanical energy as it spins a turbine in a hydroelectric plant. No matter what is happening, the first law says we should be able to account for every bit of energy as it takes part in the process under study, so that in the end, we have just as much as we had in the beginning. With proper accounting, even nuclear reactions involving conversion of mass to energy can be treated.

To apply the first law, it is necessary to define the system being studied, much as was done in the analysis of mass flows. The system (control volume) can be anything that we want to draw an imaginary boundary around; it can be an automobile engine, or a nuclear power plant, or a volume of gas emitted from a smokestack. Later when we explore the topic of global temperature equilibrium, the system will be the Earth itself. After a boundary has been defined, the rest of the universe becomes the *surroundings*. Just because a boundary has been defined, however, does not mean that energy and/or materials cannot flow across that boundary. Systems in which both energy and matter can flow across the boundary are referred to as *open systems*, whereas those in which energy is allowed to flow across the boundary, but matter is not, are called *closed systems*.

Since energy is conserved, we can write the following for whatever system we have defined:

$$\left( \begin{array}{c} \text{Total energy} \\ \text{crossing boundary} \\ \text{as heat and work} \end{array} \right) + \left( \begin{array}{c} \text{Total energy} \\ \text{of mass} \\ \text{entering system} \end{array} \right) - \left( \begin{array}{c} \text{Total energy} \\ \text{of mass} \\ \text{leaving system} \end{array} \right) = \left( \begin{array}{c} \text{Net change} \\ \text{of energy in} \\ \text{the system} \end{array} \right) \quad (46)$$

For closed systems, there is no movement of mass across the boundary, so the second and third term drop out of the equation. The accumulation of energy represented by the right side of (46) may cause changes in the observable, macroscopic forms of energy, such as kinetic and potential energies, or microscopic forms related to the atomic and molecular structure of the system. Those microscopic forms of energy include the kinetic energies of molecules and the energies associated with the forces acting between molecules, between atoms within molecules, and within atoms. The sum of those microscopic forms of energy is called the system's *internal energy* and is represented by the symbol  $U$ . The *total energy*  $E$  that a substance possesses can be described then as the sum of its internal energy  $U$ , its kinetic energy  $KE$ , and its potential energy  $PE$ :

$$E = U + KE + PE \quad (47)$$

In many applications of (46), the net energy added to a system will cause an increase in temperature. Waste heat from a power plant, for example, will raise the temperature of cooling water drawn into its condenser. The amount of energy needed to raise the temperature of a unit mass of a substance by 1 degree is called the *specific heat*. The specific heat of water is the basis for two important units of energy, namely the *British thermal unit* (Btu), which is defined to be the energy required to raise 1 lb of water by 1°F, and the *kilocalorie*, which is the energy required to raise 1 kg of water by 1°C. In the definitions just given, the assumed temperature of the water is 15°C (59°F). Since kilocalories are no longer a preferred energy unit, values of specific heat in the SI system are given in kJ/kg°C, where 1 kcal/kg°C = 1 Btu/lb°F = 4.184 kJ/kg°C.

For most applications, the specific heat of a liquid or solid can be treated as a simple quantity that varies slightly with temperature. For gases, on the other hand, the concept of specific heat is complicated by the fact that some of the heat energy absorbed by a gas may cause an increase in temperature, and some may cause the gas to expand, doing work on its environment. That means it takes more energy to raise the temperature of a gas that is allowed to expand than the amount needed if the gas is kept at constant volume. The *specific heat at constant volume*  $c_v$  is used when a gas does not change volume as it is heated or cooled, or if the volume is allowed to vary but is brought back to its starting value at the end of the process. Similarly, the *specific heat at constant pressure*  $c_p$  applies for systems that do not change pressure. For incompressible substances, that is, liquids and solids under the usual circumstances,  $c_v$  and  $c_p$  are identical. For gases,  $c_p$  is greater than  $c_v$ .

The added complications associated with systems that change pressure and volume are most easily handled by introducing another thermodynamic property of a substance called *enthalpy*. The enthalpy  $H$  of a substance is defined as

$$H = U + PV \quad (48)$$

where  $U$  is its internal energy,  $P$  is its pressure, and  $V$  is its volume. The enthalpy of a unit mass of a substance depends only on its temperature. It has energy units (kJ or Btu) and historically was referred to as a system's "heat content." Since heat is correctly defined only in terms of energy transfer across a system's boundaries, heat content is a somewhat misleading descriptor and is not used much anymore.

When a process occurs without a change of volume, the relationship between internal energy and temperature change is given by

$$\Delta U = m c_v \Delta T \quad (49)$$

The analogous equation for changes that occur under constant pressure involves enthalpy

$$\Delta H = m c_p \Delta T \quad (50)$$

For many environmental systems, the substances being heated are solids or liquids for which  $c_v = c_p = c$  and  $\Delta U = \Delta H$ . We can write the following equation for the energy needed to raise the temperature of mass  $m$  by an amount  $\Delta T$ :

$$\text{Change in stored energy} = m c \Delta T \quad (51)$$

Table 3 provides some examples of specific heat for several selected substances. It is worth noting that water has by far the highest specific heat of the substances listed; in fact, it is higher than almost all common substances. This is one

TABLE 3

| <b>Specific Heat Capacity <math>c</math> of Selected Substances</b> |                       |           |
|---------------------------------------------------------------------|-----------------------|-----------|
|                                                                     | (kcal/kg°C, Btu/lb°F) | (kJ/kg°C) |
| Water (15°C)                                                        | 1.00                  | 4.18      |
| Air                                                                 | 0.24                  | 1.01      |
| Aluminum                                                            | 0.22                  | 0.92      |
| Copper                                                              | 0.09                  | 0.39      |
| Dry soil                                                            | 0.20                  | 0.84      |
| Ice                                                                 | 0.50                  | 2.09      |
| Steam (100°C) <sup>a</sup>                                          | 0.48                  | 2.01      |
| Water vapor (20°C) <sup>a</sup>                                     | 0.45                  | 1.88      |

<sup>a</sup>Constant pressure values.

of water's very unusual properties and is in large part responsible for the major effect the oceans have on moderating temperature variations of coastal areas.

**EXAMPLE 10 A Water Heater**

How long would it take to heat the water in a 40-gallon electric water heater from 50°F to 140°F if the heating element delivers 5 kW? Assume all of the electrical energy is converted to heat in the water, neglect the energy required to raise the temperature of the tank itself, and neglect any heat losses from the tank to the environment.

**Solution** The first thing to note is that the electric input is expressed in kilowatts, which is a measure of the *rate* of energy input (*i.e.*, power). To get total energy delivered to the water, we must multiply rate by time. Letting  $\Delta t$  be the number of hours that the heating element is on gives

$$\text{Energy input} = 5 \text{ kW} \times \Delta t \text{ hrs} = 5\Delta t \text{ kWhr}$$

Assuming no losses from the tank and no water withdrawn from the tank during the heating period, there is no energy output:

$$\text{Energy output} = 0$$

The change in energy stored corresponds to the water warming from 50°F to 140°F. Using (51) along with the fact that water weighs 8.34 lb/gal gives

$$\begin{aligned} \text{Change in stored energy} &= mc\Delta T \\ &= 40 \text{ gal} \times 8.34 \text{ lb/gal} \times 1 \text{ Btu/lb°F} \times (140 - 50)°\text{F} \\ &= 30 \times 10^3 \text{ Btu} \end{aligned}$$

Setting the energy input equal to the change in internal energy and converting units using Table 1 yields

$$\begin{aligned} 5\Delta t \text{ kWhr} \times 3,412 \text{ Btu/kWhr} &= 30 \times 10^3 \text{ Btu} \\ \Delta t &= 1.76 \text{ hr} \end{aligned}$$

There are two key assumptions implicit in (51). First, the specific heat is assumed to be constant over the temperature range in question, although in actuality it does vary slightly. Second, (51) assumes that there is no change of *phase* as would occur if the substance were to freeze or melt (liquid-solid phase change) or evaporate or condense (liquid-gas phase change).

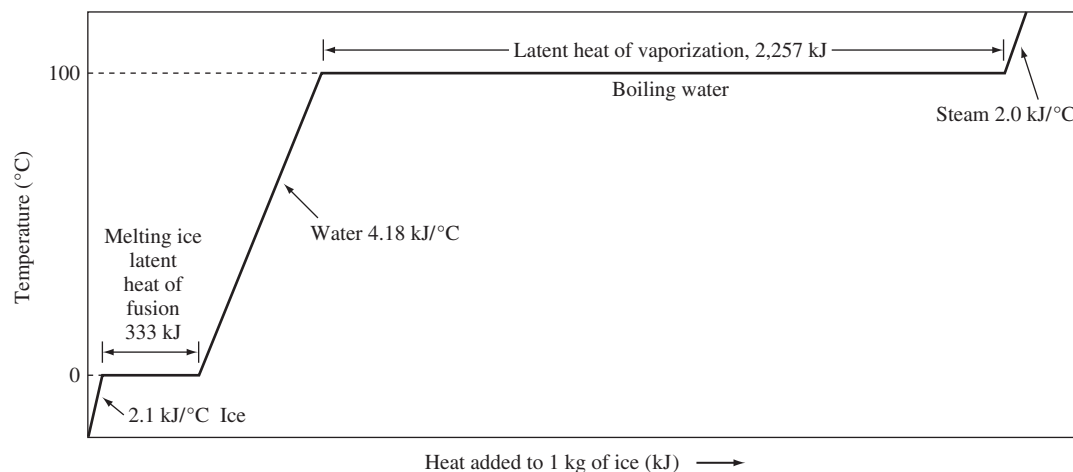
When a substance changes phase, energy is absorbed or released without a change in temperature. The energy required to cause a phase change of a unit mass from solid to liquid (melting) at the same pressure is called the *latent heat of fusion* or, more correctly, the *enthalpy of fusion*. Similarly, the energy required to change phase from liquid to vapor at constant pressure is called the *latent heat of vaporization* or the *enthalpy of vaporization*. For example, 333 kJ will melt 1 kg of ice (144 Btu/lb), whereas 2,257 kJ are required to convert 1 kg of water at 100°C to steam (970 Btu/lb). When steam condenses or when water freezes, those same amounts of energy are released. When a substance changes temperature as heat is added, the process is referred to as *sensible heating*. When the addition of heat causes a phase change, as is the case when ice is melting or water is boiling, the addition is called *latent heat*. To account for the latent heat stored in a substance, we can include the following in our energy balance:

$$\text{Energy released or absorbed in phase change} = mL \quad (52)$$

where  $m$  is the mass and  $L$  is the latent heat of fusion or vaporization.

Figure 13 illustrates the concepts of latent heat and specific heat for water as it passes through its three phases from ice, to water, to steam.

Values of specific heat, heats of vaporization and fusion, and density for water are given in Table 4 for both SI and USCS units. An additional entry has been included in the table that shows the heat of vaporization for water at 15°C. This is a useful number that can be used to estimate the amount of energy required to cause



**FIGURE 13** Heat needed to convert 1 kg of ice to steam. To change the temperature of 1 kg of ice, 2.1 kJ/°C are needed. To completely melt that ice requires another 333 kJ (heat of fusion). Raising the temperature of that water requires 4.184 kJ/°C, and converting it to steam requires another 2,257 kJ (latent heat of vaporization). Raising the temperature of 1 kg of steam (at atmospheric pressure) requires another 2.0 kJ/°C.

TABLE 4

| <b>Important Physical Properties of Water</b> |                         |                                       |
|-----------------------------------------------|-------------------------|---------------------------------------|
| Property                                      | SI Units                | USCS Units                            |
| Specific heat (15°C)                          | 4.184 kJ/kg°C           | 1.00 Btu/lb°F                         |
| Heat of vaporization (100°C)                  | 2,257 kJ/kg             | 972 Btu/lb                            |
| Heat of vaporization (15°C)                   | 2,465 kJ/kg             | 1,060 Btu/lb                          |
| Heat of fusion                                | 333 kJ/kg               | 144 Btu/lb                            |
| Density (at 4°C)                              | 1,000 kg/m <sup>3</sup> | 62.4 lb/ft <sup>3</sup> (8.34 lb/gal) |

surface water on the Earth to evaporate. The value of 15°C has been picked as the starting temperature since that is approximately the current average surface temperature of the globe.

One way to demonstrate the concept of the heat of vaporization, while at the same time introducing an important component of the global energy balance, is to estimate the energy required to power the global hydrologic cycle.

#### EXAMPLE 11 Power for the Hydrologic Cycle

Global rainfall has been estimated to average about 1 m of water per year across the entire  $5.10 \times 10^{14} \text{ m}^2$  of the Earth's surface. Find the energy required to cause that much water to evaporate each year. Compare this to the estimated 2007 world energy consumption of  $4.7 \times 10^{17} \text{ kJ}$  and compare it to the average rate at which sunlight strikes the surface of the Earth, which is about  $168 \text{ W/m}^2$ .

**Solution** In Table 4, the energy required to vaporize 1 kg of 15°C water (roughly the average global temperature) is given as 2,465 kJ. The total energy required to vaporize all of that water is

$$\begin{aligned}\text{Increase in stored energy} &= 1 \text{ m/yr} \times 5.10 \times 10^{14} \text{ m}^2 \times 10^3 \text{ kg/m}^3 \times 2,465 \text{ kJ/kg} \\ &= 1.25 \times 10^{21} \text{ kJ/yr}\end{aligned}$$

This is roughly 2,700 times the  $4.7 \times 10^{17} \text{ kJ/yr}$  of energy we use to power our society.

Averaged over the globe, the energy required to power the hydrologic cycle is

$$\frac{1.25 \times 10^{21} \text{ J/yr} \times 1 \frac{\text{W}}{\text{J/s}}}{365 \text{ day/yr} \times 24 \text{ hr/day} \times 3,600 \text{ s/hr} \times 5.10 \times 10^{14} \text{ m}^2} = 78.0 \text{ W/m}^2$$

which is equivalent to almost half of the  $168 \text{ W/m}^2$  of incoming sunlight striking the Earth's surface. It might also be noted that the energy required to raise the water vapor high into the atmosphere after it has evaporated is negligible compared to the heat of vaporization (see Problem 27 at the end of this chapter).

Many practical environmental engineering problems involve the flow of both matter and energy across system boundaries (open systems). For example, it is common for a hot liquid, usually water, to be used to deliver heat to a pollution control process or, the opposite, for water to be used as a coolant to remove heat from a process. In such cases, there are energy flow rates and fluid flow rates, and (51) needs to be modified as follows:

$$\text{Rate of change of stored energy} = \dot{m} c \Delta T \quad (53)$$

where  $\dot{m}$  is the mass flow rate across the system boundary, given by the product of fluid flow rate and density, and  $\Delta T$  is the change in temperature of the fluid that is carrying the heat to, or away from, the process. For example, if water is being used to cool a steam power plant, then  $\dot{m}$  would be the mass flow rate of coolant, and  $\Delta T$  would be the increase in temperature of the cooling water as it passes through the steam plant's condenser. Typical units for energy rates include watts, Btu/hr, or kJ/s, whereas mass flow rates might typically be in kg/s or lb/hr.

The use of a local river for power plant cooling is common, and the following example illustrates the approach that can be taken to compute the increase in river temperature that results.

#### EXAMPLE 12 Thermal Pollution of a River

A coal-fired power plant converts one-third of the coal's energy into electrical energy. The electrical power output of the plant is 1,000 MW. The other two-thirds of the energy content of the fuel is rejected to the environment as waste heat. About 15 percent of the waste heat goes up the smokestack, and the other 85 percent is taken away by cooling water that is drawn from a nearby river. The river has an upstream flow of  $100.0 \text{ m}^3/\text{s}$  and a temperature of  $20.0^\circ\text{C}$ .

- If the cooling water is only allowed to rise in temperature by  $10.0^\circ\text{C}$ , what flow rate from the stream would be required?
- What would be the river temperature just after it receives the heated cooling water?

