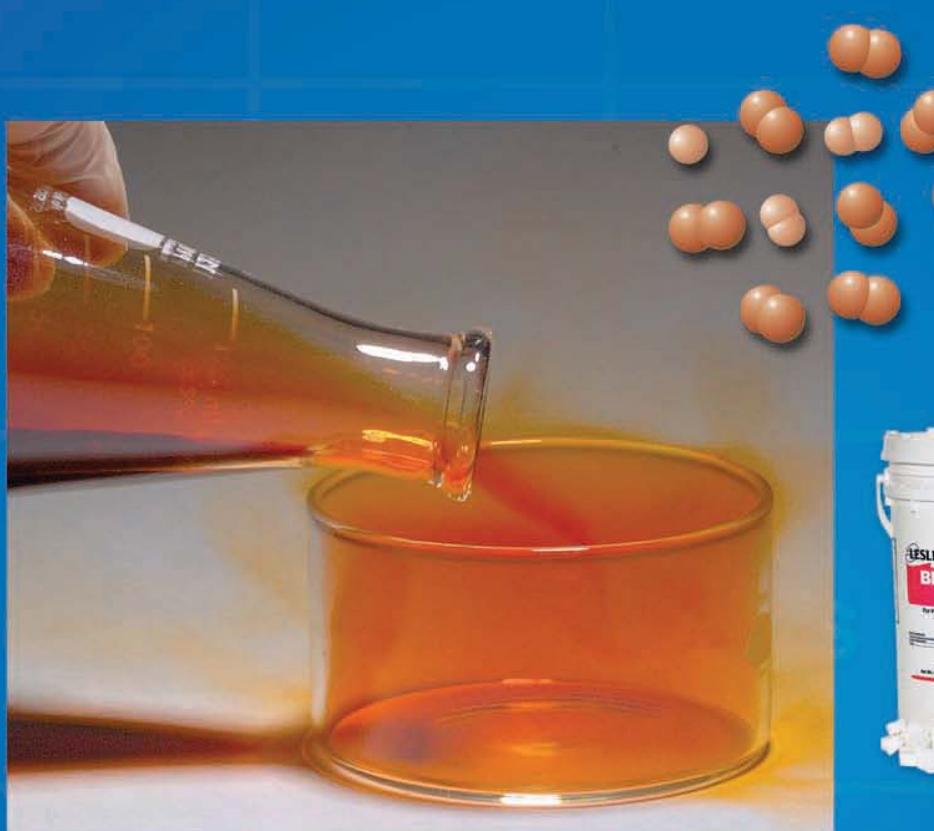


5

The Gaseous State



Bromine evaporates at room temperature to produce a dense gas, shown being poured from a flask. Compounds that contain bromine are used to disinfect swimming pools and hot tubs.

Contents and Concepts

Gas Laws

- 5.1 Gas Pressure and Its Measurement
- 5.2 Empirical Gas Laws
- 5.3 The Ideal Gas Law
- 5.4 Stoichiometry Problems Involving Gas Volumes
- 5.5 Gas Mixtures; Law of Partial Pressures

We will investigate the quantitative relationships that describe the behavior of gases.

Kinetic-Molecular Theory

- 5.6 Kinetic Theory of an Ideal Gas
- 5.7 Molecular Speeds; Diffusion and Effusion
- 5.8 Real Gases

This section will develop a model of gases as molecules in constant random motion.

Gases have several characteristics that distinguish them from liquids and solids. You can compress gases into smaller and smaller volumes. Anyone who has transported gases such as oxygen compressed in steel cylinders can appreciate this (Figure 5.1). Also, for gases, unlike for liquids and solids, you can relate pressure, volume, temperature, and molar amount of substance with fair accuracy by one simple equation, the ideal gas law. Suppose you wish to determine the amount of oxygen in a cylinder of compressed gas. You measure the pressure (with a gauge), the temperature, and the volume of gas (volume of the tank). Then, using the ideal gas law, you can calculate the amount of gas in the tank.

Kinetic-molecular theory describes a gas as composed of molecules in constant motion. This theory helps explain the simple relationship that exists among the pressure, volume, temperature, and amount of a gas. Kinetic theory has also enhanced our understanding of the flow of fluids, the transmission of sound, and the conduction of heat.

This chapter introduces the empirical gas laws, such as the ideal gas law, and the kinetic-molecular theory that explains these laws. After finishing the chapter, you will be able to answer questions such as, How many grams of oxygen are there in a 50.0-L gas cylinder at 21°C when the oxygen pressure is 15.7 atmospheres? (An atmosphere is a unit of pressure equal to that of the

normal atmosphere.) You will also be able to calculate the average speed of an oxygen molecule in this tank (479 m/s, or 1071 mi/hr).

See pages 212–213 for the Media Summary.

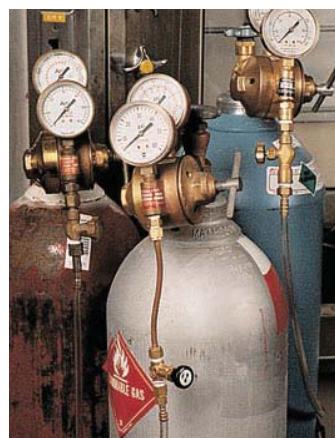


FIGURE 5.1

Cylinders of gas

Gases such as oxygen and nitrogen can be transported as compressed gases in steel cylinders. Large volumes of gas at normal pressures can be compressed into a small volume. Note the pressure gauges.

Gas Laws

Most substances composed of small molecules are gases under normal conditions or else are easily vaporized liquids. Table 5.1 lists selected gaseous substances and some of their properties.

In the first part of this chapter, we will examine the quantitative relationships, or empirical laws, governing gases. We will first consider the concept of pressure.

TABLE 5.1

Properties of Selected Gases

Name	Formula	Color	Odor	Toxicity
Ammonia	NH ₃	Colorless	Penetrating	Toxic
Carbon dioxide	CO ₂	Colorless	Odorless	Nontoxic
Carbon monoxide	CO	Colorless	Odorless	Very toxic
Chlorine	Cl ₂	Pale green	Irritating	Very toxic
Hydrogen	H ₂	Colorless	Odorless	Nontoxic
Hydrogen sulfide	H ₂ S	Colorless	Foul	Very toxic
Methane	CH ₄	Colorless	Odorless	Nontoxic
Nitrogen dioxide	NO ₂	Red-brown	Irritating	Very toxic

5.1

Gas Pressure and Its Measurement

Pressure is defined as *the force exerted per unit area of surface*. A coin resting on a table exerts a force, and therefore a pressure, downward on the table as a consequence of gravity. The air above the table exerts an additional pressure on the table, because the air is also being pulled downward by gravity.

To obtain the SI unit of pressure and a feeling for its size, let us calculate the pressure on a table from a perfectly flat coin with a radius and mass equal to that of a new penny (9.3 mm in radius and 2.5 g). The force exerted by the coin from gravity equals the mass of the coin times the constant acceleration of gravity. *Acceleration* is the change of speed per unit time, so the SI unit of acceleration is meters per second per second, abbreviated m/s^2 . The constant acceleration of gravity is 9.81 m/s^2 , and the force on the coin due to gravity is

$$\begin{aligned}\text{Force} &= \text{mass} \times \text{constant acceleration of gravity} \\ &= (2.5 \times 10^{-3} \text{ kg}) \times (9.81 \text{ m/s}^2) = 2.5 \times 10^{-2} \text{ kg} \cdot \text{m/s}^2\end{aligned}$$

The cross-sectional area of the coin is $\pi \times (\text{radius})^2 = 3.14 \times (9.3 \times 10^{-3} \text{ m})^2 = 2.7 \times 10^{-4} \text{ m}^2$. Therefore,

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{2.5 \times 10^{-2} \text{ kg} \cdot \text{m/s}^2}{2.7 \times 10^{-4} \text{ m}^2} = 93 \text{ kg}/(\text{m} \cdot \text{s}^2)$$

The SI unit of pressure, $\text{kg}/(\text{m} \cdot \text{s}^2)$, is given the name **pascal (Pa)**, after the French physicist Blaise Pascal (1623–1662), who studied fluid pressure. Note that the pressure exerted by a coin the size and mass of a penny is approximately 100 Pa. The pressure exerted by the atmosphere is about 1000 times larger, or about 100,000 Pa. Thus, the pascal is an extremely small unit.

Chemists have traditionally used two other units of pressure, based on the mercury barometer. A **barometer** is a device for measuring the pressure of the atmosphere. The mercury barometer consists of a glass tube about one meter long, filled with mercury and inverted in a dish of mercury (Figure 5.2). At sea level the mercury in the tube falls to a height of about 760 mm above the level in the dish. This height is a direct measure of the atmospheric pressure (Figure 5.3). Air pressure downward on the surface of the mercury in the dish is transmitted through the liquid and exerts a pressure upward at the base of the mercury column, supporting it. A mercury column placed in a sealed flask, as in Figure 5.4, measures the gas pressure in the flask. It acts as a **manometer**, a device that measures the pressure of a gas or liquid in a vessel.

The unit **millimeters of mercury (mmHg)**, also called the **torr** (after Evangelista Torricelli, who invented the mercury barometer in 1643), is a unit of pressure equal to that exerted by a column of mercury 1 mm high at 0.00°C . The **atmosphere (atm)** is a related unit of pressure equal to exactly 760 mmHg.

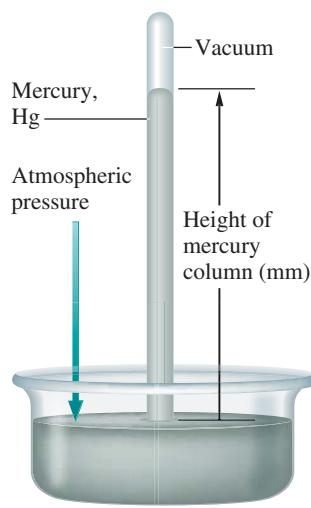


FIGURE 5.2

A mercury barometer

The height h is proportional to the barometric pressure. For that reason, the pressure is often given as the height of the mercury column, in units of millimeters of mercury, mmHg.

Atmospheric, or barometric, pressure depends not only on altitude but also on weather conditions. The “highs” and “lows” of weather reports refer to high- and low-pressure air masses. A high is associated with fair weather; a low brings unsettled weather, or storms.

FIGURE 5.3

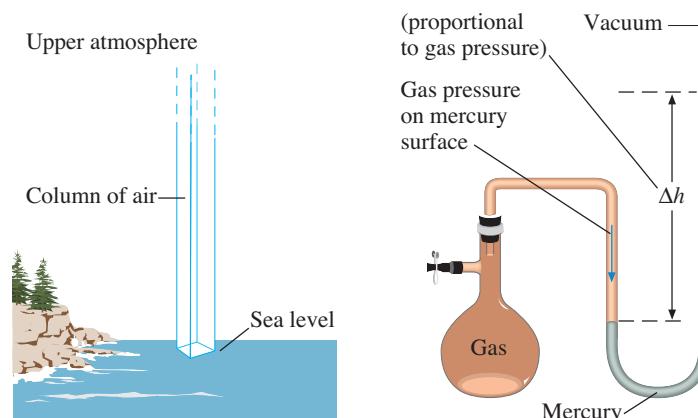
Atmospheric pressure from air mass

The force of gravity on the mass of a column of air exerts a pressure at the earth's surface. This pressure varies slightly with weather, but is approximately 101 kPa (760 mmHg, or 1 atm).

FIGURE 5.4

A flask equipped with a closed-tube manometer

The gas pressure in the flask is proportional to the difference in heights between the liquid levels in the manometer, Δh .