**Solution** Since 1,000 MW represents one-third of the power delivered to the plant by fuel, the total rate at which energy enters the power plant is

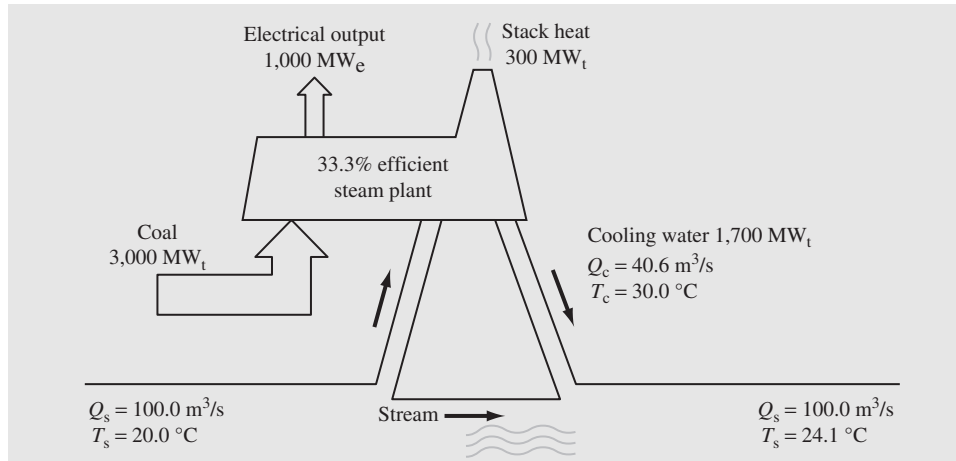
$$\text{Input power} = \frac{\text{Output power}}{\text{Efficiency}} = \frac{1,000 \text{ MW}_e}{1/3} = 3,000 \text{ MW}_t$$

Notice the subscript on the input and output power in the preceding equation. To help keep track of the various forms of energy, it is common to use  $\text{MW}_t$  for thermal power and  $\text{MW}_e$  for electrical power.

Total losses to the cooling water and stack are therefore  $3,000 \text{ MW} - 1,000 \text{ MW} = 2,000 \text{ MW}$ . Of that 2,000 MW,

$$\text{Stack losses} = 0.15 \times 2,000 \text{ MW}_t = 300 \text{ MW}_t$$





**FIGURE 14** Cooling water energy balance for the 33.3 percent efficient, 1,000 MW<sub>e</sub> power plant in Example 12.

and

$$\text{Coolant losses} = 0.85 \times 2,000 \text{ MW}_t = 1,700 \text{ MW}_t$$

- a. Finding the cooling water needed to remove 1,700 MW<sub>t</sub> with a temperature increase  $\Delta T$  of 10.0°C will require the use of (1.53) along with the specific heat of water, 4,184 J/kg°C, given in Table 4:

$$\text{Rate of change in internal energy} = \dot{m} c \Delta T$$

$$1,700 \text{ MW}_t = \dot{m} \text{ kg/s} \times 4,184 \text{ J/kg}^\circ\text{C} \times 10.0^\circ\text{C} \times 1 \text{ MW}/(10^6 \text{ J/s})$$

$$\dot{m} = \frac{1,700}{4,184 \times 10.0 \times 10^{-6}} = 40.6 \times 10^3 \text{ kg/s}$$

or, since 1,000 kg equals 1 m<sup>3</sup> of water, the flow rate is 40.6 m<sup>3</sup>/s.

- b. To find the new temperature of the river, we can use (53) with 1,700 MW<sub>t</sub> being released into the river, which again has a flow rate of 100.0 m<sup>3</sup>/s.

$$\text{Rate of change in internal energy} = \dot{m} c \Delta T$$

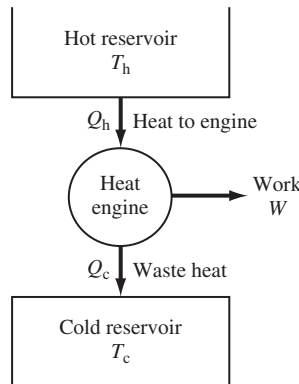
$$\Delta T = \frac{1,700 \text{ MW} \times \left( \frac{1 \times 10^6 \text{ J/s}}{\text{MW}} \right)}{100.00 \text{ m}^3/\text{s} \times 10^3 \text{ kg/m}^3 \times 4,184 \text{ J/kg}^\circ\text{C}} = 4.1^\circ\text{C}$$

so the temperature of the river will be elevated by 4.1°C making it 24.1°C. The results of the calculations just performed are shown in Figure 14.

## The Second Law of Thermodynamics

In Example 12, you will notice that a relatively modest fraction of the fuel energy contained in the coal actually was converted to the desired output, electrical power, and a rather large amount of the fuel energy ended up as waste heat rejected to the environment. The second law of thermodynamics says that there will always be some waste heat; that is, it is impossible to devise a machine that can convert heat

## Mass and Energy Transfer



**FIGURE 15** Definition of terms for a Carnot engine.

to work with 100 percent efficiency. There will always be “losses” (although, by the first law, the energy is not lost, it is merely converted into the lower quality, less useful form of low-temperature heat).

The steam-electric plant just described is an example of a *heat engine*, a device studied at some length in thermodynamics. One way to view the steam plant is that it is a machine that takes heat from a high-temperature source (the burning fuel), converts some of it into work (the electrical output), and rejects the remainder into a low-temperature reservoir (the river and the atmosphere). It turns out that the maximum efficiency that our steam plant can possibly have depends on how high the source temperature is and how low the temperature is of the reservoir accepting the rejected heat. It is analogous to trying to run a turbine using water that flows from a higher elevation to a lower one. The greater the difference in elevation, the more power can be extracted.

Figure 15 shows a theoretical heat engine operating between two heat reservoirs, one at temperature  $T_h$  and one at  $T_c$ . An amount of heat energy  $Q_h$  is transferred from the hot reservoir to the heat engine. The engine does work  $W$  and rejects an amount of waste heat  $Q_c$  to the cold reservoir.

The efficiency of this engine is the ratio of the work delivered by the engine to the amount of heat energy taken from the hot reservoir:

$$\text{Efficiency } \eta = \frac{W}{Q_h} \quad (54)$$

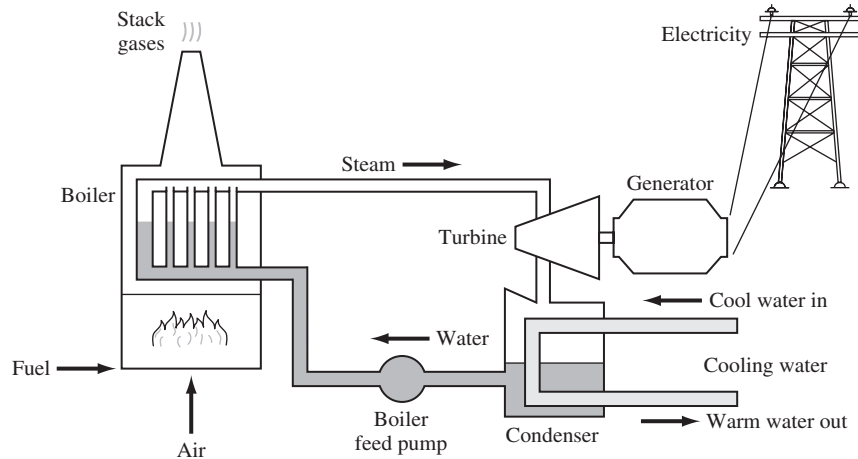
The most efficient heat engine that could possibly operate between the two heat reservoirs is called a *Carnot* engine after the French engineer Sadi Carnot, who first developed the explanation in the 1820s. Analysis of Carnot engines shows that the most efficient engine possible, operating between two temperatures,  $T_h$  and  $T_c$ , has an efficiency of

$$\eta_{\max} = 1 - \frac{T_c}{T_h} \quad (55)$$

where these are absolute temperatures measured using either the Kelvin scale or Rankine scale. Conversions from Celsius to Kelvin, and Fahrenheit to Rankine are

$$K = ^\circ\text{C} + 273.15 \quad (56)$$

$$R = ^\circ\text{F} + 459.67 \quad (57)$$



**FIGURE 16** A fuel-fired, steam-electric power plant.

One immediate observation that can be made from (55) is that the maximum possible heat engine efficiency increases as the temperature of the hot reservoir increases or the temperature of the cold reservoir decreases. In fact, since neither infinitely hot temperatures nor absolute zero temperatures are possible, we must conclude that no real engine has 100 percent efficiency, which is just a restatement of the second law.

Equation (55) can help us understand the seemingly low efficiency of thermal power plants such as the one diagrammed in Figure 16. In this plant, fuel is burned in a firing chamber surrounded by metal tubing. Water circulating through this boiler tubing is converted to high-pressure, high-temperature steam. During this conversion of chemical to thermal energy, losses on the order of 10 percent occur due to incomplete combustion and loss of heat up the smokestack. Later, we shall consider local and regional air pollution effects caused by these emissions as well as their possible role in global warming.

The steam produced in the boiler then enters a steam turbine, which is in some ways similar to a child's pinwheel. The high-pressure steam expands as it passes through the turbine blades, causing a shaft that is connected to the generator to spin. Although the turbine in Figure 16 is shown as a single unit, in actuality, turbines have many stages with steam exiting one stage and entering another, gradually expanding and cooling as it goes. The generator converts the rotational energy of a spinning shaft into electrical power that goes out onto transmission lines for distribution. A well-designed turbine may have an efficiency that approaches 90 percent, whereas the generator may have a conversion efficiency even higher than that.

The spent steam from the turbine undergoes a phase change back to the liquid state as it is cooled in the condenser. This phase change creates a partial vacuum that helps pull steam through the turbine, thereby increasing the turbine efficiency. The condensed steam is then pumped back to the boiler to be reheated.

The heat released when the steam condenses is transferred to cooling water that circulates through the condenser. Usually, cooling water is drawn from a lake or river, heated in the condenser, and returned to that body of water, which is called *once-through cooling*. A more expensive approach, which has the advantage of

requiring less water, involves the use of cooling towers that transfer the heat directly into the atmosphere rather than into a receiving body of water. In either case, the rejected heat is released into the environment. In terms of the heat engine concept shown in Figure 15, the cold reservoir temperature is thus determined by the temperature of the environment.

Let us estimate the maximum possible efficiency that a thermal power plant such as that diagrammed in Figure 16 can have. A reasonable estimate of  $T_h$  might be the temperature of the steam from the boiler, which is typically around 600°C. For  $T_c$ , we might use an ambient temperature of about 20°C. Using these values in (55) and remembering to convert temperatures to the absolute scale, gives

$$\eta_{\max} = 1 - \frac{(20 + 273)}{(600 + 273)} = 0.66 = 66 \text{ percent}$$

New fossil fuel-fired power plants have efficiencies around 40 percent. Nuclear plants have materials constraints that force them to operate at somewhat lower temperatures than fossil plants, which results in efficiencies of around 33 percent. The average efficiency of all thermal plants actually in use in the United States, including new and old (less efficient) plants, fossil and nuclear, is close to 33 percent. That suggests the following convenient rule of thumb:

*For every 3 units of energy entering the average thermal power plant, approximately 1 unit is converted to electricity and 2 units are rejected to the environment as waste heat.*

The following example uses this rule of thumb for power plant efficiency combined with other emission factors to develop a mass and energy balance for a typical coal-fired power plant.

### EXAMPLE 13 Mass and Energy Balance for a Coal-Fired Power Plant

Typical coal burned in power plants in the United States has an energy content of approximately 24 kJ/g and an average carbon content of about 62 percent. For almost all new coal plants, Clean Air Act emission standards limit sulfur emissions to 260 g of sulfur dioxide (SO<sub>2</sub>) per million kJ of heat input to the plant (130 g of elemental sulfur per 10<sup>6</sup> kJ). They also restrict particulate emissions to 13 g/10<sup>6</sup> kJ. Suppose the average plant burns fuel with 2 percent sulfur content and 10 percent unburnable minerals called *ash*. About 70 percent of the ash is released as *fly ash*, and about 30 percent settles out of the firing chamber and is collected as *bottom ash*. Assume this is a typical coal plant with 3 units of heat energy required to deliver 1 unit of electrical energy.

- Per kilowatt-hour of electrical energy produced, find the emissions of SO<sub>2</sub>, particulates, and carbon (assume all of the carbon in the coal is released to the atmosphere).
- How efficient must the sulfur emission control system be to meet the sulfur emission limitations?
- How efficient must the particulate control system be to meet the particulate emission limits?

**Solution**

- a. We first need the heat input to the plant. Because 3 kWhr of heat are required for each 1 kWhr of electricity delivered,

$$\frac{\text{Heat input}}{\text{kWhr electricity}} = 3 \text{ kWhr heat} \times \frac{1 \text{ kJ/s}}{\text{kW}} \times 3,600 \text{ s/hr} = 10,800 \text{ kJ}$$

The sulfur emissions are thus restricted to

$$\text{S emissions} = \frac{130 \text{ g S}}{10^6 \text{ kJ}} \times 10,800 \text{ kJ/kWhr} = 1.40 \text{ g S/kWhr}$$

The molecular weight of  $\text{SO}_2$  is  $32 + 2 \times 16 = 64$ , half of which is sulfur. Thus, 1.4 g of S corresponds to 2.8 g of  $\text{SO}_2$ , so 2.8 g  $\text{SO}_2$ /kWhr would be emitted. Particulate emissions need to be limited to:

$$\text{Particulate emissions} = \frac{13 \text{ g}}{10^6 \text{ kJ}} \times 10,800 \text{ kJ/kWhr} = 0.14 \text{ g/kWhr}$$

To find carbon emissions, first find the amount of coal burned per kWhr

$$\text{Coal input} = \frac{10,800 \text{ kJ/kWhr}}{24 \text{ kJ/g coal}} = 450 \text{ g coal/kWhr}$$

Therefore, since the coal is 62 percent carbon

$$\text{Carbon emissions} = \frac{0.62 \text{ g C}}{\text{g coal}} \times \frac{450 \text{ g coal}}{\text{kWhr}} = 280 \text{ g C/kWhr}$$

- b. Burning 450 g coal containing 2 percent sulfur will release  $0.02 \times 450 = 9.0$  g of S. Since the allowable emissions are 1.4 g, the removal efficiency must be

$$\text{S removal efficiency} = 1 - \frac{1.4}{9.0} = 0.85 = 85 \text{ percent}$$

- c. Since 10 percent of the coal is ash, and 70 percent of that is fly ash, the total fly ash generated will be

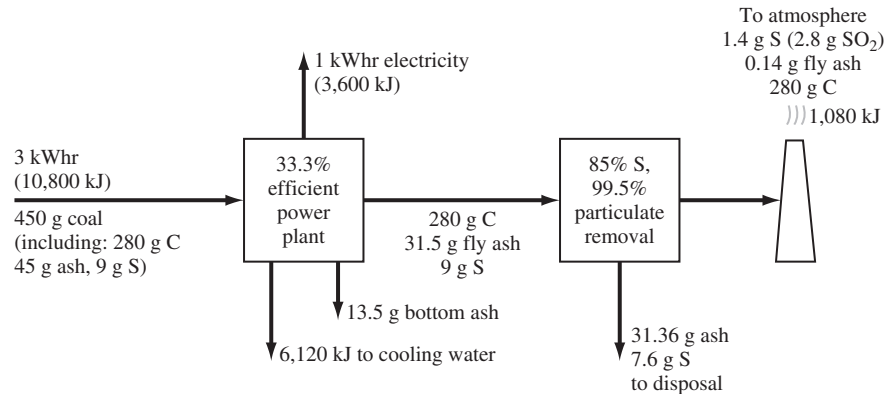
$$\begin{aligned} \text{Fly ash generated} &= 0.70 \times 0.10 \times 450 \text{ g coal/kWhr} \\ &= 31.5 \text{ g fly ash/kWhr} \end{aligned}$$

The allowable particulate matter is restricted to 0.14 g/kWhr, so controls must be installed that have the following removal efficiency:

$$\text{Particulate removal efficiency} = 1 - \frac{0.14}{31.5} = 0.995 = 99.5 \text{ percent}$$

The complete mass and energy balance for this coal plant is diagrammed in Figure 17. In this diagram, it has been assumed that 85 percent of the waste heat is removed by cooling water, and the remaining 15 percent is lost in stack gases (corresponding to the conditions given in Example 12).