In 1982, the International Union of Pure and Applied Chemistry (IUPAC) recommended that standard pressure be defined as equal to 1 **bar**, a unit of pressure equal to 1×10^5 Pa, slightly less than 1 atm. Despite this recommendation, 1 atm is still in common use by chemists as the standard pressure. Until the bar is more widely adopted by chemists as the standard unit of pressure, we will continue to use the atmosphere.

TABLE 5.2**Important Units of Pressure**

Unit	Relationship or Definition
Pascal (Pa)	$\text{kg}/(\text{m} \cdot \text{s}^2)$
Atmosphere (atm)	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} \approx 100 \text{ kPa}$
mmHg, or torr	$760 \text{ mmHg} = 1 \text{ atm}$
Bar	$1.01325 \text{ bar} = 1 \text{ atm}$

The general relationship between the pressure P and the height h of a liquid column in a barometer or manometer is

$$P = gdh$$

Here g is the constant acceleration of gravity (9.81 m/s^2) and d is the density of the liquid in the manometer. If g , d , and h are in SI units, the pressure is given in pascals. Table 5.2 summarizes the relationships among the various units of pressure. <

Example 5.1

Converting Units of Pressure

The pressure of a gas in a flask is measured to be 797.7 mmHg using a mercury-filled manometer as in Figure 5.4. What is this pressure in pascals and atmospheres?

Problem Strategy This is a unit conversion problem. To convert to the appropriate units, use the conversion factors presented in Table 5.2 and the techniques presented in Chapter 1. Keep in mind that the conversion $760 \text{ mmHg} = 1 \text{ atm}$ is exact.

Solution Conversion to pascals:

$$797.7 \text{ mmHg} \times \frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ mmHg}} = 1.064 \times 10^5 \text{ Pa}$$

Conversion to atmospheres:

$$797.7 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 1.050 \text{ atm}$$

Answer Check Pressure conversions between the units of atm and mmHg are very common, so it is helpful to remember the relationship $1 \text{ atm} = 760 \text{ mmHg}$ in order to check your answers quickly.

Exercise 5.1

A gas in a container had a measured pressure of 57 kPa. Calculate the pressure in units of atm and mmHg.

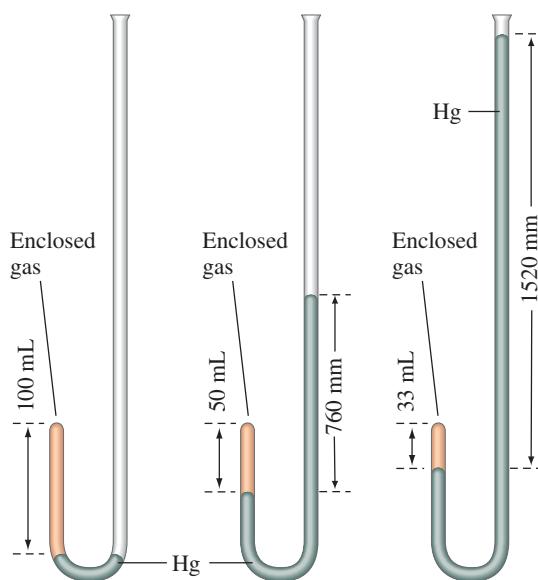
■ See Problems 5.37 and 5.38.

Concept Check 5.1

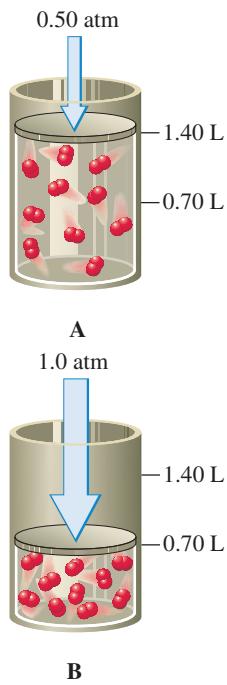
Suppose that you set up two barometers like the one shown in Figure 5.2. In one of the barometers you use mercury, and in the other you use water. Which of the barometers would have a higher column of liquid, the one with Hg or H₂O? Explain your answer.

5.2**Empirical Gas Laws**

All gases under moderate conditions behave quite simply with respect to pressure, temperature, volume, and molar amount. By holding any two of these physical properties constant, it is possible to show a simple relationship between the other two. The discovery of these quantitative relationships, the empirical gas laws, occurred from the mid-seventeenth to the mid-nineteenth century.

**FIGURE 5.5 ▲****Boyle's experiment**

The volume of the gas at normal atmospheric pressure (760 mmHg) is 100 mL. When the pressure is doubled by adding 760 mm of mercury, the volume is halved (to 50 mL). Tripling the pressure decreases the volume to one-third of the original (to 33 mL).

**FIGURE 5.6 ▲****Model of gas pressure-volume relationship at a constant temperature**

- (A) When a 1.000-g sample of O₂ gas at 0°C is placed in a container at a pressure of 0.50 atm, it occupies a volume of 1.40 L.
- (B) When the pressure on the O₂ sample is doubled to 1.0 atm, the volume is reduced to 0.70 L, which is half the original volume.

TABLE 5.3		Pressure–Volume Data for 1.000 g O₂ at 0°C
<i>P</i> (atm)	<i>V</i> (L)	<i>PV</i>
0.2500	2.801	0.7002
0.5000	1.400	0.7000
0.7500	0.9333	0.7000
1.000	0.6998	0.6998
2.000	0.3495	0.6990
3.000	0.2328	0.6984
4.000	0.1744	0.6976
5.000	0.1394	0.6970

Increasing pressure

Increasing volume

Boyle's Law: Relating Volume and Pressure

One characteristic property of a gas is its *compressibility*—its ability to be squeezed into a smaller volume by the application of pressure. By comparison, liquids and solids are relatively incompressible. The compressibility of gases was first studied quantitatively by Robert Boyle in 1661. When he poured mercury into the open end of a J-shaped tube, the volume of the enclosed gas decreased (Figure 5.5). Each addition of mercury increased the pressure on the gas, decreasing its volume. From such experiments, he formulated the law now known by his name. According to **Boyle's law**, the volume of a sample of gas at a given temperature varies inversely with the applied pressure. That is, $V \propto 1/P$, where V is the volume, P is the pressure, and \propto means “is proportional to.” Thus, if the pressure is doubled, the volume is halved.

Boyle's law can also be expressed in the form of an equation. Putting pressure and volume on the same side of the equation, you can write

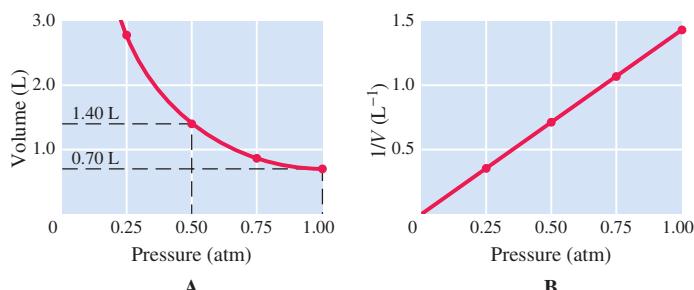
Boyle's law:
 $PV = \text{constant}$ (for a given amount of gas at fixed temperature)

That is, for a given amount of gas at a fixed temperature, the pressure times the volume equals a constant. Table 5.3 gives some pressure and volume data for 1.000 g O₂ at 0°C. Figure 5.6 presents a molecular view of the pressure–volume relationship for two data points in Table 5.3. Note that the product of the pressure and volume for each data pair is nearly constant. By plotting the volume of the oxygen at different pressures (as shown in Figure 5.7), you obtain a graph showing the inverse relationship of P and V .

You can use Boyle's law to calculate the volume occupied by a gas when the pressure changes. Consider the 50.0-L gas cylinder of oxygen mentioned in the chapter opening. The pressure of gas in the cylinder is 15.7 atm at 21°C. What volume of oxygen can you get from the cylinder at 21°C if the atmospheric pressure is 1.00 atm? You can write P_i and V_i for the initial pressure (15.7 atm) and initial volume (50.0 L), and P_f and V_f for the final pressure (1.00 atm) and final volume

FIGURE 5.7**Gas pressure–volume relationship**

(A) Plot of volume vs. pressure for a sample of oxygen. The volume (of 1.000 g O₂ at 0°C) decreases with increasing pressure. When the pressure is doubled (from 0.50 atm to 1.00 atm), the volume is halved (from 1.40 L to 0.70 L). (B) Plot of 1/V vs. pressure (at constant temperature) for the same sample. The straight line indicates that volume varies inversely with pressure.



(to be determined). Because the temperature does not change, the product of the pressure and volume remains constant. Thus, you can write

$$P_f V_f = P_i V_i$$

Dividing both sides of the equation by P_f gives

$$\frac{V_f}{P_f} = \frac{V_i}{P_i}$$

Substituting into this equation yields

$$V_f = 50.0 \text{ L} \times \frac{15.7 \text{ atm}}{1.00 \text{ atm}} = 785 \text{ L}$$

Note that the initial volume is multiplied by a ratio of pressures. You know the oxygen gas is changing to a lower pressure and will therefore expand, so this ratio will be greater than 1. The final volume, 785 L, is that occupied by all of the gas at 1.00 atm pressure. However, because the cylinder holds 50.0 L, only this volume of gas remains in the cylinder. The volume that escapes is (785 – 50.0) L = 735 L.

Example 5.2

Using Boyle's Law

A volume of air occupying 12.0 dm³ at 98.9 kPa is compressed to a pressure of 119.0 kPa. The temperature remains constant. What is the new volume?

Problem Strategy Putting the data for the problem in tabular form, you see what data you have and what you must find. This will suggest the method of solution.

$$\left. \begin{array}{ll} V_i = 12.0 \text{ dm}^3 & P_i = 98.9 \text{ kPa} \\ V_f = ? & P_f = 119.0 \text{ kPa} \end{array} \right\} \begin{array}{l} \text{Temperature and} \\ \text{moles remain} \\ \text{constant.} \end{array}$$

Because P and V vary but temperature and moles are constant, you use Boyle's law.

Solution Application of Boyle's law gives

$$V_f = V_i \times \frac{P_i}{P_f} = 12.0 \text{ dm}^3 \times \frac{98.9 \text{ kPa}}{119.0 \text{ kPa}} = 9.97 \text{ dm}^3$$

Answer Check In general, when the pressure on a gas increases, the gas is compressed and therefore occupies a smaller volume. When the pressure on a gas decreases, the gas expands—it will occupy a larger volume. Use these concepts to check your answers. In this example, since the pressure increases, the smaller final volume of the answer is what we would expect. (Note that you get the answer to this type of problem by multiplying the volume by a ratio of pressures. This ratio should be less than 1 if the volume decreases, but more than 1 if the volume increases.)

Exercise 5.2

A volume of carbon dioxide gas, CO₂, equal to 20.0 L was collected at 23°C and 1.00 atm pressure. What would be the volume of carbon dioxide collected at 23°C and 0.830 atm?

■ See Problems 5.39, 5.40, 5.41, and 5.42.

FIGURE 5.8

Effect of temperature on volume of a gas
Left: A balloon immersed in liquid nitrogen shrinks because the air inside contracts in volume. Right: When the balloon is removed from the liquid nitrogen, the balloon expands to its original size.



Before leaving the subject of Boyle's law, we should note that the pressure-volume product for a gas is not precisely constant. You can see this from the PV data given in Table 5.3 for oxygen. In fact, all gases follow Boyle's law at low to moderate pressures but deviate from this law at high pressures. The extent of deviation depends on the gas. We will return to this point at the end of the chapter.