## Mass and Energy Transfer



**FIGURE 17** Energy and mass balance for a coal-fired power plant generating 1 kWhr of electricity (see Example 13).

The Carnot efficiency limitation provides insight into the likely performance of other types of thermal power plants in addition to the steam plants just described. For example, there have been many proposals to build power plants that would take advantage of the temperature difference between the relatively warm surface waters of the ocean and the rather frigid waters found below. In some locations, the sun heats the ocean's top layer to as much as 30°C, whereas several hundred meters down, the temperature is a constant 4 or 5°C. Power plants, called *ocean thermal energy conversion* (OTEC) systems, could be designed to operate on these small temperature differences in the ocean; however, as the following example shows, they would be inefficient.

### EXAMPLE 14 OTEC System Efficiency

Consider an OTEC system operating between 30°C and 5°C. What would be the maximum possible efficiency for an electric generating station operating with these temperatures?

**Solution** Using (55), we find

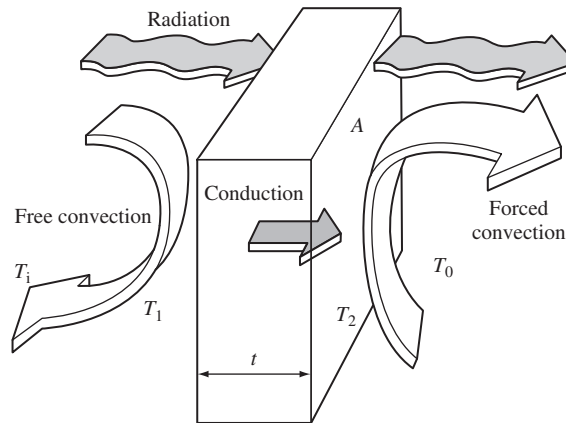
$$\eta_{\max} = 1 - \frac{(5 + 273)}{(30 + 273)} = 0.08 = 8 \text{ percent}$$

An even lower efficiency, estimated at 2 to 3 percent for a real plant, would be expected.

## Conductive and Convective Heat Transfer

When two objects are at different temperatures, heat will be transferred from the hotter object to the colder one. That heat transfer can be by *conduction*, by *convection*, or by *radiation*, which can take place even in the absence of any physical medium between the objects.

## Mass and Energy Transfer



**FIGURE 18** Heat transfer through a simple wall.

Conductive heat transfer is usually associated with solids, as one molecule vibrates the next in the lattice. The rate of heat transfer in a solid is proportional to the thermal conductivity of the material. Metals tend to be good thermal conductors, which makes them very useful when high heat-transfer rates are desired. Other materials are much less so, with some being particularly poor thermal conductors, which makes them potentially useful as thermal insulation.

Convective heat transfer occurs when a fluid at one temperature comes in contact with a substance at another temperature. For example, warm air in a house in the winter that comes in contact with a cool wall surface will transfer heat to the wall. As that warm air loses some of its heat, it becomes cooler and denser, and it will sink and be replaced by more warm air from the interior of the room. Thus there is a continuous movement of air around the room and with it a transference of heat from the warm room air to the cool wall. The cool wall, in turn, conducts heat to the cold exterior surface of the house where outside air removes the heat by convection.

Figure 18 illustrates the two processes of convection and conduction through a hypothetical wall. In addition, there is radiative heat transfer from objects in the room to the wall, and from the wall to the ambient outside. It is conventional practice to combine all three processes into a single, overall heat-transfer process that is characterized by the following simple equation:

$$q = \frac{A(T_i - T_o)}{R} \quad (58)$$

where

$q$  = heat transfer rate through the wall (W) or (Btu/hr)

$A$  = wall area ( $\text{m}^2$ ) or ( $\text{ft}^2$ )

$T_i$  = air temperature on one side of the wall ( $^{\circ}\text{C}$ ) or ( $^{\circ}\text{F}$ )

$T_o$  = ambient air temperature ( $^{\circ}\text{C}$ ) or ( $^{\circ}\text{F}$ )

$R$  = overall thermal resistance ( $\text{m}^2\text{-}^{\circ}\text{C}/\text{W}$ ) or ( $\text{hr-ft}^2\text{-}^{\circ}\text{F}/\text{Btu}$ )

The overall thermal resistance  $R$  is called the *R-value*. If you buy insulation at the hardware store, it will be designated as having an  $R$ -value in the American unit system ( $\text{hr-ft}^2\text{-}^{\circ}\text{F}/\text{Btu}$ ). For example, 3½-inch-thick fiberglass insulation is usually marked  $R$ -11, whereas 6 inches of the same material is  $R$ -19.

As the following example illustrates, improving the efficiency with which we use energy can save money as well as reduce emissions of pollutants associated with energy consumption. This important connection between energy efficiency and pollution control has in the past been overlooked and underappreciated. However, that situation has been changing. The 1990 Amendments to the Clean Air Act, for example, provide SO<sub>2</sub> emission credits for energy efficiency projects.

### EXAMPLE 15 Reducing Pollution by Adding Ceiling Insulation

A home with 1,500 ft<sup>2</sup> of poorly insulated ceiling is located in an area with an 8-month heating season during which time the outdoor temperature averages 40°F while the inside temperature is kept at 70°F (this could be Chicago, for example). It has been proposed to the owner that \$1,000 be spent to add more insulation to the ceiling, raising its total *R-value* from 11 to 40 (ft<sup>2</sup>·°F·hr/Btu). The house is heated with electricity that costs 8 cents/kWhr.

- How much money would the owner expect to save each year, and how long would it take for the energy savings to pay for the cost of insulation?
- Suppose 1 million homes served by coal plants like the one analyzed in Example 13 could achieve similar energy savings. Estimate the annual reduction in SO<sub>2</sub>, particulate, and carbon emissions that would be realized.

#### Solution

- Using (58) to find the heat loss rate with the existing insulation gives

$$q = \frac{A(T_i - T_o)}{R} = \frac{1,500 \text{ ft}^2 \times (70 - 40)^\circ\text{F}}{11 \text{ (ft}^2\text{·}^\circ\text{F·hr/Btu)}} = 4,090 \text{ Btu/hr}$$

After adding the insulation, the new heat loss rate will be

$$q = \frac{A(T_i - T_o)}{R} = \frac{1,500 \text{ ft}^2 \times (70 - 40)^\circ\text{F}}{40 \text{ (ft}^2\text{·}^\circ\text{F·hr/Btu)}} = 1,125 \text{ Btu/hr}$$

The annual energy savings can be found by multiplying the rate at which energy is being saved by the number of hours in the heating season. If we assume the electric heating system in the house is 100 percent efficient at converting electricity to heat (reasonable) and that it delivers all of that heat to the spaces that need heat (less reasonable, especially if there are heating ducts, which tend to leak), then we can use the conversion 3,412 Btu = 1 kWhr.

$$\begin{aligned} \text{Energy saved} &= \frac{(4,090 - 1,125) \text{ Btu/hr}}{3,412 \text{ Btu/kWhr}} \times 24 \text{ hr/day} \times 30 \text{ day/mo} \times 8 \text{ mo/yr} \\ &= 5,005 \text{ kWhr/yr} \end{aligned}$$

The annual savings in dollars would be

$$\text{Dollar savings} = 5,005 \text{ kWhr/yr} \times \$0.08/\text{kWhr} = \$400/\text{yr}$$

Since the estimated cost of adding extra insulation is \$1,000, the reduction in electricity bills would pay for this investment in about 2½ heating seasons.



- b. One million such houses would save a total of 5 billion kWhr/yr (nearly the entire annual output of a typical 1,000 MW<sub>e</sub> power plant). Using the emission factors derived in Example 13, the reduction in air emissions would be

$$\begin{aligned}\text{Carbon reduction} &= 280 \text{ g C/kWhr} \times 5 \times 10^9 \text{ kWhr/yr} \times 10^{-3} \text{ kg/g} \\ &= 1,400 \times 10^6 \text{ kg/yr}\end{aligned}$$

$$\begin{aligned}\text{SO}_2 \text{ reduction} &= 2.8 \text{ g SO}_2/\text{kWhr} \times 5 \times 10^9 \text{ kWhr/yr} \times 10^{-3} \text{ kg/g} \\ &= 14 \times 10^6 \text{ kg/yr}\end{aligned}$$

$$\begin{aligned}\text{Particulate reduction} &= 0.14 \text{ g/kWhr} \times 5 \times 10^9 \text{ kWhr/yr} \times 10^{-3} \text{ kg/g} \\ &= 0.7 \times 10^6 \text{ kg/yr}\end{aligned}$$

## Radiant Heat Transfer

Heat transfer by thermal radiation is the third way that one object can warm another. Unlike conduction and convection, radiant energy is transported by electromagnetic waves and does not require a medium to carry the energy. As is the case for other forms of electromagnetic phenomena, such as radio waves, x-rays, and gamma rays, thermal radiation can be described either in terms of wavelengths or, using the particle nature of electromagnetic radiation, in terms of discrete photons of energy. All electromagnetic waves travel at the speed of light. They can be described by their wavelength or their frequency, and the two are related as follows:

$$c = \lambda \nu \quad (59)$$

where

$c$  = speed of light ( $3 \times 10^8$  m/s)

$\lambda$  = wavelength (m)

$\nu$  = frequency (hertz, *i.e.*, cycles per second)

When radiant energy is described in terms of photons, the relationship between frequency and energy is given by

$$E = h \nu \quad (60)$$

where

$E$  = energy of a photon (J)

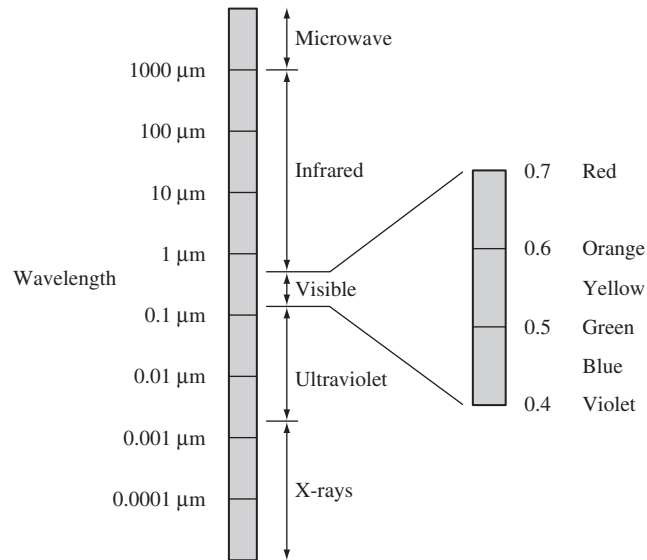
$h$  = Planck's constant ( $6.6 \times 10^{-34}$  J-s)

Equation (60) points out that higher-frequency, shorter-wavelength photons have higher energy content, which makes them potentially more dangerous when living things are exposed to them.

Consider the effects of various gases on global climate and depletion of the stratospheric ozone layer. The wavelengths of importance in that context are roughly in the range of about  $0.1 \mu\text{m}$  up to about  $100 \mu\text{m}$  ( $1 \mu\text{m}$  is  $10^{-6}$  m, also called 1 micron). For perspective, Figure 19 shows a portion of the electromagnetic spectrum.

Every object emits thermal radiation. The usual way to describe how much radiation a real object emits, as well as other characteristics of the wavelengths

## Mass and Energy Transfer



**FIGURE 19** A portion of the electromagnetic spectrum. The wavelengths of greatest interest for this text are in the range of about 0.1 μm to 100 μm.

emitted, is to compare it to a theoretical abstraction called a *blackbody*. A blackbody is defined as a perfect emitter as well as a perfect absorber. As a perfect emitter, it radiates more energy per unit of surface area than any real object at the same temperature. As a perfect absorber, it absorbs all radiation that impinges upon it; that is, none is reflected, and none is transmitted through it. Actual objects do not emit as much radiation as this hypothetical blackbody, but most are close to this theoretical limit. The ratio of the amount of radiation an actual object would emit to the amount that a blackbody would emit at the same temperature is known as the *emissivity*,  $\epsilon$ . The emissivity of desert sand, dry ground, and most woodlands is estimated to be approximately 0.90, whereas water, wet sand, and ice all have estimated emissivities of roughly 0.95. A human body, no matter what pigmentation, has an emissivity of around 0.96.

The wavelengths radiated by a blackbody depend on its temperature, as described by *Planck's law*:

$$E_{\lambda} = \frac{C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)} \quad (61)$$

where

$E_{\lambda}$  = emissive power of a blackbody (W/m<sup>2</sup>-μm)

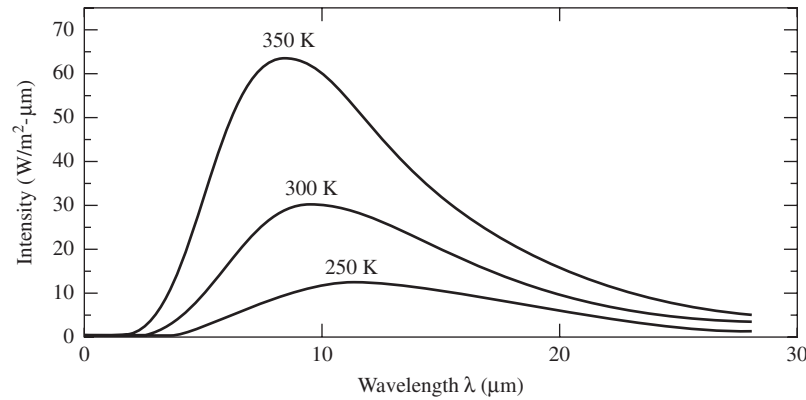
$T$  = absolute temperature of the body (K)

$\lambda$  = wavelength (μm)

$C_1 = 3.74 \times 10^8 \text{ W-}\mu\text{m}^4/\text{m}^2$

$C_2 = 1.44 \times 10^4 \mu\text{m-K}$

Figure 20 is a plot of the emissive power of radiation emitted from blackbodies at various temperatures. Curves such as these, which show the spectrum of wave-



**FIGURE 20** The spectral emissive power of a blackbody with various temperatures.

lengths emitted, have as their vertical axis an amount of power per unit-wavelength. The way to interpret such spectral diagrams is to realize that the area under the curve between any two wavelengths is equal to the power radiated by the object within that band of wavelengths. Hence the total area under the curve is equal to the total power radiated. Objects at higher temperatures emit more power and, as the figure suggests, their peak intensity occurs at shorter wavelengths.

Extraterrestrial solar radiation (just outside the Earth's atmosphere) shows spectral characteristics that are well approximated by blackbody radiation. Although the temperature deep within the sun is many millions of degrees, its effective surface temperature is about 5,800 K. Figure 21 shows the close match between the actual solar spectrum and that of a 5,800-K blackbody.

As has already been mentioned, the area under a spectral curve between any two wavelengths is the total power radiated by those wavelengths. For the solar spectrum of Figure 21, the area under the curve between 0.38 and 0.78  $\mu\text{m}$  (the wavelengths visible to the human eye) is 47 percent of the total area. That is, 47 percent of the solar energy striking the outside of our atmosphere is in the visible portion of the spectrum. The ultraviolet range contains 7 percent of the energy, and the infrared wavelengths deliver the remaining 46 percent. The total area under the solar spectrum curve is called the *solar constant*, and it is estimated to be 1,372 watts per  $\text{m}^2$ . The solar constant plays an important role in determining the surface temperature of the Earth.