Charles's Law: Relating Volume and Temperature

Temperature also affects gas volume. When you immerse an air-filled balloon in liquid nitrogen (-196°C), the balloon shrinks (Figure 5.8). After the balloon is removed from the liquid nitrogen, it returns to its original size. A gas contracts when cooled and expands when heated.

One of the first quantitative observations of gases at different temperatures was made by Jacques Alexandre Charles in 1787. Charles was a French physicist and a pioneer in hot-air and hydrogen-filled balloons. < Later, John Dalton (in 1801) and Joseph Louis Gay-Lussac (in 1802) continued these kinds of experiments, which showed that a sample of gas at a fixed pressure increases in volume *linearly* with temperature. By "linearly," we mean that if we plot the volume occupied by a given sample of gas at various temperatures, we get a straight line (Figure 5.9).

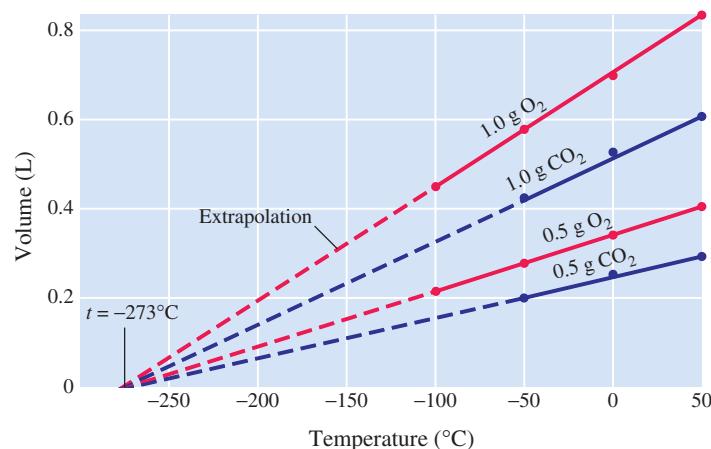
When you extend the straight lines in Figure 5.9 from the last experimental point toward lower temperatures—that is, when you *extrapolate* the straight lines backward—you find that they all intersect at a common point. This point occurs at a temperature of -273.15°C , where the graph indicates a volume of zero. This seems to say that if the substances remain gaseous, the volumes occupied will be zero at -273.15°C . This could not happen, however; all gases liquefy before they reach this temperature, and Charles's law does not apply to liquids. These extrapolations do show that we can express the volume variation of a gas with temperature more simply by choosing a different thermometer scale. Let us see how to do this.

The first ascent of a hot-air balloon carrying people was made on November 21, 1783. A few days later, Jacques Alexandre Charles made an ascent in a hydrogen-filled balloon. On landing, the balloon was attacked and torn to shreds by terrified peasants armed with pitchforks.

FIGURE 5.9

Linear relationship of gas volume and temperature at constant pressure

The graph shows gas volume versus temperature for a given mass of gas at 1.00 atm pressure. This linear relationship is independent of amount or type of gas. Note that all lines extrapolate to -273°C at zero volume.



The mathematical equation of a straight line, $y = mx + b$, is discussed in Appendix A.

The Kelvin temperature scale and a more formal equation for temperature conversion were discussed in Section 1.6.

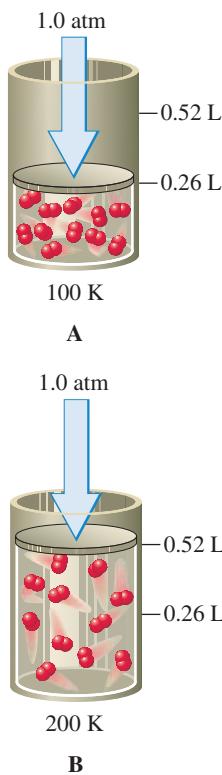


FIGURE 5.10 ▲
Model of the temperature-volume relationship for a gas at a fixed volume
(A) A 1.0-g sample of O₂ at 100 K and 1.0 atm of pressure occupies a volume of 0.26 L. (B) When the absolute temperature of the gas is doubled to 200 K, the volume of O₂ doubles to 0.52 L.

The fact that the volume occupied by a gas varies linearly with degrees Celsius can be expressed mathematically by the following equation:

$$V = bt + a$$

where t is the temperature in degrees Celsius and a and b are constants that determine the straight line. < You can eliminate the constant a by observing that $V = 0$ at $t = -273.15$ for any gas. Substituting into the preceding equation, you get

$$0 = b(-273.15) + a \quad \text{or} \quad a = 273.15b$$

The equation for the volume can now be rewritten:

$$V = bt + 273.15b = b(t + 273.15)$$

Suppose you use a temperature scale equal to degrees Celsius plus 273.15, which you may recognize as the *Kelvin scale* (an absolute scale). <

$$K = ^\circ C + 273.15$$

If you write T for the temperature on the Kelvin scale, you obtain

$$V = bT$$

This is **Charles's law**, which we can state as follows: *the volume occupied by any sample of gas at a constant pressure is directly proportional to the absolute temperature*. Thus, doubling the absolute temperature of a gas doubles its volume (Figure 5.10).

Charles's law can be rearranged into a form that is very useful for computation.

Charles's law:

$$\frac{V}{T} = \text{constant} \quad (\text{for a given amount of gas at a fixed pressure})$$

This equation says that the volume divided by the absolute temperature, for a sample of gas at a fixed pressure, remains constant.

Consider a sample of gas at a fixed pressure, and suppose the temperature changes from its initial value T_i to a final value T_f . How does the volume change? Because the volume divided by absolute temperature is constant, you can write

$$\frac{V_f}{T_f} = \frac{V_i}{T_i}$$

Or, rearranging slightly,

$$V_f = V_i \times \frac{T_f}{T_i}$$

Note that to obtain the final volume, the initial volume is multiplied by a ratio of absolute temperatures. The next example illustrates a calculation involving a change in the temperature of a gas.

Example 5.3

Using Charles's Law

Earlier we found that the total volume of oxygen that can be obtained from a particular tank at 1.00 atm and 21°C is 785 L (including the volume remaining in the tank). What would be this volume of oxygen if the temperature had been 28°C?

Problem Strategy You must first convert temperatures to the Kelvin scale. Then, list the data in tabular form so you can easily see what varies and what remains constant. You apply Charles's law when V and T vary and P is constant.

(continued)

(continued)

Solution $T_i = (21 + 273)\text{K} = 294\text{ K}$

$$T_f = (28 + 273)\text{K} = 301\text{ K}$$

Following is the data table:

$$V_i = 785\text{ L} \quad P_i = 1.00\text{ atm} \quad T_i = 294\text{ K}$$

$$V_f = ? \quad P_f = 1.00\text{ atm} \quad T_f = 301\text{ K}$$

Note that T varies and P remains constant, so V must change. These are the conditions needed to apply Charles's law.

$$V_f = V_i \times \frac{T_f}{T_i} = 785\text{ L} \times \frac{301\text{ K}}{294\text{ K}} = 804\text{ L}$$

Answer Check In general, when the temperature increases, the volume of gas increases, and when the temperature decreases, the volume of gas decreases. Applying these concepts to check the answer, we verify that when the temperature was increased, the final volume is greater than the starting volume. (Note that you get the answer to this type of problem by multiplying the volume by a ratio of absolute temperatures. This ratio should be more than 1 if the volume increases, but less than 1 if the volume decreases.)

Exercise 5.3

If you expect a chemical reaction to produce 4.38 dm^3 of oxygen, O_2 , at 19°C and 101 kPa , what will be the volume at 25°C and 101 kPa ?

■ See Problems 5.45, 5.46, 5.47, and 5.48.

Although most gases follow Charles's law fairly well, they deviate from it at high pressures and low temperatures.

Combined Gas Law: Relating Volume, Temperature, and Pressure

Boyle's law ($V \propto 1/P$) and Charles's law ($V \propto T$) can be combined and expressed in a single statement: the volume occupied by a given amount of gas is proportional to the absolute temperature divided by the pressure ($V \propto T/P$). You can write this as an equation.

$$V = \text{constant} \times \frac{T}{P} \quad \text{or} \quad \frac{PV}{T} = \text{constant} \quad (\text{for a given amount of gas})$$

Consider a problem in which you wish to calculate the final volume of a gas when the pressure and temperature are changed. PV/T is constant for a given amount of gas, so you can write

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i}$$

which rearranges to

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i}$$

Thus, the final volume is obtained by multiplying the initial volume by ratios of pressures and absolute temperatures.

Example 5.4

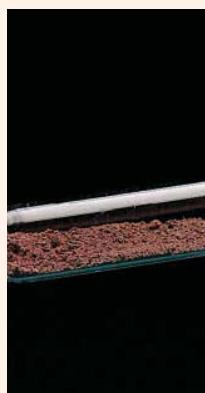
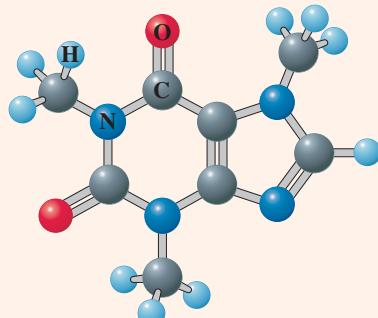
Using the Combined Gas Law

Modern determination of %N in an organic compound is an automated version of one developed by the French chemist Jean-Baptiste Dumas in 1830. The Dumas method uses hot copper(II) oxide to oxidize C and H in the compound to CO_2 and H_2O (both are trapped chemically) and to convert N in the compound to N_2 gas (Figure 5.11). Using the Dumas

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(continued)

method, 39.8 mg of caffeine gives 10.1 cm³ of nitrogen gas at 23°C and 746 mmHg. What is the volume of nitrogen at 0°C and 760 mmHg?

**FIGURE 5.11****Oxidation of an organic compound with copper(II) oxide**

Left: Molecular model of caffeine, an organic compound. *Center:* A chemist heats caffeine with copper(II) oxide, CuO. CuO oxidizes C and H in the compound to CO₂ and H₂O, and converts N to N₂. *Right:* Copper metal produced by the reaction.

Problem Strategy As always, you will need to convert temperature to the Kelvin scale and put the data in tabular form to determine the law(s) that apply. In this case, since both pressure and temperature are changing, we should expect to use more than one law to arrive at an answer.

Solution You first express the temperatures in kelvins:

$$T_i = (23 + 273) \text{ K} = 296 \text{ K}$$

$$T_f = (0 + 273) \text{ K} = 273 \text{ K}$$

Now you put the data for the problem in tabular form:

$$V_i = 10.1 \text{ cm}^3 \quad P_i = 746 \text{ mmHg} \quad T_i = 296 \text{ K}$$

$$V_f = ? \quad P_f = 760 \text{ mmHg} \quad T_f = 273 \text{ K}$$

From the data, you see that you need to use Boyle's and Charles's laws combined to find how *V* varies as *P* and *T* change. Note that the increase in pressure decreases the volume, making the pressure ratio less than 1. The decrease in temperature also decreases the volume, and the ratio of absolute temperatures is less than 1.

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i} = 10.1 \text{ cm}^3 \times \frac{746 \text{ mmHg}}{760 \text{ mmHg}} \times \frac{273 \text{ K}}{296 \text{ K}} = 9.14 \text{ cm}^3$$

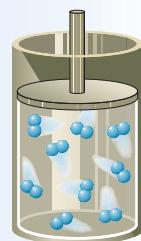
Answer Check This gas sample is undergoing a temperature decrease and a pressure increase. These two changes will have opposite effects on the final gas volume. Considering the magnitude of the changes in temperature and pressure in this problem, we can conclude that the final volume of the gas should not be greatly different from its initial volume.