The equation describing Planck's law (61) is somewhat tricky to manipulate, especially for calculations involving the area under a spectral curve. Two other radiation equations, however, are straightforward and are often all that is needed. The first, known as the *Stefan-Boltzmann law of radiation*, gives the total radiant energy emitted by a blackbody with surface area  $A$  and absolute temperature  $T$ :

$$E = \sigma AT^4 \quad (62)$$

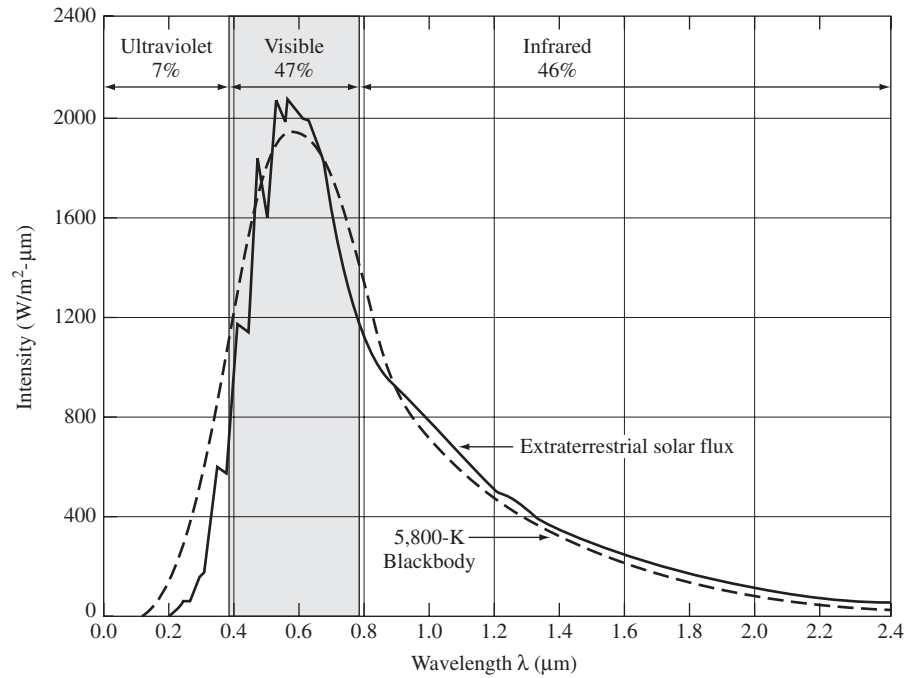
where

$E$  = total blackbody emission rate (W)

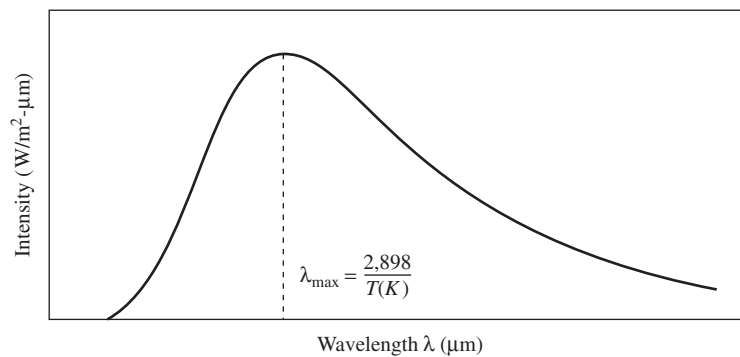
$\sigma$  = the Stefan-Boltzmann constant =  $5.67 \times 10^{-8} \text{ W/m}^2\text{-K}^4$

$T$  = absolute temperature (K)

$A$  = surface area of the object ( $\text{m}^2$ )



**FIGURE 21** The extraterrestrial solar spectrum (solid line) compared with the spectrum of a 5,800-K blackbody (dashed).



**FIGURE 22** Wien's rule for finding the wavelength at which the spectral emissive power of a blackbody reaches its maximum value.

The second is *Wien's displacement rule*, which tells us the wavelength at which the spectrum reaches its maximum point:

$$\lambda_{\max} (\mu\text{m}) = \frac{2,898}{T(K)} \quad (63)$$

where wavelength is specified in micrometers and temperature is in kelvins. Figure 22 illustrates this concept, and Example 16 shows how it can be used.

**EXAMPLE 16** The Earth's Spectrum

Consider the Earth to be a blackbody with average temperature  $15^{\circ}\text{C}$  and surface area equal to  $5.1 \times 10^{14} \text{ m}^2$ . Find the rate at which energy is radiated by the Earth and the wavelength at which maximum power is radiated. Compare this peak wavelength with that for a 5,800-K blackbody (the sun).

**Solution** Using (62), the Earth radiates

$$\begin{aligned} E &= \sigma AT^4 \\ &= 5.67 \times 10^{-8} \text{ W/m}^2\text{-K}^4 \times 5.1 \times 10^{14} \text{ m}^2 \times (15.0 + 273.15 \text{ K})^4 \\ &= 2.0 \times 10^{17} \text{ Watts} \end{aligned}$$

The wavelength at which the maximum point is reached in the Earth's spectrum is

$$\lambda_{\max}(\mu\text{m}) = \frac{2,898}{T(\text{K})} = \frac{2,898}{288.15} = 10.1 \mu\text{m} \text{ (Earth)}$$

For the 5,800-K sun,

$$\lambda_{\max}(\mu\text{m}) = \frac{2,898}{5,800} = 0.48 \mu\text{m} \text{ (sun)}$$

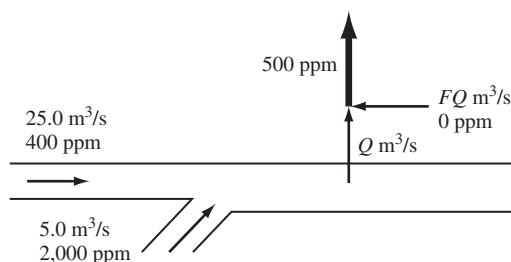
This tremendous rate of energy emission by the Earth is balanced by the rate at which the Earth absorbs energy from the sun. As shown in Example 16, however, the solar energy striking the Earth has much shorter wavelengths than energy radiated back to space by the Earth. This wavelength shift plays a crucial role in the greenhouse effect. Carbon dioxide and other greenhouse gases are relatively transparent to the incoming short wavelengths from the sun, but they tend to absorb the outgoing, longer wavelengths radiated by the Earth. As those greenhouse gases accumulate in our atmosphere, they act like a blanket that envelops the planet, upsets the radiation balance, and raises the Earth's temperature.

**PROBLEMS**

- 1 The proposed air quality standard for ozone ( $\text{O}_3$ ) is 0.08 ppm.
  - (a) Express that standard in  $\mu\text{g}/\text{m}^3$  at 1 atm of pressure and  $25^{\circ}\text{C}$ .
  - (b) At the elevation of Denver, the pressure is about 0.82 atm. Express the ozone standard at that pressure and at a temperature of  $15^{\circ}\text{C}$ .
- 2 Suppose the exhaust gas from an automobile contains 1.0 percent by volume of carbon monoxide. Express this concentration in  $\text{mg}/\text{m}^3$  at  $25^{\circ}\text{C}$  and 1 atm.
- 3 Suppose the average concentration of  $\text{SO}_2$  is measured to be  $400 \mu\text{g}/\text{m}^3$  at  $25^{\circ}\text{C}$  and 1 atm. Does this exceed the (24-hr) air quality standard of 0.14 ppm?
- 4 A typical motorcycle emits about 20 g of CO per mile.
  - (a) What volume of CO would a 5-mile trip produce after the gas cools to  $25^{\circ}\text{C}$  (at 1 atm)?
  - (b) Per meter of distance traveled, what volume of air could be polluted to the air quality standard of 9 ppm?

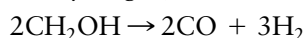
- 5 If we approximate the atmosphere to be 79 percent nitrogen ( $N_2$ ) by volume and 21 percent oxygen ( $O_2$ ), estimate the density of air ( $kg/m^3$ ) at STP conditions ( $0^\circ C$ , 1 atm).
- 6 Five million gallons per day (MGD) of wastewater, with a concentration of 10.0 mg/L of a conservative pollutant, is released into a stream having an upstream flow of 10 MGD and pollutant concentration of 3.0 mg/L.
  - (a) What is the concentration in ppm just downstream?
  - (b) How many pounds of substance per day pass a given spot downstream? (The conversions 3.785 L/gal and 2.2 kg/lbm may be helpful.)
- 7 A river with 400 ppm of salts (a conservative substance) and an upstream flow of  $25.0\ m^3/s$  receives an agricultural discharge of  $5.0\ m^3/s$  carrying 2,000 mg/L of salts (see Figure P7). The salts quickly become uniformly distributed in the river. A municipality just downstream withdraws water and mixes it with enough pure water (no salt) from another source to deliver water having no more than 500 ppm salts to its customers.
 

What should be the mixture ratio  $F$  of pure water to river water?



**FIGURE P7**

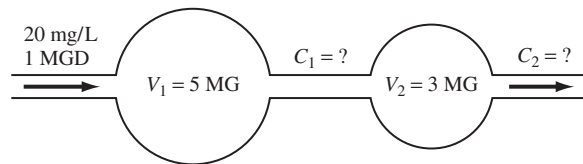
- 8 A home washing machine removes grease and dirt from clothes in a nearly first-order process in which 12 percent of the grease on the clothes is removed per minute. The washing machine holds 50.0 L of water and has a wash cycle of 5.00 minutes before discharging the wash water. What will be the grease concentration (in mg/L) in the discharge water if the clothes initially contain 0.500 g of grease?
- 9 Plateau Creek carries  $5.0\ m^3/s$  of water with a selenium (Se) concentration of 0.0015 mg/L. A farmer starts withdrawing  $1.0\ m^3/s$  of the creek water to irrigate the land. During irrigation, the water picks up selenium from the salts in the soil. One-half of the irrigation water is lost to the ground and plants, and the other half is returned to Plateau Creek. The irrigation run-off to the creek contains 1.00 mg/L of selenium. Selenium is a conservative, nonreactive substance (it does not degrade in the stream), and the stream does not pick up more selenium from any other source.
  - (a) If the farmer irrigates continuously, what will be the steady-state concentration of selenium in the stream downstream from the farm (after the irrigation run-off returns to the stream)?
  - (b) Fish are sensitive to selenium levels over 0.04 mg/L. The farmer agrees not to use more water than will keep the stream selenium level below this critical concentration. How much water can the farmer withdraw from the stream to use for irrigation?
- 10 When methanol is used to generate hydrogen, it reacts with the following reaction:



The reaction is second order in methanol ( $CH_3OH$ ), and it is observed that 100 g of carbon monoxide (CO) can be produced in one day in a batch reactor, if you start with 200 g of methanol. What is the rate constant for this reaction?

- 11 A lake with constant volume  $10 \times 10^6 \text{ m}^3$  is fed by a pollution-free stream with flow rate  $50 \text{ m}^3/\text{s}$ . A factory dumps  $5 \text{ m}^3/\text{s}$  of a nonconservative waste with concentration  $100 \text{ mg/L}$  into the lake. The pollutant has a reaction rate coefficient  $K$  of  $0.25/\text{day}$ . Assuming the pollutant is well mixed in the lake, find the steady-state concentration of pollutant in the lake.
- 12 The two-pond system shown in Figure P12 is fed by a stream with flow rate  $1.0 \text{ MGD}$  (millions gallons per day) and BOD (a nonconservative pollutant) concentration  $20.0 \text{ mg/L}$ . The rate of decay of BOD is  $0.30/\text{day}$ . The volume of the first pond is  $5.0$  million gallons, and the second is  $3.0$  million.

Assuming complete mixing within each pond, find the BOD concentration leaving each pond.

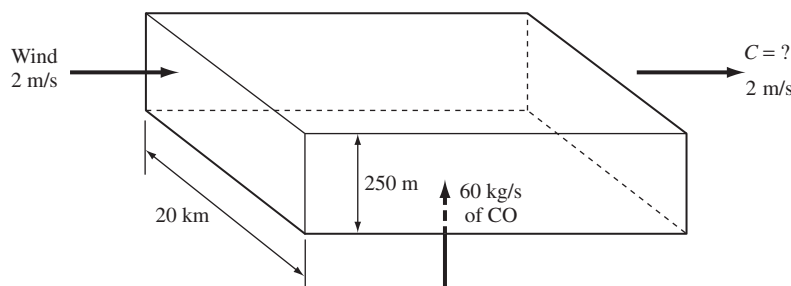


**FIGURE P12**

- 13 A lagoon is to be designed to accommodate an input flow of  $0.10 \text{ m}^3/\text{s}$  of nonconservative pollutant with concentration  $30.0 \text{ mg/L}$  and reaction rate  $0.20/\text{day}$ . The effluent from the lagoon must have pollutant concentration of less than  $10.0 \text{ mg/L}$ . Assuming complete mixing, how large must the lagoon be?
- 14 Ozone is sometimes used as a disinfectant for drinking water. Ozone is highly reactive. It will react with many benign species found in water, as well as the pathogens it is intended to kill. It is found that ozone reaction in water nearly follows first-order kinetics in ozone concentration, such that its concentration decreases by 50 percent in 12 minutes ( $t_{1/2} = 12 \text{ min}$ ). A water supplier wants to inject ozone into a pipe bringing water to the water treatment plant to pre-disinfect the influent. The  $3.0\text{-ft.}$  diameter pipe is  $3,400$  feet long with a steady flow rate of  $10,000 \text{ gal/min}$ . What concentration of ozone (in  $\text{mg/L}$ ) should be injected at the head of the pipe so that there will be an ozone concentration of  $1.0 \text{ mg/L}$  at the pipe's exit into the plant? The pipe may be realistically assumed to act as an ideal PFR.
- 15 Your stomach is a chemical reactor. When you devour a fast food  $99\text{¢}$  special hamburger in about a minute, it acts like an instantaneous input of  $325 \text{ g}$  of food entering the stomach. In response, the stomach starts producing gastric liquids (acids), which are continuously excreted into the stomach at a rate of  $12.0 \text{ mL/min}$  as the hamburger is digested. The fluid also leaves the stomach to the small intestine at a flow rate of  $12.0 \text{ mL/min}$ , so the volume of liquid in the stomach stays constant at  $1.15 \text{ L}$ . The hamburger digestion rate constant is  $1.33 \text{ hr}^{-1}$ .
  - (a) What kind of ideal reactor would you model your stomach as?
  - (b) What fraction of the hamburger's mass will remain undigested in your stomach one hour after you eat the hamburger?
- 16 A simple way to model air pollution over a city is with a box model that assumes complete mixing and limited capability for the pollution to disperse horizontally or vertically except in the direction of the prevailing winds (for example, a town located in a valley

with an inversion layer above it). Consider a town having an inversion at 250 m, a 20-km horizontal distance perpendicular to the wind, a windspeed of 2 m/s, and a carbon monoxide (CO) emission rate of 60 kg/s (see Figure P16). Assume the CO is conservative and completely mixed in the box.

What would be the CO concentration in the box?