Exercise 5.4 A balloon contains 5.41 dm³ of helium, He, at 24°C and 101.5 kPa. Suppose the gas in the balloon is heated to 35°C. If the helium pressure is now 102.8 kPa, what is the volume of the gas?

■ See Problems 5.51 and 5.52.

Concept Check 5.2

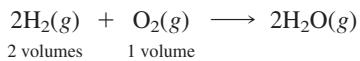
To conduct some experiments, a 10.0-L flask equipped with a movable plunger, as illustrated here, is filled with enough H₂ gas to come to a pressure of 20 atm.



- In the first experiment, we decrease the temperature in the flask by 10°C and then increase the volume. Predict how the pressure in the flask changes during each of these events and, if possible, how the final pressure compares to your starting pressure.
- Once again we start with the pressure in the flask at 20 atm. The flask is then heated 10°C, followed by a volume decrease. Predict how the pressure in the flask changes during each of these events and, if possible, how the final pressure compares to your starting pressure.

Avogadro's Law: Relating Volume and Amount

In 1808 the French chemist Joseph Louis Gay-Lussac (1778–1850) concluded from experiments on gas reactions that the volumes of reactant gases at the same pressure and temperature are in ratios of small whole numbers (*the law of combining volumes*). For example, two volumes of hydrogen react with one volume of oxygen gas to produce water.



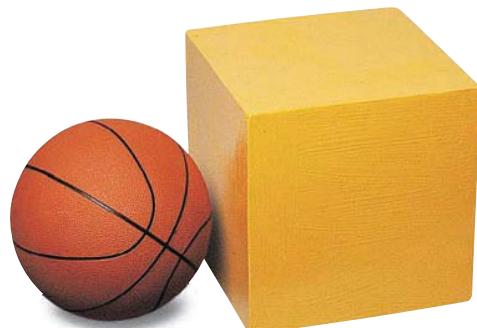
Three years later, the Italian chemist Amedeo Avogadro (1776–1856) interpreted the law of combining volumes in terms of what we now call **Avogadro's law: equal volumes of any two gases at the same temperature and pressure contain the same number of molecules**. Thus, two volumes of hydrogen contain twice the number of molecules as in one volume of oxygen, in agreement with the chemical equation for the reaction.

One mole of any gas contains the same number of molecules (Avogadro's number = 6.02×10^{23}) and by Avogadro's law must occupy the same volume at a given temperature and pressure. This *volume of one mole of gas* is called the **molar gas volume, V_m** . Volumes of gases are often compared at **standard temperature and pressure (STP)**, the reference conditions for gases chosen by convention to be 0°C and 1 atm pressure. At STP, the molar gas volume is found to be 22.4 L/mol (Figure 5.12).

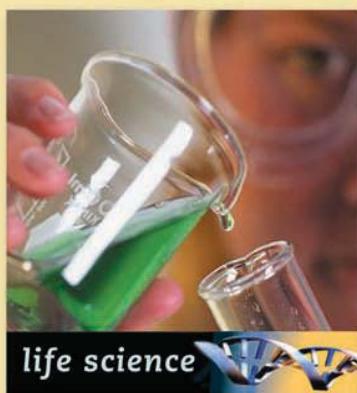
FIGURE 5.12

The molar volume of a gas

The box has a volume of 22.4 L, equal to the molar volume of a gas at STP. The basketball is shown for comparison.



A Chemist Looks at . . .



In 1998, the Nobel committee awarded its prize in physiology or medicine to three scientists for the astounding discovery that nitrogen monoxide (nitric oxide) gas, NO, functions as the signaling agent between biological cells in a wide variety of chemical processes. Until this discovery, biochemists had thought that the major chemical reactions in a cell always involved very large molecules. Now they discovered that a simple gas, NO, could play a central role in cell chemistry.

Prizewinners Robert Furchtgott and Louis Ignarro, independently, unraveled the role of nitrogen monoxide in blood-pressure regulation. Cells in the lining of arteries detect increased blood pressure and respond by producing nitrogen monoxide. NO rapidly diffuses through the artery wall to cells in the surrounding muscle tissue. In response, the muscle tissue relaxes, the blood vessel expands, and the blood pressure drops.

Nitrogen Monoxide Gas and Biological Signaling

In a related discovery, another prizewinner, Ferid Murad, explained how nitroglycerin works to alleviate the intense chest pain of an angina attack, which results from reduced blood flow to the heart muscle as a result of partial blockage of arteries by plaque. Physicians have prescribed nitroglycerin for angina for more than a century, knowing only that it works. Murad found that nitroglycerin breaks down in the body to form nitrogen monoxide, which relaxes the arteries, allowing greater blood flow to the heart. Alfred Nobel, were he alive today, would no doubt be stunned by this news. Nobel, who established the prizes bearing his name, made his fortune in the nineteenth century from his invention of dynamite, a mixture of nitroglycerin with clay

FIGURE 5.13 ►

Nitroglycerin patch

Nitroglycerin has been used for more than a hundred years to treat and prevent angina attacks. Here a patient wears a patch that dispenses nitroglycerin steadily over a period of time.

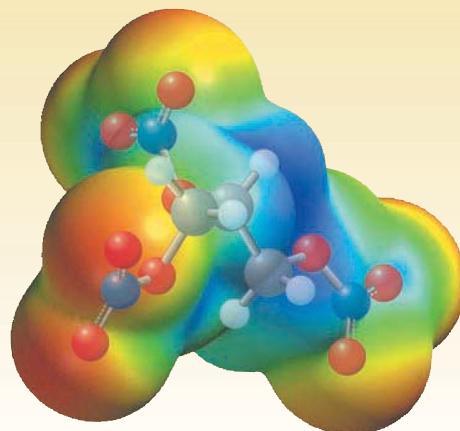


TABLE 5.4
Molar Volumes of Several Gases at 0.0°C and 1.00 atm

Gas	Molar Volume (L)
He	22.40
H ₂	22.43
O ₂	22.39
CO ₂	22.29
NH ₃	22.09
Ideal gas*	22.41

*An ideal gas follows the empirical gas laws.

We can re-express Avogadro's law as follows: the molar gas volume at a given temperature and pressure is a specific constant independent of the nature of the gas.

Avogadro's law:
 $V_m = \text{specific constant} (= 22.4 \text{ L/mol at STP})$
(depending on T and P but independent of the gas)

Table 5.4 lists the molar volumes of several gases. The values agree within about 2% of the value expected from the empirical gas laws (the "ideal gas" value). We will discuss the reason for the deviations from this value at the end of this chapter, in the section on real gases.

that tamed the otherwise hazardous explosive. When Nobel had heart trouble, his physician recommended that he eat a small quantity of nitroglycerin; he refused. In a letter, he wrote, “It is ironical that I am now ordered by my physician to eat nitroglycerin.” Today, a patient may either take nitroglycerin pills (containing tenths of a milligram of compound in a stabilized mixture) for occasional use or apply a chest patch to dispense nitroglycerin continuously to the skin, where it is absorbed (Figure 5.13).

Research papers on the biological role of nitrogen monoxide now number in the tens of thousands. For example,

scientists have found that white blood cells use nitrogen monoxide in a kind of chemical warfare. These cells emit concentrated clouds of NO that surround bacterial or tumor cells, killing them by interfering with certain cell processes. Researchers have also discovered that nitrogen monoxide plays a role in penile erection. Pharmacologists found that the drug Viagra (Figure 5.14) assists in the action of NO in dilating arteries, leading to erection.

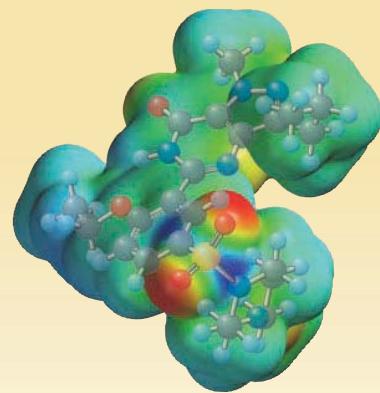


FIGURE 5.14

Viagra

Viagra is marketed as an aid to erectile dysfunction. Sexual stimulation produces nitrogen monoxide, which in turn aids an enzyme in the production of a substance called cGMP that relaxes arterial muscles, allowing blood to flow to the penis. Viagra enhances the action of NO by inhibiting an enzyme that degrades cGMP.

■ See Problems 5.105 and 5.106.

5.3 The Ideal Gas Law

In the previous section, we discussed the empirical gas laws. Here we will show that these laws can be combined into one equation, called the *ideal gas equation*. Earlier we combined Boyle’s law and Charles’s law into the equation

$$V = \text{constant} \times \frac{T}{P} \quad (\text{for a given amount of gas})$$

This “constant” is independent of the temperature and pressure but does depend on the amount of gas. For one mole, the constant will have a specific value, which we will denote as R . The molar volume, V_m , is

$$V_m = R \times \frac{T}{P}$$

TABLE 5.5 Molar Gas Constant in Various Units	
Value of R	
0.082058 L·atm/(K·mol)	
8.3145 J/(K·mol)*	
8.3145 kg·m ² /(s ² ·K·mol)	
8.3145 kPa·dm ³ /(K·mol)	
1.9872 cal/(K·mol)*	

*The units of pressure times volume are the units of energy—for example, joules (J) or calories (cal).

According to Avogadro's law, the molar volume at a specific value of T and P is a constant independent of the nature of the gas, and this implies that R is a constant independent of the gas. The **molar gas constant, R** , is the constant of proportionality relating the molar volume of a gas to T/P . Values of R in various units are given in Table 5.5.

The preceding equation can be written for n moles of gas by multiplying both sides by n .

$$\underbrace{nV_m}_V = \frac{nRT}{P} \quad \text{or} \quad PV = nRT$$

Because V_m is the volume per mole, nV_m is the total volume V . The equation $PV = nRT$, which combines all of the gas laws, is called the **ideal gas law**.

Ideal gas law:
 $PV = nRT$

The ideal gas law includes all the information contained in Boyle's, Charles's, and Avogadro's laws. In fact, starting with the ideal gas law, you can derive any of the other gas laws.

Example 5.5

Deriving Empirical Gas Laws from the Ideal Gas Law

Prove the following statement: the pressure of a given amount of gas at a fixed volume is proportional to the absolute temperature. This is sometimes called *Amontons's law*. In 1702 Guillaume Amontons constructed a thermometer based on measurement of the pressure of a fixed volume of air. The principle he employed is now used in special gas thermometers to establish the Kelvin scale.

Problem Strategy Because we need a relationship between pressure and temperature, the ideal gas law is a logical starting place.

Solution From the ideal gas law,

$$PV = nRT$$

Solving for P , you get

$$P = \left(\frac{nR}{V} \right) T$$

Note that everything in parentheses in this equation is constant. Therefore, you can write

$$P = \text{constant} \times T$$

Or, expressing this as a proportion,

$$P \propto T$$

Boyle's law and Charles's law follow from the ideal gas law by a similar derivation.

Answer Check We can apply common experience to qualitatively verify this relationship. Think about what happens to the pressure in a tire when the temperature is increased: the hotter the tire gets, the more the pressure increases.

Exercise 5.5 Show that the moles of gas are proportional to the pressure for constant volume and temperature.

■ See Problems 5.55 and 5.56.

No gas is "ideal." But the ideal gas law is very useful even though it is only an approximation. The behavior of real gases is described at the end of this chapter.

The limitations that apply to Boyle's, Charles's, and Avogadro's laws also apply to the ideal gas law. That is, the ideal gas law is most accurate for low to moderate pressures and for temperatures that are not too low. <

Calculations Using the Ideal Gas Law

The type of problem to which Boyle's and Charles's laws are applied involves a change in conditions (P , V , or T) of a gas. The ideal gas law allows us to solve another

type of problem: given any three of the quantities P , V , n , and T , calculate the unknown quantity. Example 5.6 illustrates such a problem.

Example 5.6

Using the Ideal Gas Law

Answer the question asked in the chapter opening: how many grams of oxygen, O_2 , are there in a 50.0-L gas cylinder at 21°C when the oxygen pressure is 15.7 atm?

Problem Strategy In asking for the mass of oxygen, we are in effect asking for moles of gas, n , because mass and moles are directly related. The problem gives P , V , and T , so you can use the ideal gas law to solve for n . The proper value to use for R depends on the units of P and V . Here they are in atmospheres and liters, respectively, so you use $R = 0.0821 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol})$ from Table 5.5. Once you have solved for n , convert to mass by using the molar mass of oxygen.

Solution The data given in the problem are

Variable	Value
P	15.7 atm
V	50.0 L
T	(21 + 273) K = 294 K
n	?

Solving the ideal gas law for n gives

$$n = \frac{PV}{RT}$$

Substituting the data gives

$$n = \frac{15.7 \text{ atm} \times 50.0 \text{ L}}{0.0821 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol}) \times 294 \text{ K}} = 32.5 \text{ mol}$$

and converting moles to mass of oxygen yields

$$32.5 \text{ mol } O_2 \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 1.04 \times 10^3 \text{ g } O_2$$

Answer Check If you were to forget that oxygen is a diatomic gas with the formula O_2 , you would not get this problem right. Keep in mind, too, that the other gaseous diatomic elements are N_2 , F_2 , and Cl_2 .

Exercise 5.6

What is the pressure in a 50.0-L gas cylinder that contains 3.03 kg of oxygen, O_2 , at 23°C?

■ See Problems 5.57, 5.58, 5.59, 5.60, 5.61, and 5.62.

Gas Density; Molecular-Mass Determination

The density of a substance is its mass divided by its volume, and because the volume of a gas varies with temperature and pressure, the density of a gas also varies with temperature and pressure (Figure 5.15). In the next example, we use the ideal gas law to calculate the density of a gas at any temperature and pressure. We do this by calculating the moles, and from this the mass, in a liter of gas at the given temperature and pressure; the mass per liter of gas is its density. At the end of this section, we will give an alternative method of solving this problem, using a formula relating density to temperature, pressure, and molecular weight.

Example 5.7

Calculating Gas Density

What is the density of oxygen, O_2 , in grams per liter at 25°C and 0.850 atm?

Problem Strategy The density of a gas is often expressed in g/L. Using the ideal gas law, you can calculate the moles of O_2 in 1 L of O_2 . Next, you can convert the moles of O_2 to a mass of O_2 , keeping in mind that this mass is the amount of O_2 per liter of O_2 (g/1 L), which is the density.

(continued)

(continued)

Solution The data given are

Variable	Value
P	0.850 atm
V	1 L (exact value)
T	(25 + 273) K = 298 K
n	?

Therefore,

$$n = \frac{PV}{RT} = \frac{0.850 \text{ atm} \times 1 \text{ L}}{0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 298 \text{ K}} = 0.0347 \text{ mol}$$

Now convert mol O₂ to grams:

$$0.0347 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 1.11 \text{ g O}_2$$

Therefore, the density of O₂ at 25°C and 0.850 atm is **1.11 g/L**.Suppose you wanted the density of Cl₂, instead of O₂, at this T and P. Only the conversion of moles to mass is affected. The previous calculation becomes

$$0.0347 \text{ mol Cl}_2 \times \frac{70.9 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 2.46 \text{ g Cl}_2$$

The density of Cl₂ at 25°C and 0.850 atm is 2.46 g/L. Note that the density of a gas is directly proportional to its molecular mass.**Answer Check** Because gases consist of molecules spread very far apart, you should expect any reasonable answer for gas density to be very low when compared to values for liquids and solids. Therefore, gas densities should be on the order of this answer.**Exercise 5.7** Calculate the density of helium, He, in grams per liter at 21°C and 752 mmHg. The density of air under these conditions is 1.188 g/L. What is the difference in mass between 1 liter of air and 1 liter of helium? (This mass difference is equivalent to the buoyant, or lifting, force of helium per liter.)

See Problems 5.63, 5.64, 5.65, and 5.66.

**FIGURE 5.15****Hot-air ballooning**

A propane gas burner on board a balloon heats the air. The heated air expands, occupying a larger volume; it therefore has a lower density than the surrounding air. The hot air and balloon rise.

**FIGURE 5.16****A gas whose density is greater than that of air**

The reddish-brown gas being poured from the flask is bromine. Note how the gas, which is denser than air, hugs the bottom of the beaker.

The previous example demonstrates that the density of a gas is directly proportional to its molecular mass. Bromine, whose molecular mass is five times that of oxygen, is therefore more than five times as dense as air. Figure 5.16 shows bromine gas being poured into a beaker where it displaces the air and fills the beaker.

The relation between density and molecular mass of a gas suggests that you could use a measurement of gas density to determine its molecular mass. In fact, gas-density (vapor-density) measurements provided one of the first methods of determining molecular mass. The method was worked out by the French chemist Jean-Baptiste André Dumas in 1826. It can be applied to any substance that can be vaporized without decomposing.

As an illustration, consider the determination of the molecular mass of halothane, an inhalation anesthetic. The density of halothane vapor at 71°C (344 K) and 768 mmHg (1.01 atm) is 7.05 g/L. To obtain the molecular mass, you calculate the moles of vapor in a given volume. The molar mass equals mass divided by the moles

in the same volume. From the density, you see that one liter of vapor has a mass of 7.05 g. The moles in this volume are obtained from the ideal gas law.

$$n = \frac{PV}{RT} = \frac{1.01 \text{ atm} \times 1 \text{ L}}{0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 344 \text{ K}} = 0.0358 \text{ mol}$$

Therefore, the molar mass, M_m , is

$$M_m = \frac{m}{n} = \frac{7.05 \text{ g}}{0.0358 \text{ mol}} = 197 \text{ g/mol}$$

Thus, the molecular mass is 197 amu.

If you look at what we have done, you will see that all you need to have is the mass of vapor in *any* given volume (for a given T and P). An explicit determination of density is not necessary. You determine the moles of vapor from the volume using the ideal gas law, then determine the molar mass by dividing the mass by moles for this volume. The next example illustrates this. At the end of this section, we will derive an explicit formula for the molecular mass in terms of the density of a gas, which will provide an alternative way to solve this problem.

Example 5.8

Determining the Molecular Mass of a Vapor

Using the apparatus described in Figure 5.17, a 200.0-mL flask at 99°C and a pressure of 733 mmHg is filled with the vapor of a volatile (easily vaporized) liquid. The mass of the substance in the flask is 0.970 g. What is the molecular mass of the liquid?

Problem Strategy You can calculate the moles of vapor from the ideal gas law and then calculate the molar mass by dividing mass by moles. Note that the temperature of the vapor is the same as the temperature of the boiling water and that the pressure of the vapor equals the barometric pressure.

Solution You have the following data for the vapor.

Variable Value

P	$733 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.964 \text{ atm}$
V	200.0 mL = 0.2000 L
T	(99 + 273) K = 372 K
n	?

From the ideal gas law, $PV = nRT$, you obtain

$$n = \frac{PV}{RT} = \frac{0.964 \text{ atm} \times 0.2000 \text{ L}}{0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 372 \text{ K}}$$

$$n = 0.00631 \text{ mol}$$

Dividing the mass of the vapor by moles gives you the mass per mole (the molar mass).

$$\text{Molar mass} = \frac{\text{grams vapor}}{\text{moles vapor}} = \frac{0.970 \text{ g}}{0.00631 \text{ mol}} = 154 \text{ g/mol}$$

Thus, the molecular mass is **154 amu**.

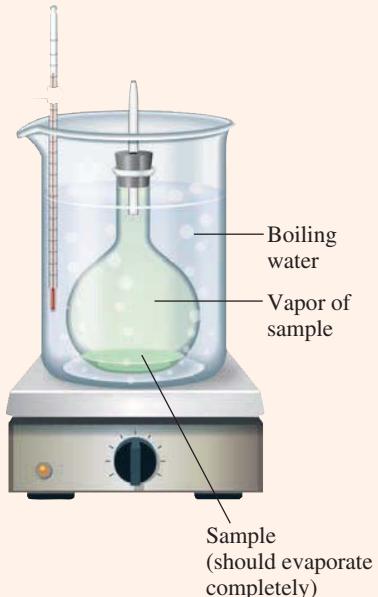


FIGURE 5.17

Finding the vapor density of a substance

After the flask fills with the vapor of the substance at the temperature of the boiling water, you allow the flask to cool so that the vapor condenses. You obtain the mass of the substance (which was vapor) by weighing the flask and substance and then subtracting the mass of the empty flask. The pressure of the vapor equals the barometric pressure, and the temperature equals that of the boiling water.

(continued)

(continued)

Answer Check No gas has a smaller molar mass than H₂ at 2 g/mol. Therefore, if you obtain an answer that is smaller than this, it must be incorrect. The upper limit on molar masses that you would expect is less definite, but solids and liquids that readily vaporize will have molar masses not much larger than a few hundred. An answer much larger than this should be regarded with suspicion.

Exercise 5.8 A sample of a gaseous substance at 25°C and 0.862 atm has a density of 2.26 g/L. What is the molecular mass of the substance?

■ See Problems 5.67, 5.68, 5.69, and 5.70.

From the ideal gas law, you can obtain an explicit relationship between the molecular mass and density of a gas. Recall that the molar mass ($M_m = m/n$) when expressed in grams per mole is numerically equal to the molecular mass. If you substitute $n = m/M_m$ into the ideal gas law, $PV = nRT$, you obtain

$$PV = \frac{m}{M_m} RT \quad \text{or} \quad PM_m = \frac{m}{V} RT$$

But m/V equals the density, d . Substituting this gives

$$PM_m = dRT$$

We can illustrate the use of this equation by solving Examples 5.7 and 5.8 again. In Example 5.7, we asked, “What is the density of oxygen, O₂, in grams per liter at 25°C (298 K) and 0.850 atm?” You rearrange the previous equation to give an explicit formula for the density and then substitute into this formula.

$$d = \frac{PM_m}{RT} = \frac{0.850 \text{ atm} \times 32.0 \text{ g/mol}}{0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 298 \text{ K}} = 1.11 \text{ g/L}$$

Note that by giving M_m in g/mol and R in L·atm/(K·mol), you obtain the density in g/L.

The question in Example 5.8 is equivalent to the following. What is the molecular mass of a substance weighing 0.970 g whose vapor occupies 200.0 mL (0.2000 L) at 99°C (372 K) and 733 mmHg (0.964 atm)? The density of the vapor is 0.970 g/0.2000 L = 4.85 g/L. To obtain the molecular mass directly, you rearrange the equation $PM_m = dRT$ to give an explicit formula for M_m , then substitute into it.

$$M_m = \frac{dRT}{P} = \frac{4.85 \text{ g/L} \times 0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 372 \text{ K}}{0.964 \text{ atm}} = 154 \text{ g/mol}$$

Concept Check 5.3

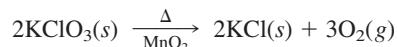
Three 3.0-L flasks, each at a pressure of 878 mmHg, are in a room. The flasks contain He, Ar, and Xe, respectively.

- Which of the flasks contains the most atoms of gas?
- Which of the flasks has the greatest density of gas?
- If the He flask were heated and the Ar flask cooled, which of the three flasks would be at the highest pressure?
- Say the temperature of the He was lowered while that of the Xe was raised. Which of the three flasks would have the greatest number of moles of gas?