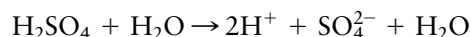
**FIGURE P16**

- 17 Consider the air over a city to be a box 100 km on a side that reaches up to an altitude of 1.0 km. Clean air is blowing into the box along one of its sides with a speed of 4 m/s. Suppose an air pollutant with reaction rate  $k = 0.20/\text{hr}$  is emitted into the box at a total rate of 10.0 kg/s. Find the steady-state concentration if the air is assumed to be completely mixed.
- 18 If the windspeed in Problem 17 suddenly drops to 1 m/s, estimate the concentration of pollutants two hours later.
- 19 A lagoon with volume  $1,200 \text{ m}^3$  has been receiving a steady flow of a conservative waste at a rate of  $100 \text{ m}^3/\text{day}$  for a long enough time to assume that steady-state conditions apply. The waste entering the lagoon has a concentration of 10 mg/L. Assuming completely mixed conditions,
  - (a) What would be the concentration of pollutant in the effluent leaving the lagoon?
  - (b) If the input waste concentration suddenly increased to 100 mg/L, what would the concentration in the effluent be 7 days later?
- 20 Repeat Problem 19 for a nonconservative pollutant with reaction rate  $k = 0.20/\text{d}$ .
- 21 A nuclear power station is situated in Coal Valley, which is a roughly rectangular valley that is 5 km long, 2 km wide, and 200 m deep. You have been asked to evaluate the effects of a worst-case scenario where the reactor housing fails, and radiation is released to the atmosphere. In your evaluation, you determine that 120 kg of Iodine-131 (a radioisotope that causes thyroid gland and liver damage) could be released into the atmosphere.
  - (a) Assuming the release of Iodine-131 was very rapid and all of it was uniformly distributed through the valley's atmosphere with none escaping the valley, what would the concentration of Iodine-131 be in the valley's air? Your answer should be expressed in units of ppmv, and you may assume an atmospheric pressure of 1.0 atm and a temperature of  $20^\circ\text{C}$ .
  - (b) Assuming the Iodine-131 concentration you calculated in part (a) is the initial concentration in the valley, you now want to determine the time it will take for the concentration to decrease to the safe limit of  $1.0 \times 10^{-5}$  ppmv. The average windspeed through the valley (entering at one end and exiting at the other) is only 1.5 m/min. However, Iodine-131 also is removed by two other processes: 1) radioactive decay



with a half life of 8.1 days, and 2) sedimentation to the ground with a rate constant of  $0.02 \text{ d}^{-1}$ . Draw a picture of the situation, and label the appropriate variables.

- (c) Now derive an equation that expresses the concentration of Iodine-131 in the valley's air as a function of the time since the accident. Use the equation to determine the time needed for the concentration to decrease to a safe level.
- 22 When a strong acid is added to water, it completely dissociates its protons ( $\text{H}^+$ ). For example, the dissociation of sulfuric acid in water is



Or more simply:



A similar type of reaction occurs if a strong base is added to water, except hydroxide ions ( $\text{OH}^-$ ) are dissociated. For example, the dissociation of the strong base, sodium hydroxide ( $\text{NaOH}$ ), in water is



Or more simply:

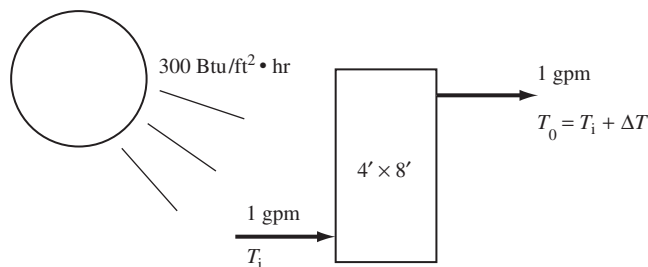


When both a strong acid and a strong base are added to water together, the protons from the acid react with the hydroxides from the base to produce more water molecules until the supply of either excess protons or hydroxides is used up. The reaction is



The rate constant for reaction (P3) is  $1.4 \times 10^{11} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .\*

- (a) 8.00 mg of  $\text{H}_2\text{SO}_4$  is added to 1.00 L of water in a flask. How much  $\text{NaOH}$  (in mg) must be added to neutralize the acid? Neutralization means conversion of all of the protons from the acid to water as shown in reaction (P3).
- (b) If the 8.00 mg of  $\text{H}_2\text{SO}_4$  and the amount of base you calculated in part (a) are added to the flask's water at the same instant, what will be the half-life of the added protons in the water?
- 23 A  $4 \times 8$ -ft solar collector has water circulating through it at the rate of 1.0 gallon per minute (gpm) while exposed to sunlight with intensity 300 Btu/ft<sup>2</sup>-hr (see Figure P23).



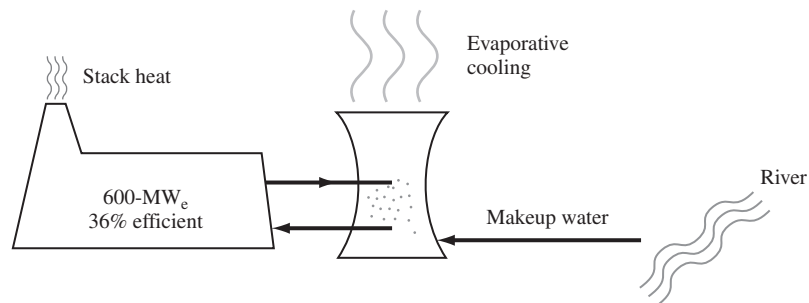
**FIGURE P23**

\*From Moore and Pearson, *Kinetics and Mechanism*, 3rd ed., 1981, Wiley-Interscience, New York, NY.

Fifty percent of that sunlight is captured by the collector and heats the water flowing through it. What would be the temperature rise of the water as it leaves the collector?

- 24 An uncovered swimming pool loses 1.0 in of water off of its 1,000 ft<sup>2</sup> surface each week due to evaporation. The heat of vaporization for water at the pool temperature is 1,050 Btu/lb. The cost of energy to heat the pool is \$10.00 per million Btu. A salesman claims that a \$500 pool cover that reduces evaporative losses by two-thirds will pay for itself in one 15-week swimming season. Can it be true?
- 25 Two-thirds of the energy content of fuel entering a 1,000-MW<sub>e</sub> nuclear power plant is removed by condenser cooling water that is withdrawn from a local river (there are no stack losses, as is the case for a fossil fuel-fired plant). The river has an upstream flow of 100 m<sup>3</sup>/s and a temperature of 20°C.
  - (a) If the cooling water is only allowed to rise in temperature by 10°C, what flow rate from the river would be required? Compare it to the coal plant in Example 12.
  - (b) How much would the river temperature rise as it receives the heated cooling water? Again, compare it to Example 12.
- 26 Consider a 354-mL can of soda cold enough to cause moisture from the air to condense on the outside of the can. If all of the heat released when 5 ml of vapor condenses on the can is transferred into the soda, how much would the soda temperature increase? Assume the density and specific heat of the soda are the same as water, neglect the thermal capacitance of the can itself, and use 2,500 kJ/kg as the latent heat of vaporization (condensation).
- 27 Compare the energy required to evaporate a kilogram of water at 15°C to that required to raise it 3 km into the air. (Recall that 1 kg on Earth weighs 9.8 N, and 1 J = 1 N-m.)
- 28 Compare the potential energy represented by 1 lb of water vapor at 59°F (15°C) and an elevation of 5,000 ft to the energy that would be released when it condenses into rain (1 Btu = 778 ft-lb).
- 29 A 600-MW<sub>e</sub> power plant has an efficiency of 36 percent with 15 percent of the waste heat being released to the atmosphere as stack heat and the other 85 percent taken away in the cooling water (see Figure P29). Instead of drawing water from a river, heating it, and returning it to the river, this plant uses an evaporative cooling tower wherein heat is released to the atmosphere as cooling water is vaporized.

At what rate must 15°C makeup water be provided from the river to offset the water lost in the cooling tower?



**FIGURE P29**

- 30 An electric water heater held at 140°F is kept in a 70°F room. When purchased, its insulation is equivalent to R-5. An owner puts a 25-ft<sup>2</sup> blanket on the water heater, raising its

- total  $R$  value to 15. Assuming 100 percent conversion of electricity into heated water, how much energy (kWhr) will be saved each year? If electricity costs 8.0 cents/kWhr, how much money will be saved in energy each year?
- 31 A 15-W compact fluorescent lightbulb (CFL) produces the same amount of light as a 60-W incandescent while using only one-fourth the power. Over the 9,000-hr lifetime of one CFL, compute carbon,  $\text{SO}_2$ , and particulate emissions that would be saved if one CFL replaces incandescents and the electricity comes from the coal-fired power plant described in Example 13.
  - 32 Suppose a utility generates electricity with a 36 percent efficient coal-fired power plant emitting the legal limit of 0.6 lb of  $\text{SO}_2$  per million Btus of heat into the plant. Suppose the utility encourages its customers to replace their 75-W incandescents with 18-W compact fluorescent lamps (CFLs) that produce the same amount of light. Over the 10,000-hr lifetime of a single CFL,
    - (a) How many kilowatt-hours of electricity would be saved?
    - (b) How many 2,000-lb tons of  $\text{SO}_2$  would not be emitted?
    - (c) If the utility can sell its rights to emit  $\text{SO}_2$  at \$800 per ton (these are called “allowances”; see Chapter 7), how much money could the utility earn by selling the  $\text{SO}_2$  saved by a single CFL?
  - 33 No. 6 fuel oil has a carbon content of 20 kg carbon per  $10^9$  J. If it is burned in a 40 percent efficient power plant, find the carbon emissions per kilowatt-hour of electricity produced, assuming all of the carbon in the fuel is released into the atmosphere. By law, new oil-fired power plant emissions are limited to 86 mg of  $\text{SO}_2$  per million joules (MJ) of thermal input and 130 mg  $\text{NO}_x$ /MJ. Estimate the maximum allowable  $\text{SO}_2$  and  $\text{NO}_x$  emissions per kilowatt-hour.
  - 34 Mars radiates energy with a peak wavelength of  $13.2 \mu\text{m}$ .
    - (a) Treating it as a blackbody, what would its temperature be?
    - (b) What would be the frequency and energy content of a photon at that wavelength?
  - 35 The rate at which sunlight reaches the outer edge of the atmosphere of Earth is  $1,370 \text{ W/m}^2$  (the solar constant for Earth). The Earth’s orbit has an average radius of  $150 \times 10^6 \text{ km}$ . Solar radiation decreases as the square of the distance from the sun. Estimate the solar constants for
    - (a) Mars, whose orbit has a radius of  $228 \times 10^6 \text{ km}$ .
    - (b) Venus, whose orbit has a radius of  $108 \times 10^6 \text{ km}$ .
  - 36 Objects not only radiate energy, but they absorb radiant energy as well. The net black-body radiation for an object at temperature  $T_1$  in an environment with temperature  $T_2$  is given by
 
$$E_{\text{net}} = \sigma A[(T_1)^4 - (T_2)^4]$$

Suppose an unclothed human body has a surface area of  $1.35 \text{ m}^2$ , an average skin temperature of  $32^\circ\text{C}$ , and is in a room with surfaces at  $15^\circ\text{C}$ . Treating this person as a black-body (a very good approximation), find the net heat loss by radiation (watts).
  - 37 A hot-water radiator has a surface temperature of  $80^\circ\text{C}$  and a surface area of  $2 \text{ m}^2$ . Treating it as a blackbody, find the net rate at which it will radiate energy to a  $20^\circ\text{C}$  room (see Problem 36).

# Environmental Chemistry

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|   |                              |
|---|------------------------------|
| 1 | Introduction                 |
| 2 | Stoichiometry                |
| 3 | Enthalpy in Chemical Systems |
| 4 | Chemical Equilibria          |
| 5 | Organic Chemistry            |
| 6 | Nuclear Chemistry            |
|   | Problems                     |
|   | References                   |

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It often matters much how given atoms combine, in what arrangement, with what others, what impulse they receive, and what impart. The same ones make up earth, sky, sea, and stream; the same the sun, the animals, grain and trees, but mingling and moving in ever different ways.

—*Lucretius (95–52 B.C.) in The Nature of Things*

## 1 | Introduction

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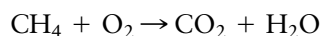
Almost every pollution problem that we face has a chemical basis. Even the most qualitative descriptions of such problems as the greenhouse effect, ozone depletion, toxic wastes, groundwater contamination, air pollution, and acid rain, to mention a few, require at least a rudimentary understanding of some basic chemical concepts. And, of course, an environmental engineer who must design an emission control system or a waste treatment plant must be well grounded in chemical principles and the techniques of chemical engineering. In this brief chapter, the topics have been selected with the goal of providing only the essential chemical principles required to understand the nature of the pollution problems that we face and the engineering approaches to their solutions.

## 2 | Stoichiometry

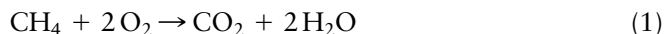
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When a chemical reaction is written down, it provides both qualitative and quantitative information. Qualitatively, we can see which chemicals are interacting to produce which end products. Quantitatively, the principle of conservation of mass can be applied to give information about how much of each compound is involved to produce the results shown. The balancing of equations so that the same number of each kind of atom appears on each side of the equation and the subsequent calculations, which can be used to determine amounts of each compound involved, is known as *stoichiometry*.

The first step is to balance the equation. For example, suppose we want to investigate the combustion of methane ( $\text{CH}_4$ ), the principal component of natural gas and a major greenhouse gas. Methane combines with oxygen to produce carbon dioxide and water as the following reaction suggests:



The equation is not balanced. One atom of carbon appears on each side, which is fine, but there are four atoms of hydrogen on the left and only two on the right, and there are only two atoms of oxygen on the left while there are three on the right. We might try to double the water molecules on the right to balance the hydrogen on each side, but then there would be an imbalance of oxygen with two on the left and four on the right. So try doubling the oxygen on the left. This sort of trial-and-error approach to balancing simple reactions usually converges pretty quickly. In this instance, the following is a balanced equation with the same number of C, H, and O atoms on each side of the arrow:



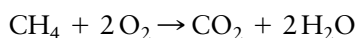
This balanced chemical equation can be read as: One molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water. It is of more use, however, to be able to describe this reaction in terms of the mass of each substance, that is, how many grams of oxygen are required to react with how many grams of methane, and so on. To do so requires that we know something about the mass of individual atoms and molecules.

The *atomic weight* of an atom is the mass of the atom measured in *atomic mass units* (amu) where one amu is defined to be exactly one-twelfth the mass of a carbon atom having six protons and six neutrons in its nucleus. Although this might suggest that if we look up the atomic weight of carbon, we would expect to find it to be exactly 12 amu, that is not the case. All carbon atoms do have six protons, but they do not all have six neutrons, so they do not all have the same atomic weight. Atoms having the same number of protons but differing numbers of neutrons are called *isotopes*. What is reported in tables of atomic weights, is the average based on the relative abundance of different isotopes found in nature. The *atomic number* is the number of protons in the nucleus. All isotopes of a given element have the same atomic number.

The *molecular weight* of a molecule is simply the sum of the atomic weights of all of the constituent atoms. If we divide the mass of a substance by its molecular weight, the result is the mass expressed in *moles* (mol). Usually the mass is expressed in grams, in which case 1 mole contains  $6.02 \times 10^{23}$  molecules (Avogadro's number).

$$\text{Moles} = \frac{\text{Mass (g)}}{\text{Molecular weight}} \quad (2)$$

The special advantage of expressing amounts in moles is that 1 mole of any substance contains exactly the same number of molecules, which gives us another way to interpret a chemical equation. Consider (1), repeated here:



On a molecular level, we can say that 1 molecule of methane reacts with 2 molecules of oxygen to produce 1 molecule of carbon dioxide and 2 molecules of water. On a larger (and more environmentally relevant) scale, we can say that 1 mole of methane reacts with 2 moles of oxygen to produce 1 mole of carbon dioxide and 2 moles of water. Because we know how many grams are contained in each mole, we can express our mass balance in those terms as well.

To express the preceding methane reaction in grams, we need first to find the number of grams per mole for each substance. The atomic weight of C is 12, H is 1, and O is 16. Notice that these values have been rounded slightly, which is common engineering practice. Thus, the molecular weights and hence the number of grams per mole, are

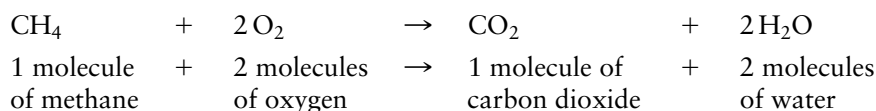
$$\text{CH}_4 = 12 + 4 \times 1 = 16 \text{ g/mol}$$

$$\text{O}_2 = 2 \times 16 = 32 \text{ g/mol}$$

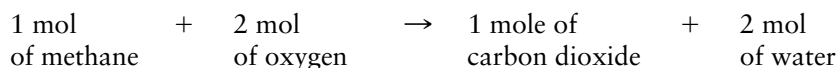
$$\text{CO}_2 = 12 + 2 \times 16 = 44 \text{ g/mol}$$

$$\text{H}_2\text{O} = 2 \times 1 + 16 = 18 \text{ g/mol}$$

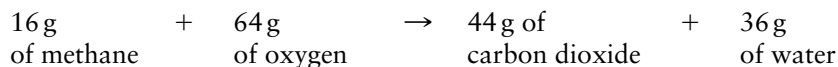
Summarizing these various ways to express the oxidation of methane, we can say



or,



or,

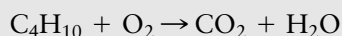


Notice that mass is conserved in the last expression; that is, there are 80 grams on the left and 80 grams on the right.

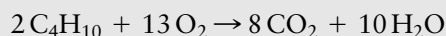
**EXAMPLE 1** Combustion of Butane

What mass of carbon dioxide would be produced if 100 g of butane ( $\text{C}_4\text{H}_{10}$ ) is completely oxidized to carbon dioxide and water?

**Solution** First write down the reaction:



then balance it



Find the grams per mole for butane:

$$\text{C}_4\text{H}_{10} = 4 \times 12 + 10 \times 1 = 58 \text{ g/mol}$$

We already know that there are 44 grams per mole of  $\text{CO}_2$ , so we don't need to recalculate that. Two moles of butane ( $2 \text{ mol} \times 58 \text{ g/mol} = 116 \text{ g}$ ) yields 8 moles of carbon dioxide ( $8 \text{ mol} \times 44 \text{ g/mol} = 352 \text{ g CO}_2$ ). So, we can set up the following proportion:

$$\frac{116 \text{ g C}_4\text{H}_{10}}{352 \text{ g CO}_2} = \frac{100 \text{ g C}_4\text{H}_{10}}{\text{X g CO}_2}$$

Thus,

$$\text{X} = 100 \times 352/116 = 303 \text{ g of CO}_2 \text{ produced}$$

Many environmental problems involve concentrations of substances dissolved in water. We introduce two common sets of units: mg/L and ppm. However, it is also useful to express concentrations in terms of *molarity*, which is simply the number of moles of substance per liter of solution. A 1 molar (1 M) solution has 1 mole of substance dissolved into enough water to make the mixture have a volume of 1 L. Molarity is related to mg/L concentrations by the following:

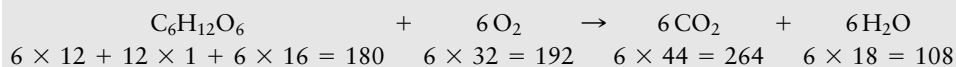
$$\text{mg/L} = \text{Molarity (mol/L)} \times \text{Molecular Weight (g/mol)} \times 10^3 \text{ (mg/g)} \quad (3)$$

The following example illustrates the use of molarity, and at the same time, introduces another important concept having to do with the amount of oxygen required to oxidize a given substance.

**EXAMPLE 2** Theoretical Oxygen Demand

Consider a  $1.67 \times 10^{-3} \text{ M}$  glucose solution ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) that is completely oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Find the amount of oxygen required to complete the reaction.

**Solution** To find the oxygen required to completely oxidize this glucose, we first write a balanced equation, determine molecular weights, and find the mass of each constituent in the reaction:



Thus it takes 192 g of oxygen to oxidize 180 g of glucose. From (3), the concentration of glucose is

$$\text{mg/L} = 1.67 \times 10^{-3} \text{ mol/L} \times 180 \text{ g/mol} \times 10^3 \text{ mg/g} = 301 \text{ mg/L}$$

so the oxygen requirement would be

$$300 \text{ mg/L glucose} \times \frac{192 \text{ g O}_2}{180 \text{ g glucose}} = 321 \text{ mg/L O}_2$$

If the chemical composition of a substance is known, then the amount of oxygen required to oxidize it to carbon dioxide and water can be calculated using stoichiometry, as was done in the preceding example. That oxygen requirement is known as the *theoretical oxygen demand*. If that oxidation is carried out by bacteria using the substance for food, then the amount of oxygen required is known as the *biochemical oxygen demand* or *BOD*. The BOD will be somewhat less than the theoretical oxygen demand because some of the original carbon is incorporated into bacterial cell tissue rather than being oxidized to carbon dioxide. Oxygen demand is an important measure of the likely impact that wastes will have on a receiving body of water.

The convenience of using moles to describe amounts of substances also helps when calculating atmospheric concentrations of pollutants. It was Avogadro's hypothesis, made in 1811, that equal volumes of all gases, at a specified temperature and pressure, contain equal numbers of molecules. In fact, since 1 mole of any substance has Avogadro's number of molecules, it follows that 1 mole of gas, at a specified temperature and volume, will occupy a predictable volume. At standard temperature and pressure (STP), corresponding to 0°C and 1 atm. (760 mm of mercury, 101.3 kPa), 1 mole of an ideal gas occupies 22.4 L, or 0.0224 m<sup>3</sup>, and contains  $6.02 \times 10^{23}$  molecules.

Let us demonstrate the usefulness of Avogadro's hypothesis for gases by applying it to a very modern concern; that is, the rate at which we are pouring carbon dioxide into the atmosphere as we burn up our fossil fuels.

### EXAMPLE 3 Carbon Emissions from Natural Gas

Worldwide combustion of methane, CH<sub>4</sub> (natural gas), provides about  $10.9 \times 10^{16}$  kJ of energy per year. If methane has an energy content of  $39 \times 10^3$  kJ/m<sup>3</sup> (at STP), what mass of CO<sub>2</sub> is emitted into the atmosphere each year? Also, express that emission rate as metric tons of carbon (not CO<sub>2</sub>) per year. A metric ton, which is 1,000 kg, is usually written as *tonne* to distinguish it from the 2,000-lb American, or short, *ton*.

**Solution** We first need to express that consumption rate in moles. Converting kJ of energy into moles of methane is straightforward:

$$\text{moles CH}_4 = \frac{10.9 \times 10^{16} \text{ kJ/yr}}{39 \times 10^3 \text{ kJ/m}^3} \times \frac{1}{22.4 \times 10^{-3} \text{ m}^3/\text{mol}} = 12.5 \times 10^{13} \text{ mol/yr}$$



We know from the balanced chemical reaction given in (1) that each mole of  $\text{CH}_4$  yields 1 mole of  $\text{CO}_2$ , so there will be  $12.5 \times 10^{13}$  moles of  $\text{CO}_2$  emitted. Since the molecular weight of  $\text{CO}_2$  is 44, the mass of  $\text{CO}_2$  emitted is

$$\text{mass CO}_2 = 12.5 \times 10^{13} \text{ mol/yr} \times 44 \text{ g/mol} = 5.5 \times 10^{15} \text{ g/yr}$$

To express these emissions as tonnes of C per year, we must convert grams to tonnes and then sort out the fraction of  $\text{CO}_2$  that is carbon. The fraction of  $\text{CO}_2$  that is C is simply the ratio of the atomic weight of carbon (12) to the molecular weight of carbon dioxide (44):

$$\begin{aligned} \text{C emissions} &= 5.5 \times 10^{15} \text{ g CO}_2/\text{yr} \times \frac{1 \text{ kg}}{1,000 \text{ g}} \times \frac{1 \text{ tonne}}{1,000 \text{ kg}} \times \frac{12 \text{ g C}}{44 \text{ g CO}_2} \\ &= 1.5 \times 10^9 \text{ tonnes/yr} = 1.5 \text{ gigatonne/yr} = 1.5 \text{ GtC/yr} \end{aligned}$$

The  $1.5 \times 10^9$  tonnes of carbon found in the preceding example is about 20 percent of the total, worldwide carbon emissions entering the atmosphere each year when fossil fuels (coal, oil, natural gas) are burned. “Global Atmospheric Change” the main worry about these emissions is their potential to enhance the Earth’s greenhouse effect.

### 3 | Enthalpy in Chemical Systems

Just as we used conservation of mass to balance chemical equations, we can use the conservation of energy to learn something about heat absorbed or released during chemical reactions. Since energy must be conserved, we should be able to track it from beginning to end. The first law of thermodynamics lets us say that the energy in the reactants on the left side of the equation, plus any heat added to the system, should equal the energy contained in the reaction products on the right side, plus any work done during the reaction.

$$U_1 + Q = U_2 + W \quad (4)$$

where

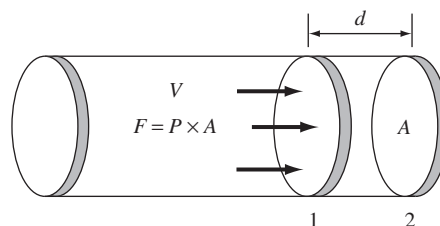
$U_1$  = internal energy of the chemical system at the beginning

$U_2$  = internal energy at the end

$Q$  = heat absorbed during the reaction

$W$  = work done by the system during the reaction

Although many forms of work could be included in (4), our concern will be only with work that occurs when a system changes volume under constant pressure, which is typical of chemical reactions. Any possibility of electrical, magnetic, gravitational, or other forms of work will be ignored. To analyze this work done by expansion, consider the cylinder in Figure 1 containing a volume of gas  $V$  exerting a pressure  $P$  against a piston with area  $A$ . The force exerted by the gas on the piston is



**FIGURE 1** Work done when a substance expands at constant pressure is  $P\Delta V$ .

$P \times A$ . If the piston moves a distance  $d$ , then, since work is force  $\times$  distance, we can write

$$W = Fd = PAd = P(V_2 - V_1) \quad (5)$$

Substituting (5) into (4) and rearranging terms gives

$$(U_2 + PV_2) - (U_1 + PV_1) = Q \quad (6)$$

If we define the *enthalpy*,  $H$ , of a system as

$$H = U + PV \quad (7)$$

then

$$H_2 - H_1 = \Delta H = Q \quad (8)$$

That is, the change in enthalpy during a constant pressure reaction is equal to the heat absorbed by the system. When  $\Delta H$  is positive, heat is absorbed and the reaction is said to be *endothermic*. When  $\Delta H$  is negative, heat is liberated and the reaction is called *exothermic*. The change in enthalpy,  $H_2 - H_1$ , is called the *heat of reaction*.

As is usually the case for discussions about energy, it is changes in energy, or in this case enthalpy, that are of interest. For example, we can talk about the potential energy of an object as being its weight times its height above some reference elevation. Our choice of reference elevation doesn't matter as long as we are only interested in the change in potential energy as an object is raised against gravity from one height to another. Similarly, since changes in enthalpy during a chemical reaction are of interest, it doesn't really matter what reference conditions are chosen. Tabulated values of enthalpy are usually based on 1 atm of pressure and 25°C (298 K); in which case, they are designated with the notation

$$H_{298}^0 = \text{standard enthalpy} = \text{enthalpy at 1 atm and 298 K (kJ/mol)} \quad (9)$$

It is also assumed that the reference condition for pure elements is the stable state of the substance at 1 atm and 25°C. For example, the stable state of oxygen at 1 atm and 25°C, is gaseous  $O_2$ , so the standard enthalpy for  $O_2(g)$ , where (g) just means it is in the gaseous state, is defined to be 0. Similarly, mercury under those conditions is a liquid, so the standard enthalpy for  $Hg(l)$  is 0, where (l) means the liquid state. A table of standard enthalpies for a number of substances is presented in Table 1. More extensive lists can be found in chemical handbooks or more advanced environmental engineering texts.

The sum of the enthalpies of the reaction products minus the sum of the enthalpies of the reactants is called the *heat of reaction*. When it is negative, heat is

TABLE 1

| Standard Enthalpies for Selected Species (kJ/mol) |                    |             |                               |                    |             |
|---------------------------------------------------|--------------------|-------------|-------------------------------|--------------------|-------------|
| Substance                                         | State <sup>a</sup> | $H_{298}^0$ | Substance                     | State <sup>a</sup> | $H_{298}^0$ |
| Ca <sup>2+</sup>                                  | <i>aq</i>          | -543.0      | HCO <sub>3</sub> <sup>-</sup> | <i>aq</i>          | -691.1      |
| CaCO <sub>3</sub>                                 | <i>s</i>           | -1207       | H <sub>2</sub> O              | <i>l</i>           | -285.8      |
| Ca(OH) <sub>2</sub>                               | <i>s</i>           | -986.6      | H <sub>2</sub> O              | <i>g</i>           | -241.8      |
| C                                                 | <i>s</i>           | 0           | NO                            | <i>g</i>           | 90.4        |
| CO                                                | <i>g</i>           | -110.5      | NO <sub>2</sub>               | <i>g</i>           | 33.9        |
| CO <sub>2</sub>                                   | <i>g</i>           | -393.5      | NO <sub>2</sub> <sup>-</sup>  | <i>aq</i>          | -106.3      |
| CO <sub>2</sub>                                   | <i>aq</i>          | -412.9      | N                             | <i>g</i>           | 472.6       |
| CH <sub>4</sub>                                   | <i>g</i>           | -74.9       | N <sub>2</sub>                | <i>g</i>           | 0           |
| C <sub>2</sub> H <sub>4</sub>                     | <i>g</i>           | 52.3        | N <sub>2</sub> O              | <i>g</i>           | 81.55       |
| CH <sub>3</sub> COOH                              | <i>aq</i>          | -488.5      | NH <sub>3</sub>               | <i>aq</i>          | -80.8       |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub>          | <i>g</i>           | -124.7      | O                             | <i>g</i>           | 247.5       |
| <i>i</i> -C <sub>4</sub> H <sub>10</sub>          | <i>g</i>           | -131.6      | O <sub>2</sub>                | <i>g</i>           | 0           |
| H                                                 | <i>g</i>           | 217.9       | O <sub>3</sub>                | <i>g</i>           | 142.9       |
| H <sup>+</sup>                                    | <i>aq</i>          | 0           | OH <sup>-</sup>               | <i>aq</i>          | -229.9      |
| H <sub>2</sub>                                    | <i>g</i>           | 0           | SO <sub>2</sub>               | <i>g</i>           | -296.9      |

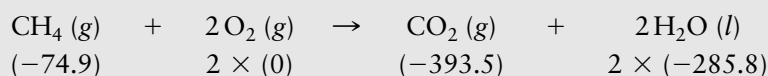
<sup>a</sup>*g* = gas, *aq* = aqueous, *s* = solid, *l* = liquid.

liberated during the reaction; when it is positive, heat is absorbed. Since standard enthalpies are expressed as energy per mole, we must first balance the chemical reaction, and then for each species, multiply the number of moles by the standard enthalpy to get its total enthalpy.

#### EXAMPLE 4 Gross Heat of Combustion for Methane

Find the heat of reaction when methane CH<sub>4</sub> is oxidized to CO<sub>2</sub> and liquid H<sub>2</sub>O.

**Solution** The reaction is written here, and enthalpies taken from Table 1 appear below it.



Notice we have used the enthalpy of liquid water for this calculation. The heat of reaction is the difference between the total enthalpy of the reaction products and reactants:

$$[(-393.5) + 2 \times (-285.8)] - [(-74.9) + 2 \times (0)] = -890.2 \text{ kJ/mol of CH}_4$$

Since the heat of reaction is negative, heat is released during combustion (*i.e.*, it is exothermic).

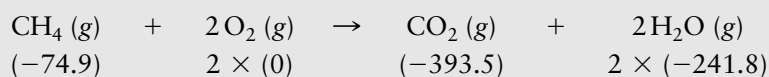
When a fuel is burned, some of the energy released ends up as latent heat in the water vapor produced. Usually that water vapor, along with the latent heat it contains, exits the stack along with all the other combustion gases, and its heating value is, in essence, lost. That leads to two different values of what is called the *heat of combustion*. The *higher heating value* (HHV) includes the heat released when water

condenses to liquid form, as was the case in Example 4. The HHV is also known as the *gross heat of combustion*. In the United States, the heat content of fossil fuels is usually expressed as this gross amount. The *lower heating value* (LHV), or *net heat of combustion*, is based on the heat of reaction when water is assumed to remain in the vapor state. The most fuel-efficient, modern furnaces used for space-heating buildings achieve their high efficiencies (above 90 percent) by causing the combustion gases to cool enough to condense the water vapor before it leaves the stack. Not unexpectedly, these are called *condensing furnaces*.