5.4**Stoichiometry Problems Involving Gas Volumes**

In Chapter 3 you learned how to find the mass of one substance in a chemical reaction from the mass of another substance in the reaction. Now that you know how to use the ideal gas law, we can extend these types of problems to include gas volumes.

Consider the following reaction, which is often used to generate small quantities of oxygen gas:



Suppose you heat 0.0100 mol of potassium chlorate, KClO_3 , in a test tube. How many liters of oxygen can you produce at 298 K and 1.02 atm?

You solve such a problem by breaking it into two problems, one involving stoichiometry and the other involving the ideal gas law. You note that 2 mol KClO_3 yields 3 mol O_2 . Therefore,

$$0.0100 \frac{\text{mol KClO}_3}{2 \text{ mol KClO}_3} \times \frac{3 \text{ mol O}_2}{1 \text{ mol KClO}_3} = 0.0150 \text{ mol O}_2$$

Now that you have the moles of oxygen produced, you can use the ideal gas law to calculate the volume of oxygen under the conditions given. You rearrange the ideal gas law, $PV = nRT$, and solve for the volume.

$$V = \frac{nRT}{P}$$

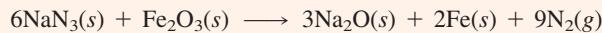
Then you substitute for n , T , and P . Because the pressure is given in units of atmospheres, you choose the value of R in units of $\text{L}\cdot\text{atm}/(\text{K}\cdot\text{mol})$. The answer comes out in liters.

$$V = \frac{0.0150 \text{ mol} \times 0.0821 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol}) \times 298 \text{ K}}{1.02 \text{ atm}} = 0.360 \text{ L}$$

The next example further illustrates this method.

Example 5.9**Solving Stoichiometry Problems Involving Gas Volumes**

Automobiles are being equipped with air bags that inflate on collision to protect the occupants from injury (Figure 5.18). Many such air bags are inflated with nitrogen, N_2 , using the rapid reaction of sodium azide, NaN_3 , and iron(III) oxide, Fe_2O_3 , which is initiated by a spark. The overall reaction is



How many grams of sodium azide would be required to provide 75.0 L of nitrogen gas at 25°C and 748 mmHg?

Problem Strategy This is a stoichiometry problem and a gas-law problem. The chemical equation relates the moles of NaN_3 to moles of N_2 . You can use the ideal gas law to relate the volume of N_2 to moles of N_2 and hence moles of NaN_3 . Then you can obtain the grams of NaN_3 from the moles of NaN_3 .

Solution Here are the available data:

Variable **Value**

$$P \quad 748 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.984 \text{ atm}$$

$$V \quad 75.0 \text{ L}$$

$$T \quad (25 + 273) \text{ K} = 298 \text{ K}$$

$$n \quad ?$$

(continued)

(continued)

Note that the pressure was converted from mmHg to atmospheres and the temperature from degrees Celsius to kelvins. Rearrange the ideal gas law to obtain n .

$$n = \frac{PV}{RT}$$

Substituting from the data gives you the moles of N₂,

$$n = \frac{0.984 \text{ atm} \times 75.0 \text{ L}}{0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 298 \text{ K}} = 3.02 \text{ mol}$$

From the moles of N₂, you use the chemical equation to obtain moles of NaN₃.

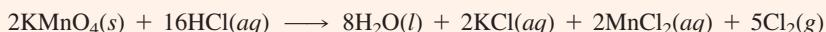
$$3.02 \text{ mol N}_2 \times \frac{6 \text{ mol NaN}_3}{9 \text{ mol N}_2} = 2.01 \text{ mol NaN}_3$$

Now you can calculate the grams of NaN₃. The molecular mass of NaN₃ is 65.01 amu.

$$2.01 \text{ mol NaN}_3 \times \frac{65.01 \text{ g NaN}_3}{1 \text{ mol NaN}_3} = 131 \text{ g NaN}_3$$

Answer Check As with any problem, see whether the context can help you evaluate your answer. Here we determined the mass of a substance used to inflate an airbag. Using this problem context, we would expect the amount of NaN₃ not to be many kilograms; otherwise, it wouldn't fit in a steering wheel. Also, it shouldn't be some minuscule amount (1 mol of gas will occupy a volume of about 22 L at STP), because the airbag has a large volume to fill (75.0 L in this case).

Exercise 5.9 How many liters of chlorine gas, Cl₂, can be obtained at 40°C and 787 mmHg from 9.41 g of hydrogen chloride, HCl, according to the following equation?



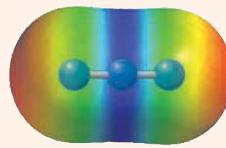
■ See Problems 5.73, 5.74, 5.75, 5.76, 5.77, and 5.78.



FIGURE 5.18

Automobile air bag

Automobiles are equipped with air bags that inflate during collisions. Most air bags are inflated with nitrogen obtained from the rapid reaction of sodium azide, NaN₃ (the azide ion is N₃⁻).



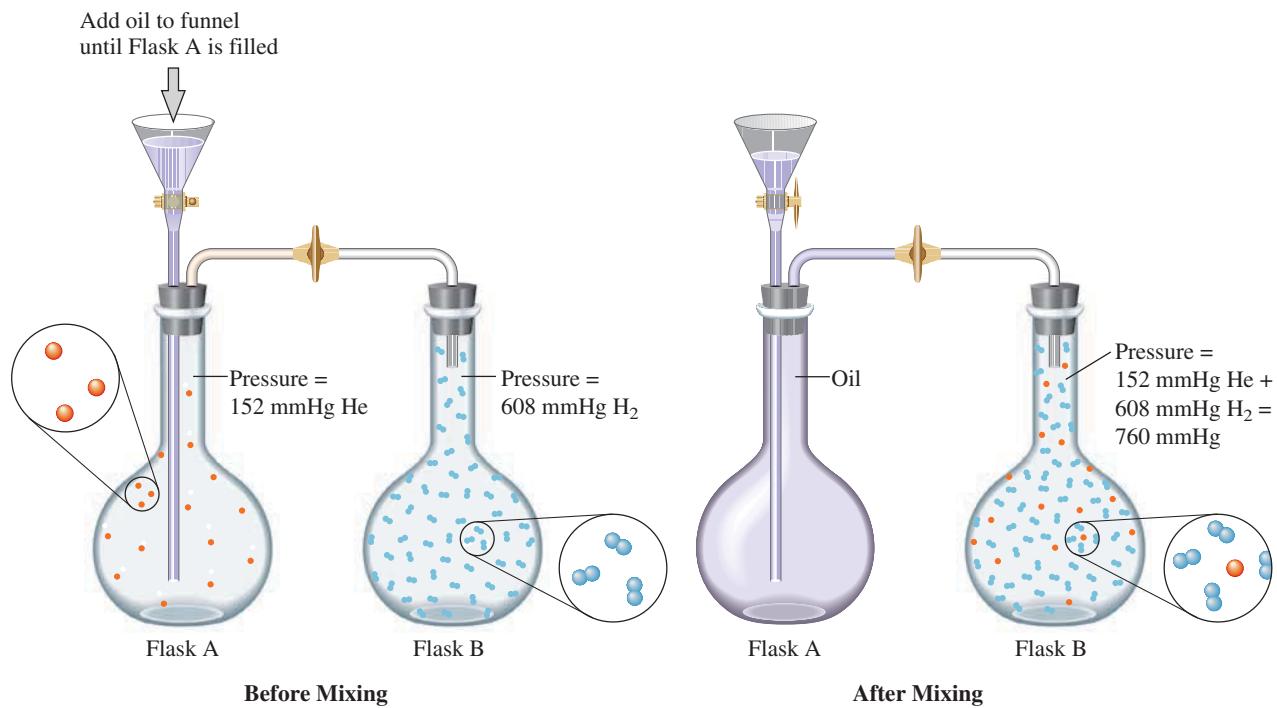
Azide ion

5.5

Gas Mixtures; Law of Partial Pressures

While studying the composition of air, John Dalton concluded in 1801 that each gas in a mixture of unreactive gases acts, as far as its pressure is concerned, as though it were the only gas in the mixture. To illustrate, consider two 1-L flasks, one filled with helium to a pressure of 152 mmHg at a given temperature and the other filled with hydrogen to a pressure of 608 mmHg at the same temperature. Suppose all of the helium in the one flask is put in with the hydrogen in the other flask (see Figure 5.19). After the gases are mixed in one flask, each gas occupies a volume of one liter, just as before, and has the same temperature.

According to Dalton, each gas exerts the same pressure it would exert if it were the only gas in the flask. Thus, the pressure exerted by helium in the mixture is 152 mmHg, and the pressure exerted by hydrogen in the mixture is 608 mmHg. The total pressure exerted by the gases in the mixture is 152 mmHg + 608 mmHg = 760 mmHg.

**FIGURE 5.19****An illustration of Dalton's law of partial pressures**

The valve connecting the flasks and the valve at the funnel are opened so that flask A fills with mineral oil. The helium flows into flask B (having the same volume as flask A), where it mixes with hydrogen. Each gas exerts the pressure it would exert if the other were not there.

Partial Pressures and Mole Fractions

The pressure exerted by a particular gas in a mixture is the **partial pressure** of that gas. The partial pressure of helium in the preceding mixture is 152 mmHg; the partial pressure of hydrogen in the mixture is 608 mmHg. According to **Dalton's law of partial pressures**, the sum of the partial pressures of all the different gases in a mixture is equal to the total pressure of the mixture.

If you let P be the total pressure and P_A , P_B , P_C , . . . be the partial pressures of the component gases in a mixture, the law of partial pressures can be written as

Dalton's law of partial pressures:

$$P = P_A + P_B + P_C + \dots$$

The individual partial pressures follow the ideal gas law. For component A ,

$$P_A V = n_A R T$$

where n_A is the number of moles of component A .

The composition of a gas mixture is often described in terms of the mole fractions of component gases. The **mole fraction** of a component gas is the fraction of moles of that component in the total moles of gas mixture (or the fraction of molecules that are component molecules). Because the pressure of a gas is proportional to moles, for fixed volume and temperature ($P = nRT/V \propto n$), the mole fraction also equals the partial pressure divided by total pressure.

$$\text{Mole fraction of } A = \frac{n_A}{n} = \frac{P_A}{P}$$

Mole percent equals mole fraction \times 100. Mole percent is equivalent to the percentage of the molecules that are component molecules.

Example 5.10

Calculating Partial Pressures and Mole Fractions of a Gas in a Mixture

A 1.00-L sample of dry air at 25°C and 786 mmHg contains 0.925 g N₂, plus other gases including oxygen, argon, and carbon dioxide. a. What is the partial pressure (in mmHg) of N₂ in the air sample? b. What is the mole fraction and mole percent of N₂ in the mixture?

Problem Strategy The key to understanding how to solve this problem is to assume that each gas in the container is independent of other gases; that is, it occupies the entire volume of the sample. Therefore, each gas in the mixture follows the ideal gas law. Using the ideal gas law, we can solve for the pressure of just the N₂, which is its partial pressure. The mole fraction of N₂ can be calculated from the partial pressure of N₂ and the total pressure of all the gases in the sample.