#### EXAMPLE 5 The Net Heat of Combustion

Find the net heat of combustion when methane is burned.

**Solution** We just repeat the procedure of Example 4, but this time, the water will remain in the gaseous state. Again, using values from Table 1,



The net heat of combustion is

$$[(-393.5) + 2 \times (-241.8)] - [(-74.9) + 2 \times (0)] = -802.2 \text{ kJ/mol of CH}_4$$

Again, the sign tells us this is an exothermic reaction. Notice about 10 percent of the gross heating value is lost when water vapor is not condensed.

There is another application of the concept of enthalpy that is useful in describing photochemical smog reactions in the atmosphere and for analyzing the chemical reactions that affect the stratospheric ozone layer. When a molecule is dissociated by absorbing a photon of energy, the process is called a *photochemical reaction*, *photochemical dissociation*, or more simply *photolysis*. We can use enthalpies to determine the amount of energy a photon must have to cause photolysis, and from the photon's energy, we can determine the maximum wavelength that the photon can have.

For a photon to be able to cause photolysis, it must have at least as much energy as the change in enthalpy for the reaction. It is important to realize that when a molecule absorbs a photon, the energy must be used almost immediately for photolysis or else the energy will be dissipated as waste heat as the molecule collides with neighboring molecules. Molecules cannot store up energy from a series of photon encounters, waiting until enough energy is accumulated to cause photolysis. That means a *single* photon has to have sufficient energy to cause photolysis all by itself.

The following relationship between energy contained in 1 photon and the wavelength and frequency associated with that photon is introduced:

$$E = h\nu = \frac{hc}{\lambda} \quad (10)$$

where

$E$  = Energy of a photon (J)  
 $h$  = Planck's constant ( $6.6 \times 10^{-34}$  J·s)  
 $\nu$  = frequency (hertz, *i.e.*, cycles per second)  
 $c$  = speed of light ( $3 \times 10^8$  m/s)  
 $\lambda$  = wavelength (m)

We are interested in the maximum wavelength that a photon can have and still have enough energy for photolysis, so rearranging (10) gives

$$\lambda \leq \frac{hc}{E} \quad (11)$$

Before we can equate the energy in a photon with the enthalpy change, we have to be sure the units are consistent. The reaction's enthalpy change  $\Delta H^0$  has units of kJ/mol, and  $E$  is joules per photon. Using Avogadro's number, along with the fact that 1 photon dissociates 1 molecule, lets us write:

$$\lambda \leq \frac{6.6 \times 10^{-34} \text{ J} \cdot \text{s} \times 3 \times 10^8 \text{ m/s} \times 6.02 \times 10^{23} \text{ molecules/mol} \times 1 \text{ photon/molecule}}{\Delta H^0 \text{ (kJ/mol)} \times 10^3 \text{ J/kJ}}$$

$$\lambda(\text{m}) \leq \frac{1.19 \times 10^{-4} \text{ (kJ} \cdot \text{m/mol)}}{\Delta H^0 \text{ (kJ/mol)}} \quad (12)$$

#### EXAMPLE 6 Photolysis of Ozone

What maximum wavelength of light would be capable of causing photolysis of ozone  $\text{O}_3$  into  $\text{O}_2$  and  $\text{O}$ ?

**Solution** First write the reaction, including enthalpies from Table 1. Even though those enthalpies are for standard conditions (1 atm, 298 K), they can be used under stratospheric pressure and temperature conditions with only modest error.



The enthalpy change is

$$\Delta H^0 = 247.5 - 142.9 = 104.6 \text{ kJ/mol}$$

Since the sign of  $\Delta H^0$  is positive, this is an endothermic reaction that needs to absorb energy for it to take place. That energy comes from the photon.

From Equation (12),

$$\lambda \leq \frac{1.19 \times 10^{-4} \text{ kJ} \cdot \text{m/mol}}{104.6 \text{ kJ/mol}} = 1.13 \times 10^{-6} \text{ m} = 1.13 \mu\text{m}$$

Absorption of incoming solar radiation by ozone, as described in Example 6, is part of the shielding that the stratospheric ozone layer provides for Earth.

## 4 | Chemical Equilibria

In the reactions considered so far, the assumption has been that they proceed in one direction only. Most chemical reactions are, to some extent, reversible, proceeding in both directions at once. When the rates of reaction are the same—that is products are being formed on the right at the same rate as they are being formed on the left—the reaction is said to have reached *equilibrium*.

In this generalized reversible reaction



the small letters  $a$ ,  $b$ ,  $c$ , and  $d$  are coefficients corresponding to the number of molecules or ions of the respective substances that result in a balanced equation. The capital letters A, B, C, and D are the chemical species. The double arrow designation indicates that the reaction proceeds in both directions at the same time.

At equilibrium, we can write that

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K \quad (14)$$

where the [ ] designation represents concentrations of the substances at equilibrium, expressed in moles per liter (molarity). Do not use concentrations in mg/L!  $K$  is called the *equilibrium constant*. Informally, the equilibrium constant is spoken of as the products over reactants or the ratio of products to reactants. It should also be emphasized that (14) is valid only when chemical equilibrium is established, if ever. Natural systems are often subject to constantly changing inputs, and since some reactions occur very slowly, equilibrium may never be established. A practicing environmental engineer must therefore use this important equation with a certain degree of caution.

Equilibrium constants are used in so many ways in water chemistry that they often are given specific names to describe a particular equilibrium process. Many molecules, when dissolved in water, separate into positively charged ions, called *cations*, and negatively charged ions, called *anions*. Equation (14) can be applied to the dissociation of such molecules, in which case  $K$  is referred to as a *dissociation constant* or an *ionization constant*. The quantity on the left in (13) may be a solid, and the problem is to determine the degree to which that solid enters solution. In such cases, the equilibrium constant is called the *solubility product* and is often denoted  $K_{sp}$ . In another process of environmental interest where a gas dissolves in water, the equilibrium constant describing the concentration of gas in the water in equilibrium with the concentration of the gas in the air is termed *Henry's constant* and denoted  $K_H$ . These and other equilibrium constants will be discussed in the next few sections. To lessen confusion, the kinetic rate constants are typically signified using a lowercase  $k$ , whereas equilibrium constants are written with an uppercase  $K$ .

Finally, often when dealing with very large and very small numbers, it is helpful to introduce the following logarithmic measure:

$$X = 10^{-pX} \quad (15)$$

or

$$pX = -\log X \quad (16)$$

where  $X$  is any number or a variable denoting any number.

## Acid-Base Reactions

Water dissociates slightly into hydrogen ions ( $\text{H}^+$ ) and hydroxide ions ( $\text{OH}^-$ ) as the following reaction suggests



The hydrogen ions,  $\text{H}^+$ , are also known as protons because when a hydrogen atom loses an electron—is ionized—all that remains is a proton. The corresponding equilibrium expression for this reaction is

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K \quad (18)$$

The molar concentration of water  $[\text{H}_2\text{O}]$  is 1,000 g/L divided by 18 g/mol, or 55.56 mol/L. Since water dissociates only slightly, the molar concentration after ionization is not changed enough to be of significance, so  $[\text{H}_2\text{O}]$  is essentially a constant that can be included in the equilibrium constant. The result is

$$[\text{H}^+][\text{OH}^-] = K_w = 1 \times 10^{-14} \quad \text{at } 25^\circ\text{C} \quad (19)$$

where  $K_w$  is the dissociation constant for water. For dilute aqueous solutions in general,  $[\text{H}_2\text{O}]$  is considered constant and is included in the equilibrium constant.  $K_w$  is slightly temperature dependent, but unless otherwise stated, the value given in (19) at  $25^\circ\text{C}$  is the assumed value.

Note that (19) holds, no matter what the source of hydrogen ions or hydroxide ions. That is, the equation is valid even if other substances dissolved in the water make their own contributions to the hydrogen and hydroxide supplies. It is always one of the equations that must be satisfied when chemical equilibria problems in water are analyzed.

$[\text{H}^+]$  and  $[\text{OH}^-]$  concentrations are customarily expressed using the logarithmic measure introduced in (15) and (16). To express hydrogen ion concentrations (also known as proton concentrations), the pH scale is used, where

$$\text{pH} = -\log[\text{H}^+] \quad (20)$$

or,

$$[\text{H}^+] = 10^{-\text{pH}} \quad (21)$$

With the pH scale, it is easy to specify whether a solution is acidic, basic, or neutral. In a *neutral* solution, the concentration of hydrogen ions  $[\text{H}^+]$  equals the concentration of hydroxide ions  $[\text{OH}^-]$ . From (19), for a neutral solution

$$[\text{H}^+][\text{OH}^-] = [\text{H}^+][\text{H}^+] = [\text{H}^+]^2 = 10^{-14}$$

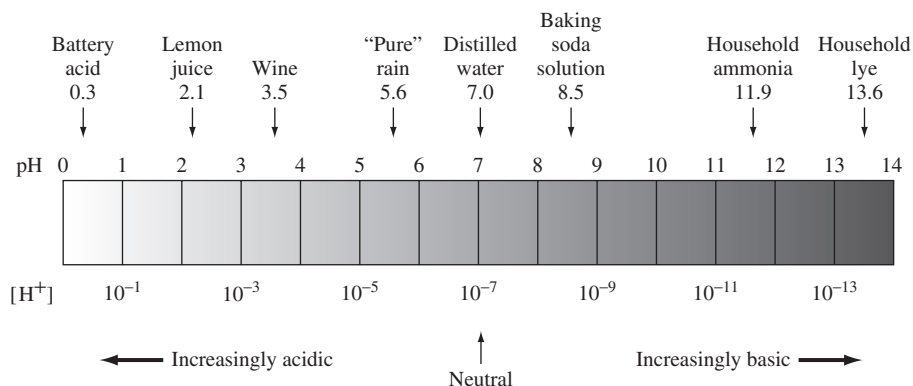
so

$$[\text{H}^+] = 10^{-7}$$

and a neutral solution has a pH of 7 (written pH 7).

An *acidic* solution is one in which  $[\text{H}^+]$  is greater than  $[\text{OH}^-]$ ; that is, the hydrogen ion concentration is greater than  $10^{-7}$  mol/L, and its pH is less than 7. A *basic* solution is the other way around with more hydroxide ions than hydrogen ions and a pH greater than 7. Notice for every unit change in pH, the concentration of hydrogen ions changes by a factor of 10.

## Environmental Chemistry



**FIGURE 2** The pH scale.

Figure 2 illustrates the pH scale, showing example values of pH for several common solutions. Notice in the figure that a distinction is made between distilled water and “pure” rainfall. As will be seen in a later section on carbonates, as rain-water falls, it absorbs carbon dioxide from the air and carbonic acid is formed. Unpolluted rainfall then has a natural pH of around 5.6. By the usual definition, acid rain, caused by industrial pollutants, has pH lower than 5.6. Actual acid rain and acid fog have been recorded with pH below 2.0.

### EXAMPLE 7 pH of Tomato Juice

Find the hydrogen ion concentration and the hydroxide ion concentration in tomato juice having a pH of 4.1.

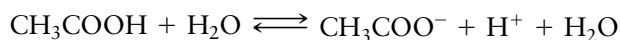
**Solution** From (21), the hydrogen ion concentration is

$$[H^+] = 10^{-\text{pH}} = 10^{-4.1} = 7.94 \times 10^{-5} \text{ mol/L}$$

From (19), the hydroxide ion concentration is

$$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{7.94 \times 10^{-5}} = 1.26 \times 10^{-10} \text{ mol/L}$$

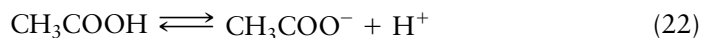
Water is not the only source of hydrogen ions or hydroxide ions. When a chemical dissociates in water and produces a hydrogen ion, it is an acid. As you would expect, any chemical that dissociates and gives off a hydroxide ion is a base. In other words, acids add protons (or subtract hydroxide ions) in water, whereas bases add hydroxide ions (or subtract protons). For instance, when acetic acid ( $C_2H_4O_2$ ), the main component in vinegar, is dissolved in water, some of it dissociates to protons ( $H^+$ ) and acetate ( $C_2H_3O_2^-$ ). At equilibrium,



The chemical composition of acetic acid is usually written as  $CH_3COOH$  rather than  $C_2H_4O_2$  to emphasize the presence of the carboxylic acid group ( $-COOH$ ), an organic functional group that will be explained later in this chapter. Since  $H_2O$



appears as both a reactant and product, it is usually dropped from the equation, so the equilibrium expression is written as



and the dissociation constant (with a subscript “a” for acidity constant) is

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 10^{-4.76} \quad (23)$$

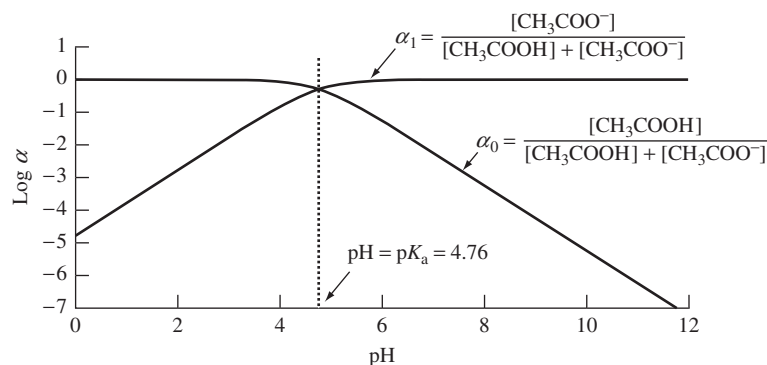
The degree of dissociation of an acid is a function of pH. This can be seen by rearranging (23) and using (21) to get

$$\frac{K_a}{[\text{H}^+]} = \frac{K_a}{10^{-\text{pH}}} = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad (24)$$

As pH goes up, that is, the  $\text{H}^+$  concentration goes down, then the ratio of concentration of acetate to acetic acid goes up. This is true for all acids; as the pH increases the degree of dissociation increases. In addition, when  $[\text{H}^+] = K_a$  ( $\text{pH} = \text{p}K_a$ ), then by (24),  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$ . Figure 3 shows this graphically in what is called an  $\alpha$  (*alpha*) diagram. In an  $\alpha$  diagram,  $\alpha_0$  denotes the fraction of total acid-derived species present (for this example,  $[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$ ) in the undissociated form (in this example,  $\text{CH}_3\text{COOH}$ ), whereas  $\alpha_1$  is the fraction that is in the dissociated or singly deprotonated form (in this example,  $\text{CH}_3\text{COO}^-$ ). Remember if we had added acetate rather than acetic acid to the water, the acetate would have been a base because some of it would have withdrawn hydrogen ions from the water to form acetic acid to satisfy the (24) equilibrium between  $\text{CH}_3\text{COO}^-$  and  $\text{CH}_3\text{COOH}$ . In fact, we call acetate the conjugate base of acetic acid.

Acetic acid is an example of a *monoprotic acid*, meaning it can lose 1 proton ( $\text{H}^+$ ) when dissolved in water. There are also *diprotic*, *triprotic*, and even *quadriprotic acids*. Table 2 shows some of the acids of environmental importance. As you would expect, the number of dissociation constants corresponds to the number of hydrogen ions an acid can lose, so the dissociation constant for dissociating the first proton is  $K_{a1}$ , for the second proton is  $K_{a2}$ , and so on. The behavior of a very important diprotic acid system, the carbonate system, will be discussed later in this chapter.

Acid-base reactions are among the most important in environmental engineering. Most aquatic forms of life, for example, are very sensitive to the pH of their



**FIGURE 3**  $\alpha$  diagram for acetic acid in water.

TABLE 2

| <b>Dissociation Constants and Chemical Formulas for Some Acids of Environmental Importance</b> |                                                |           |           |           |
|------------------------------------------------------------------------------------------------|------------------------------------------------|-----------|-----------|-----------|
| Acid                                                                                           | Formula                                        | $pK_{a1}$ | $pK_{a2}$ | $pK_{a3}$ |
| Nitric acid                                                                                    | $\text{HNO}_3$                                 | -1.30     | —         | —         |
| Hydrochloric acid                                                                              | $\text{HCl}$                                   | <0        | —         | —         |
| Sulfuric acid                                                                                  | $\text{H}_2\text{SO}_4$                        | <0        | 1.99      | —         |
| Phosphoric acid                                                                                | $\text{H}_3\text{PO}_4$                        | 2.16      | 7.20      | 12.35     |
| Arsenic acid                                                                                   | $\text{H}_3\text{AsO}_4$                       | 2.24      | 6.76      | —         |
| Citric acid                                                                                    | $\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3$ | 3.13      | 4.72      | 6.33      |
| Acetic acid                                                                                    | $\text{CH}_3\text{COOH}$                       | 4.76      | —         | —         |
| Carbonic acid                                                                                  | $\text{H}_2\text{CO}_3$                        | 6.35      | 10.33     | —         |
| Hydrogen sulfide                                                                               | $\text{H}_2\text{S}$                           | 6.99      | 12.92     | —         |
| Hypochlorous acid                                                                              | $\text{HOCl}$                                  | 7.60      | —         | —         |
| Ammonium ion                                                                                   | $\text{NH}_4^+$                                | 9.26      | —         | —         |
| Silicic acid                                                                                   | $\text{H}_4\text{SiO}_4$                       | 9.84      | 13.20     | —         |

habitat. To protect local ecosystems, waste neutralization before release is common. In other circumstances, by manipulating pH, unwanted substances can be driven out of a solution as precipitates or gases before the effluent is released.

#### EXAMPLE 8 Drinking Water Disinfection Using Chlorine

Chlorine is the active ingredient in most household bleach and is one of the most commonly used and inexpensive chemical disinfectants for water. The chlorine is in the hypochlorous acid form,  $\text{HOCl}$ , and hypochlorous acid is a much better disinfectant than hypochlorite,  $\text{OCl}^-$ , its conjugate base. If bleach is used to disinfect water, below what pH should the water be maintained so that at least 95 percent of the chlorine added is in the hypochlorous acid form?

**Solution** From Table 2 and inspection, we know hypochlorous acid is a monoprotic acid. Its equilibrium reaction is



The equilibrium constant equation is

$$K_{a1} = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} = 10^{-7.60} \quad (26)$$

which rearranges to

$$[\text{H}^+] = \frac{[\text{HOCl}]K_{a1}}{[\text{OCl}^-]}$$

We can then solve for  $[\text{H}^+]$  when  $[\text{HOCl}]/[\text{OCl}^-] = 95/5 = 19$ , so

$$[\text{H}^+] = 19 \times 10^{-7.60} = 4.77 \times 10^{-7} = 10^{-6.32}$$

If the pH is kept below 6.3, then more than 95 percent of the chlorine will be in the  $\text{HOCl}$  form.

TABLE 3

| Selected Solubility Product Constants at 25°C                                       |                     |                           |
|-------------------------------------------------------------------------------------|---------------------|---------------------------|
| Equilibrium Equation                                                                | $K_{sp}$ at 25°C    |                           |
| $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$                | $5 \times 10^{-9}$  | Hardness removal, scaling |
| $\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$                | $2 \times 10^{-5}$  | Flue gas desulfurization  |
| $\text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^-$                  | $2 \times 10^{-19}$ | Heavy metal removal       |
| $\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$                  | $1 \times 10^{-32}$ | Coagulation               |
| $\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$ | $1 \times 10^{-27}$ | Phosphate removal         |
| $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$                      | $3 \times 10^{-11}$ | Fluoridation              |

Source: Sawyer et al., 1994.

## Solubility Product

All solids are to some degree soluble, although some are much more so than others. A generalized equation describing the equilibrium condition in which a solid is dissociating into its ionic components (*dissolution*) at the same rate that ionic components are recombining into the solid form (*precipitation*) is



where A and B are the ionic components that make up the solid. Applying (14) yields

$$\frac{[\text{A}]^a[\text{B}]^b}{[\text{solid}]} = K \quad (28)$$

As long as there is still solid present at equilibrium, its effect can be incorporated into the equilibrium constant

$$[\text{A}]^a[\text{B}]^b = K_{sp} \quad (29)$$

where  $K_{sp}$  is called the *solubility product*. Table 3 gives a short list of solubility products of particular importance in environmental engineering.

As an example of the use of (29), consider the fluoridation of water with calcium fluoride,  $\text{CaF}_2$ .

### EXAMPLE 9 Fluoride Solubility

Find the equilibrium concentration of fluoride ions in pure water caused by the dissociation of  $\text{CaF}_2$ . Express the answer both in units of mol/L and mg/L.

**Solution** From Table 3, the reaction and solubility product are



Remembering to square the term for the fluoride ion, the mass action equation (29) becomes

$$[\text{Ca}^{2+}][\text{F}^-]^2 = 3 \times 10^{-11} \quad (30)$$

If we let  $s$  (mol/L) represent the concentration of  $\text{Ca}^{2+}$ , then the concentration of  $\text{F}^-$  will be  $2s$ , since 2 moles of  $\text{F}^-$  are dissociated for every mole of  $\text{Ca}^{2+}$  dissociated. Thus

$$[\text{Ca}^{2+}] = s$$

$$[\text{F}^-] = 2s$$

and from (30)

$$K_{\text{sp}} = s \times (2s)^2 = 4s^3 = 3 \times 10^{-11}$$

$$s = [\text{Ca}^{2+}] = 2 \times 10^{-4} \text{ mol/L}$$

$$2s = [\text{F}^-] = 4 \times 10^{-4} \text{ mol/L}$$

To find the concentration of fluoride ions in mg/L, we need the atomic weight of fluorine, which is 19.

$$[\text{F}^-] = 4 \times 10^{-4} \text{ mol/L} \times 19 \text{ g/mol} \times 10^3 \text{ mg/g} = 7.6 \text{ mg/L}$$

The fluoride concentration obtained in Example 9 is above recommended drinking water levels of 1.8 mg/L. Fluoride concentrations of approximately 1 mg/L in drinking water help prevent cavities in children, but discoloration of teeth, called *mottling*, is relatively common when concentrations exceed 2.0 mg/L.

## Solubility of Gases in Water

When air comes in contact with water, some of it dissolves into the water. Different constituents of air dissolve to different degrees and in amounts that vary with temperature and water purity. The behavior of gases in contact with water was reported by W. Henry in England in 1903, and the resulting relationship is known as *Henry's law*:

$$[\text{gas}] = K_{\text{H}} P_{\text{g}} \quad (31)$$

where

$[\text{gas}]$  = concentration of dissolved gas (mol/L)

$K_{\text{H}}$  = Henry's law constant (mol/L · atm)

$P_{\text{g}}$  = the partial pressure of the gas in air (atm)

The quantity  $P_{\text{g}}$  is the partial pressure of the gas in air, which is simply its volumetric concentration times the atmospheric pressure. The units suggested in the preceding list for pressure are atmospheres (atm), where 1 atm corresponds to 101,325 pascals (Pa), and 1 Pa equals 1 newton per square meter. For example, oxygen makes up about 21 percent of the atmosphere, so at 1 atm  $P_{\text{g}}$  would be  $0.21 \times 1 \text{ atm} = 0.21 \text{ atm}$ .

Each gas-liquid system has its own value for Henry's coefficient. The coefficient varies both with temperature (solubility decreases as temperature increases) and with concentration of other dissolved gases and solids (the solubility decreases as other dissolved material in the liquid increases). Note that Henry's law is expressed in various ways with different units for the coefficient depending on the

TABLE 4

| Henry's Law Coefficients, $K_H$ (mol/L · atm) |                 |                |
|-----------------------------------------------|-----------------|----------------|
| T (°C)                                        | CO <sub>2</sub> | O <sub>2</sub> |
| 0                                             | 0.076425        | 0.0021812      |
| 5                                             | 0.063532        | 0.0019126      |
| 10                                            | 0.053270        | 0.0016963      |
| 15                                            | 0.045463        | 0.0015236      |
| 20                                            | 0.039172        | 0.0013840      |
| 25                                            | 0.033363        | 0.0012630      |

method of expression. The user must be careful, then, to check the units given for Henry's constant before applying the law. Table 4 gives some values of  $K_H$  for CO<sub>2</sub> and O<sub>2</sub>, two of the gases that we will be most concerned with.

Because atmospheric pressure changes with altitude,  $P_g$  will change as well. One estimate for atmospheric pressure as a function of altitude is the following (Thomann and Mueller, 1987):

$$P = P_o - 1.15 \times 10^{-4}H \quad (32)$$

where

$P$  = atmospheric pressure at altitude  $H$  (atm)

$H$  = altitude (m)

$P_o$  = atmospheric pressure at sea level (atm)

#### EXAMPLE 10 Solubility of Oxygen in Water

By volume, the concentration of oxygen in air is about 21 percent. Find the equilibrium concentration of O<sub>2</sub> in water (in mol/L and mg/L) at 25°C and 1 atmosphere of pressure. Recalculate it for Denver at an altitude of 1,525 m.

**Solution** Air is 21 percent oxygen, so its partial pressure at 1 atm is

$$P_g = 0.21 \times 1 \text{ atm} = 0.21 \text{ atm}$$

From Table 4, at 25°C,  $K_H = 0.0012630 \text{ mol/L} \cdot \text{atm}$ ; so, from (31),

$$\begin{aligned} [\text{O}_2] &= K_H P_g = 0.0012630 \text{ mol/L} \cdot \text{atm} \times 0.21 \text{ atm} \\ &= 2.65 \times 10^{-4} \text{ mol/L} \\ &= 2.65 \times 10^{-4} \text{ mol/L} \times 32 \text{ g/mol} \times 10^3 \text{ mg/g} = 8.5 \text{ mg/L} \end{aligned}$$

In Denver, at 1,525 m, atmospheric pressure can be estimated using (32):

$$P = P_o - 1.15 \times 10^{-4}H = 1 - 1.15 \times 10^{-4} \times 1,525 = 0.825 \text{ atm}$$

so

$$\begin{aligned} [\text{O}_2] &= 0.0012630 \text{ mol/L} \cdot \text{atm} \times 0.21 \times 0.825 \text{ atm} = 2.19 \times 10^{-4} \text{ mol/L} \\ &= 2.19 \times 10^{-4} \text{ mol/L} \times 32 \text{ g/mol} \times 10^3 \text{ mg/g} = 7.0 \text{ mg/L} \end{aligned}$$

Calculations based on Henry's law provide equilibrium concentrations of dissolved gases, or, as they are frequently called, *saturation* values. Often, actual values differ considerably from those at equilibrium. There may be more than the saturation value of a dissolved gas, as when photosynthesis by plants pumps oxygen into the water at a faster rate than it can leave through the air/water interface. It is more common for dissolved gases to be less than the saturation value, as occurs when bacteria decompose large quantities of waste, drawing oxygen from the water (possibly leading to an oxygen deficiency that can kill fish). In either case, when an excess or a deficiency of a dissolved gas occurs, pressures act to try to bring the amount dissolved back to the saturation level.

As an example of the value of being able to engineer pH and utilize gas transfer across the air/water interface, consider the problem of removing nitrogen from wastewater. Nitrogen is a nutrient that can degrade water quality by stimulating excessive algal growth in receiving bodies of water. Nitrogen in the form of nitrate  $\text{NO}_3^-$  also poses another problem, especially in groundwater. When babies drink water with high nitrate content, a potentially lethal condition known as methemoglobinemia can result.

One way to remove nitrogen during wastewater treatment is with a process known as *ammonia stripping*. When organic matter decomposes, nitrogen is first released in the form of ammonia  $\text{NH}_3$  or ammonium ion  $\text{NH}_4^+$ . Ammonium ions are acids, whereas  $\text{NH}_3$  is ammonia gas, which dissolves in water with a Henry's constant of  $57 \text{ mol/L} \cdot \text{atm}$  at  $25^\circ\text{C}$ . Even though ammonia is much more soluble in water than, for instance, the oxygen in the preceding example, the concentration of ammonia in the air is near zero so ammonia is readily driven from water (stripped) and transferred to the air as the system tries to reach the air/water equilibrium state. By driving the acid/base equilibrium reaction



toward the right, more of the nitrogen will be in the ammonia gas form, which can then be stripped from solution and enter the air in a gas stripping tower. In such a tower, contaminated water is allowed to trickle downward over slats or corrugated surfaces while clean air is blown in from the bottom to aerate the dripping water. Gas stripping can be used in wastewater treatment facilities to remove such gases as ammonia and hydrogen sulfide, and it can also be used to remove *volatile organic chemicals* (VOCs) from contaminated groundwater.

To strip ammonia, the reaction given in (33) must be driven toward the right, which can be done by increasing the concentration of  $\text{OH}^-$ . This may be more easily seen by adding a hydroxide ion ( $\text{OH}^-$ ) to both sides of (33), which gives



Thus, by adding  $\text{OH}^-$ , in other words raising the pH, (34) is driven to the right so that more of the nitrogen is in the ammonia and strippable form.

### EXAMPLE 11 Ammonia Stripping

Nitrogen in a wastewater treatment plant is in the form of ammonia and ammonium ion and has a total concentration of  $7.1 \times 10^{-4} \text{ M}$ . The Henry's constant (at  $25^\circ\text{C}$ ) is  $57 \text{ mol/L} \cdot \text{atm}$ .

- Find the fraction of the nitrogen that is in the ammonia form (and hence strippable) as a function of pH, and draw a graph.
- If the wastewater pH is raised to 10 and the atmospheric ammonia concentration is  $5.0 \times 10^{-10}$  atm, what would be the equilibrium concentration of total nitrogen in the wastewater after air stripping?

**Solution** From (33) and Table 2, the equilibrium equation for the reaction is

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 10^{-9.26} \quad (35)$$

- What we want to find is the fraction of nitrogen in the form of ammonia, or

$$\text{NH}_3 \text{ fraction} = \frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]} = \frac{1}{1 + [\text{NH}_4^+]/[\text{NH}_3]} \quad (36)$$

Rearranging (35) gives

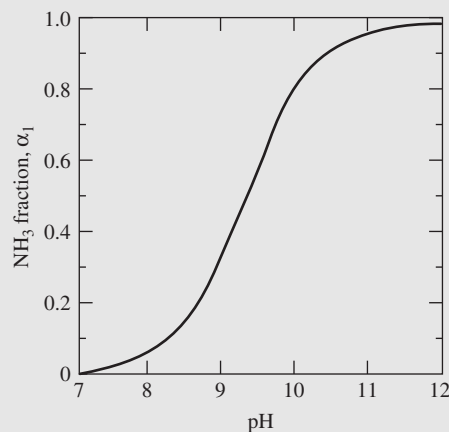
$$\frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{[\text{H}^+]}{K_a} \quad (37)$$

and putting this into (36) gives

$$\begin{aligned} \text{NH}_3 \text{ fraction} &= \frac{1}{1 + [\text{H}^+]/K_a} \\ &= \frac{1}{1 + 10^{-\text{pH}}/10^{-9.26}} \\ &= \frac{1}{1 + 10^{(9.26-\text{pH})}} \end{aligned} \quad (38)$$

A table of values for this fraction can easily be generated from (38); the results are plotted in Figure 4.

| pH | $\frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]}$ |
|----|---------------------------------------------------------|
| 4  | 0.000005                                                |
| 6  | 0.0005                                                  |
| 8  | 0.052                                                   |
| 9  | 0.35                                                    |
| 10 | 0.85                                                    |
| 12 | 0.99                                                    |



**FIGURE 4** Dependence of the ammonia fraction,  $\alpha_1$ , on pH.