Solution a. Each gas in a mixture follows the ideal gas law. To calculate the partial pressure of N₂, you convert 0.925 g N₂ to moles N₂.

$$0.925 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} = 0.0330 \text{ mol N}_2$$

You substitute into the ideal gas law (noting that 25°C is 298 K).

$$\begin{aligned} P_{\text{N}_2} &= \frac{n_{\text{N}_2}RT}{V} \\ &= \frac{0.0330 \text{ mol} \times 0.0821 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol}) \times 298 \text{ K}}{1.00 \text{ L}} \\ &= 0.807 \text{ atm} (= 613 \text{ mmHg}) \end{aligned}$$

b. The mole fraction of N₂ in air is

$$\text{Mole fraction of N}_2 = \frac{P_{\text{N}_2}}{P} = \frac{613 \text{ mmHg}}{786 \text{ mmHg}} = 0.780$$

Air contains **78.0 mole percent** of N₂.

Answer Check Whenever you are solving for the mole fraction of a substance in a mixture, the number must always be less than 1 (as it was in this problem). Therefore, if you obtain a value greater than 1, it is a sure sign that you have made an error.

Exercise 5.10

A 10.0-L flask contains 1.031 g O₂ and 0.572 g CO₂ at 18°C. What are the partial pressures of oxygen and carbon dioxide? What is the total pressure? What is the mole fraction of oxygen in the mixture?

■ See Problems 5.81, 5.82, 5.83, and 5.84.

Concept Check 5.4

A flask equipped with a valve contains 3.0 mol of H₂ gas. You introduce 3.0 mol of Ar gas into the flask via the valve and then seal the flask.

- What happens to the pressure of just the H₂ gas in the flask after the introduction of the Ar? If it changes, by what factor does it do so?
- How do the pressures of the Ar and the H₂ in the flask compare?
- How does the total pressure in the flask relate to the pressures of the two gases?

Collecting Gases over Water

A useful application of the law of partial pressures arises when you collect gases over water (a method used for gases that do not dissolve appreciably in water). Figure 5.20 shows how a gas, produced by chemical reaction in the flask, is collected by leading it to an inverted tube, where it displaces water. As gas bubbles through the water, the gas picks up molecules of water vapor that mix with it. The partial pressure of water vapor in the gas mixture in the collection tube depends only on the temperature. This partial pressure of water vapor is called the *vapor pressure* of water. < Values of the

Vapor pressure is the maximum partial pressure of the vapor in the presence of the liquid. It is defined more precisely in Chapter 11.

TABLE 5.6
Vapor Pressure of Water at Various Temperatures*

Temperature (°C)	Pressure (mmHg)
0	4.6
10	9.2
15	12.8
17	14.5
19	16.5
21	18.7
23	21.1
25	23.8
27	26.7
30	31.8
40	55.3
60	149.4
80	355.1
100	760.0

*Appendix B contains a more complete table.

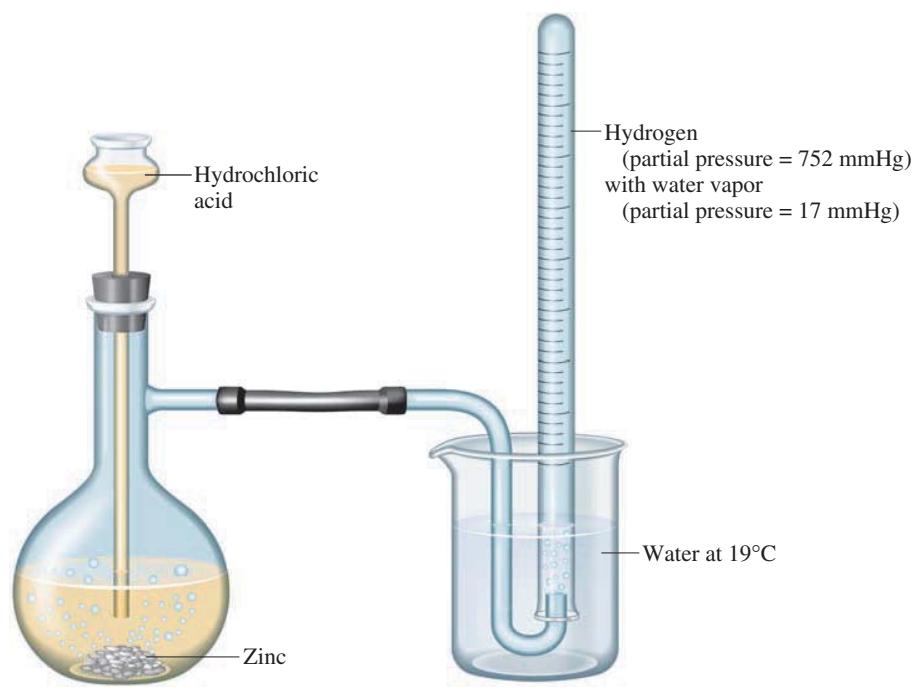


FIGURE 5.20 ▲
Collection of gas over water

Hydrogen, prepared by the reaction of zinc with hydrochloric acid, is led to an inverted tube initially filled with water. When the gas-collection tube is adjusted so that the water level in the tube is at the same height as the level in the beaker, the gas pressure in the tube equals the barometric pressure (769 mmHg). The total gas pressure equals the sum of the partial pressure of the hydrogen (752 mmHg) and the vapor pressure of water (17 mmHg). For clarity, hydrochloric acid is shown in light brown and hydrogen gas in light blue.

vapor pressure of water at various temperatures are listed in Table 5.6 (see Appendix B for a more complete table). The following example shows how to find the partial pressure and then the mass of the collected gas.

Example 5.11

Calculating the Amount of Gas Collected over Water

Hydrogen gas is produced by the reaction of hydrochloric acid, HCl, on zinc metal.



The gas is collected over water. If 156 mL of gas is collected at 19°C (two significant figures) and 769 mmHg total pressure, what is the mass of hydrogen collected?

Problem Strategy The gas collected is hydrogen mixed with water vapor. To obtain the amount of hydrogen, you must first find its partial pressure in the mixture, using Dalton's law (Step 1). Then you can calculate the moles of hydrogen from the ideal gas law (Step 2). Finally, you can obtain the mass of hydrogen from the moles of hydrogen (Step 3).

Solution

Step 1: The vapor pressure of water at 19°C is 16.5 mmHg. From Dalton's law of partial pressures, you know that the total gas pressure equals the partial pressure of hydrogen, P_{H_2} , plus the partial pressure of water, $P_{\text{H}_2\text{O}}$.

$$P = P_{\text{H}_2} + P_{\text{H}_2\text{O}}$$

(continued)

(continued)

Substituting and solving for the partial pressure of hydrogen, you get

$$P_{\text{H}_2} = P - P_{\text{H}_2\text{O}} = (769 - 16.5) \text{ mmHg} = 752 \text{ mmHg}$$

Step 2: Now you can use the ideal gas law to find the moles of hydrogen collected. The data are

Variable	Value
P	$752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.989 \text{ atm}$
V	$156 \text{ mL} = 0.156 \text{ L}$
T	$(19 + 273) \text{ K} = 292 \text{ K}$
n	?

From the ideal gas law, $PV = nRT$, you have

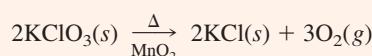
$$n = \frac{PV}{RT} = \frac{0.989 \text{ atm} \times 0.156 \text{ L}}{0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 293 \text{ K}} = 0.00644 \text{ mol}$$

Step 3: You convert moles of H_2 to grams of H_2 .

$$0.00664 \text{ mol H}_2 \times \frac{2.02 \text{ g H}_2}{1 \text{ mol H}_2} = \mathbf{0.0130 \text{ g H}_2}$$

Answer Check Note that this problem assumes that the water level in the collection tube is the same as the water level in the beaker (Figure 5.20). This enables us to equate the gas pressure in the collection tube to atmospheric pressure.

Exercise 5.11 Oxygen can be prepared by heating potassium chlorate, KClO_3 , with manganese dioxide as a catalyst. The reaction is



How many moles of O_2 would be obtained from 1.300 g KClO_3 ? If this amount of O_2 were collected over water at 23°C and at a total pressure of 745 mmHg, what volume would it occupy?

See Problems 5.87 and 5.88.

Kinetic-Molecular Theory

In the following sections, you will see how the interpretation of a gas in terms of the **kinetic-molecular theory** (or simply **kinetic theory**) leads to the ideal gas law. According to this theory, *a gas consists of molecules in constant random motion*. The word *kinetic* describes something in motion. Kinetic energy, E_k , is the energy associated with the motion of an object of mass m . From physics,

$$E_k = \frac{1}{2}m \times (\text{speed})^2$$

We will use the concept of kinetic energy in describing the kinetic theory.



5.6

Kinetic Theory of an Ideal Gas

Our present explanation of gas pressure is that it results from the continual bombardment of the container walls by constantly moving molecules (Figure 5.21). This kinetic interpretation of gas pressure was first put forth in 1676 by Robert Hooke, who had been an assistant of Boyle. Hooke did not pursue this idea, however, so the generally accepted interpretation of gas pressure remained the one given by Isaac Newton, a contemporary of Hooke.

According to Newton, the pressure of a gas was due to the mutual repulsions of the gas particles (molecules). These repulsions pushed the molecules against the walls of the gas container, much as coiled springs packed tightly in a box would push against the walls of the box. This interpretation continued to be the dominant view of gas pressure until the mid-nineteenth century.

Despite the dominance of Newton's view, some people followed the kinetic interpretation. In 1738, Daniel Bernoulli, a Swiss mathematician and physicist, gave a quantitative explanation of Boyle's law using the kinetic interpretation. He even suggested that molecules move faster at higher temperatures, in order to explain Amontons's experiments on the temperature dependence of gas volume and pressure. However, Bernoulli's paper attracted little notice. A similar kinetic interpretation of gases was submitted for publication to the Royal Society of London in 1848 by John James Waterston. His paper was rejected as "nothing but nonsense." <

Soon afterward, the scientific climate for the kinetic view improved. The kinetic theory of gases was developed by a number of influential physicists, including James Clerk Maxwell (1859) and Ludwig Boltzmann (in the 1870s). Throughout the last half of the nineteenth century, research continued on the kinetic theory, making it a cornerstone of our present view of molecular substances.

FIGURE 5.21

Kinetic-theory model of gas pressure

According to kinetic theory, gas pressure is the result of the bombardment of the container walls by constantly moving molecules.

Waterston's paper, with the reviewers' comments, was discovered in the Royal Society's files by Lord Rayleigh in 1892. (Rayleigh codiscovered argon and received the 1904 Nobel Prize in physics.)

The statements that there are no intermolecular forces and that the volume of molecules is negligible are simplifications that lead to the ideal gas law. But intermolecular forces are needed to explain how we get the liquid state from the gaseous state; it is intermolecular forces that hold molecules together in the liquid state.

Postulates of Kinetic Theory

Physical theories are often given in terms of *postulates*: the basic statements from which all conclusions or predictions of a theory are deduced. The postulates are accepted as long as the predictions from the theory agree with experiment. If a particular prediction did not agree with experiment, we would limit the area to which the theory applies, modify the postulates, or start over with a new theory.

The kinetic theory of an *ideal gas* (a gas that follows the ideal gas law) is based on five postulates.

Postulate 1: *Gases are composed of molecules whose size is negligible compared with the average distance between them.* Most of the volume occupied by a gas is empty space. This means that you can usually ignore the volume occupied by the molecules.

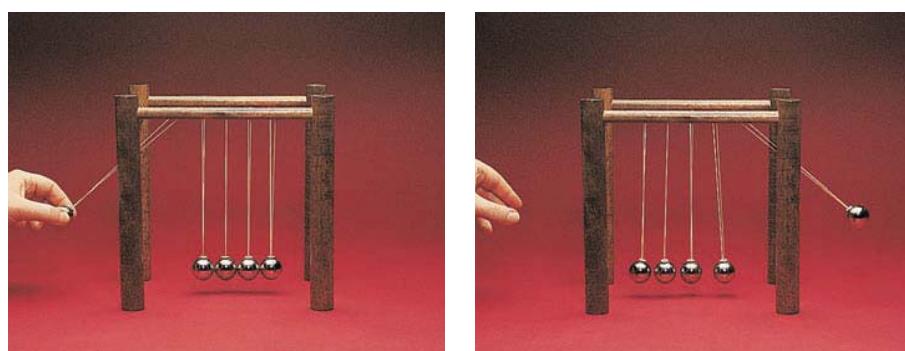
Postulate 2: *Molecules move randomly in straight lines in all directions and at various speeds.* This means that properties of a gas that depend on the motion of molecules, such as pressure, will be the same in all directions.

Postulate 3: *The forces of attraction or repulsion between two molecules (intermolecular forces) in a gas are very weak or negligible, except when they collide.* < This means that a molecule will continue moving in a straight line with undiminished speed until it collides with another gas molecule or with the walls of the container.

Postulate 4: *When molecules collide with one another, the collisions are elastic.* In an elastic collision, the total kinetic energy remains constant; no kinetic energy is lost. To understand the difference between an elastic and an inelastic collision, compare the collision of two hard steel spheres with

FIGURE 5.22**Elastic collision of steel balls**

Left: The steel ball at the left is lifted to give it energy. *Right:* When the steel ball is released, the energy is transmitted through elastic collisions to the ball on the right.



the collision of two masses of putty. The collision of steel spheres is nearly elastic (that is, the spheres bounce off each other and continue moving), but that of putty is not (Figure 5.22). Postulate 4 says that unless the kinetic energy of molecules is removed from a gas—for example, as heat—the molecules will forever move with the same average kinetic energy per molecule.

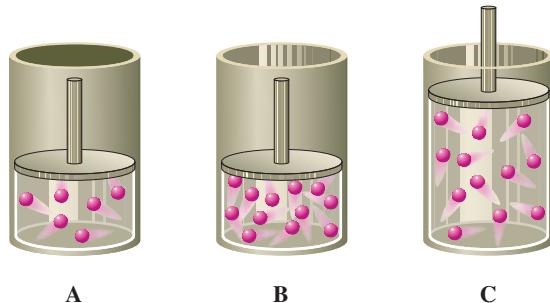
Postulate 5: *The average kinetic energy of a molecule is proportional to the absolute temperature.* This postulate establishes what we mean by temperature from a molecular point of view: the higher the temperature, the greater the molecular kinetic energy.

Qualitative Interpretation of the Gas Laws

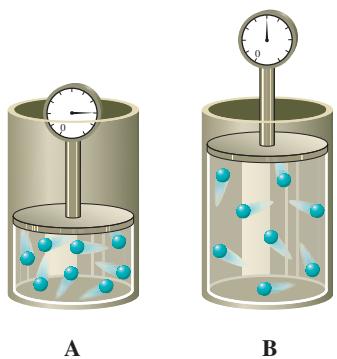
According to the kinetic theory, the pressure of a gas results from the bombardment of container walls by molecules. Both the concentration of molecules (number per unit volume) and the average speed of the molecules are factors in determining this pressure. Molecular concentration and average speed determine the frequency of collisions with the wall. Average molecular speed determines the average force of a collision.

Let's consider how these terms apply to Avogadro's law, which relates the volume of gas to the moles of gas at constant (fixed) temperature and pressure. Constant temperature means that the average kinetic energy of a molecule is constant (Postulate 5). Therefore, the average molecular speed and thus the average molecular force from collision remain constant. Gas pressure depends on the force and frequency of molecular collisions with container walls. Consider the container depicted in Figure 5.23A, where the pressure of the gas molecules in the container equals atmospheric pressure. What happens when you introduce more gas molecules into the container? More moles of gas increase the number of molecules per unit volume (concentration) and therefore increase the frequency of collisions with the container walls. If the volume of the container were fixed, the pressure would increase (Figure 5.23B). However, Avogadro's law requires that the pressure remain constant, so the container volume expands until the concentration and, therefore, the frequency of collisions with container walls decrease (Figure 5.23C). The result is that when you increase the number of moles of gas in a container at a constant pressure and temperature, the volume increases.

The same concepts can be used to discuss Boyle's law. Suppose you increase the volume of a gas while holding both the temperature

**FIGURE 5.23****Molecular description of Avogadro's law**

(A) A container where the gas molecules are at atmospheric pressure ($P_{\text{inside}} = P_{\text{atm}}$). The pressure in the container is due to the force and frequency of molecular collisions with the container walls. (B) The container after increasing the number of gas molecules while not allowing the piston to move. Due to the greater concentration of gas (more moles of gas in the same volume), the frequency of collisions of the gas molecules with the walls of the container has increased, causing the pressure to increase ($P_{\text{inside}} > P_{\text{atm}}$). (C) Container after the molecules are allowed to move the piston and increase the volume. The concentration of gas molecules and frequency of collisions with the container walls have decreased, and the pressure of the gas molecules inside the container is again equal to atmospheric pressure ($P_{\text{inside}} = P_{\text{atm}}$).

**FIGURE 5.24****Molecular description of Boyle's law**

(A) A fixed number of moles of gas in a container at room temperature. The pressure in the container is due to the force and frequency of molecular collisions with the container walls. (B) The same number of moles of gas at the same temperature as A, but in a container of greater volume. Because of the larger container volume, the gas concentration is now lower, which leads to a decrease in the frequency of molecular collisions per unit of wall area, resulting in a lower pressure.

This derivation is essentially the one given by Daniel Bernoulli.

Consistent with kinetic theory, we assume that the duration of collision of a molecule with a container wall is the same, regardless of the type of molecule.

Recall that kinetic energy is defined as $\frac{1}{2}m$ multiplied by (speed)².

and number of moles of gas constant (Figure 5.24). This decreases the concentration of molecules and the frequency of collisions per unit wall area; the pressure must decrease. Thus, when you increase the volume of a gas while keeping the temperature constant, the pressure decreases.

Now consider Charles's law. If you raise the temperature, you increase the average molecular speed. The average force of a collision increases. If all other factors remained fixed, the pressure would increase. For the pressure to remain constant as it does in Charles's law, it is necessary for the volume to increase so that the number of molecules per unit volume decreases and the frequency of collisions decreases. Thus, when you raise the temperature of a gas while keeping the pressure constant, the volume increases.

The Ideal Gas Law from Kinetic Theory

One of the most important features of kinetic theory is its explanation of the ideal gas law. To show how you can get the ideal gas law from kinetic theory, we will first find an expression for the pressure of a gas. <

According to kinetic theory, the pressure of a gas, P , will be proportional to the frequency of molecular collisions with a surface and to the average force exerted by a molecule in collision.

$$P \propto \text{frequency of collisions} \times \text{average force}$$

The average force exerted by a molecule during a collision depends on its mass m and its average speed u —that is, on its average momentum mu . < In other words, the greater the mass of the molecule and the faster it is moving, the greater the force exerted during collision. The frequency of collisions is also proportional to the average speed u , because the faster a molecule is moving, the more often it strikes the container walls. Frequency of collisions is inversely proportional to the gas volume V , because the larger the volume, the less often a given molecule strikes the container walls. Finally, the frequency of collisions is proportional to the number of molecules N in the gas volume. Putting these factors together gives

$$P \propto \left(u \times \frac{1}{V} \times N \right) \times mu$$

Bringing the volume to the left side, you get

$$PV \propto Nmu^2$$

Because the average kinetic energy of a molecule of mass m and average speed u is $\frac{1}{2}mu^2$, PV is proportional to the average kinetic energy of a molecule. < Moreover, the average kinetic energy is proportional to the absolute temperature (Postulate 5). Noting that the number of molecules, N , is proportional to the moles of molecules, n , you have

$$PV \propto nT$$

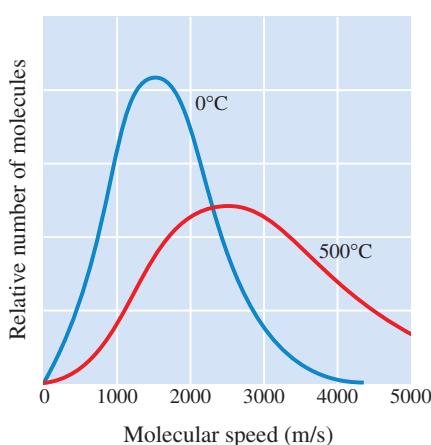
You can write this as an equation by inserting a constant of proportionality, R , which you can identify as the molar gas constant.

$$PV = nRT$$

The next two sections give additional deductions from kinetic theory.

5.7**Molecular Speeds; Diffusion and Effusion**

The principal tenet of kinetic theory is that molecules are in constant random motion. Now we will look at the speeds of molecules and at some conclusions of kinetic theory regarding molecular speeds.

**FIGURE 5.25****Maxwell's distribution of molecular speeds**

The distributions of speeds of H_2 molecules are shown for 0°C and 500°C. Note that the speed corresponding to the maximum in the curve (the most probable speed) increases with temperature.

According to kinetic theory, the total kinetic energy of a mole of any gas equals $\frac{3}{2}RT$. The average kinetic energy of a molecule, which by definition is $\frac{1}{2}mu^2$, is obtained by dividing $\frac{3}{2}RT$ by Avogadro's number, N_A . Therefore, the kinetic energy is $\frac{1}{2}mu^2 = 3RT/(2N_A)$. Hence $u^2 = 3RT/(N_A m)$. Or, noting that $N_A m$ equals the molar mass M_m , you get $u^2 = 3RT/M_m$, from which you get the text equation.

Molecular Speeds

According to kinetic theory, the speeds of molecules in a gas vary over a range of values. The British physicist James Clerk Maxwell (1831–1879) showed theoretically—and it has since been demonstrated experimentally—that molecular speeds are distributed as shown in Figure 5.25. This distribution of speeds depends on the temperature. At any temperature, the molecular speeds vary widely, but most are close to the average speed, which is close to the speed corresponding to the maximum in the distribution curve. As the temperature increases, the average speed increases.

The **root-mean-square (rms) molecular speed**, u , is a type of average molecular speed, equal to the speed of a molecule having the average molecular kinetic energy. It is given by the following formula:

$$u = \sqrt{\frac{3RT}{M_m}} = \left(\frac{3RT}{M_m}\right)^{\frac{1}{2}}$$

where R is the molar gas constant, T is the absolute temperature, and M_m is the molar mass for the gas. This result follows from Postulate 5 of kinetic theory. < Note that of two gases, the one with the higher molar mass will have the lower rms speed.

In applying this equation, care must be taken to use consistent units. If SI units are used for R ($= 8.31 \text{ kg}\cdot\text{m}^2/(\text{s}^2\cdot\text{K}\cdot\text{mol})$), T (K), and M_m (kg/mol), as in the following example, the rms speed will be in meters per second. Note that in these units, H_2 , whose molecular weight is 2.02 amu, has a molar mass of 2.02×10^{-3} kg/mol.

Values of the rms speed calculated from this formula indicate that molecular speeds are astonishingly high. For example, the rms speed of H_2 molecules at 20°C is 1.90×10^3 m/s (over 4000 mi/hr).

Example 5.12

Calculating the rms Speed of Gas Molecules

Calculate the rms speed of O_2 molecules in a cylinder at 21°C and 15.7 atm. See Table 5.5 for the appropriate value of R .

Problem Strategy The rms speed of a gas can be determined by substituting the appropriate values into the preceding equation.

Solution The rms molecular speed is independent of pressure but does depend on the absolute temperature, which is $(21 + 273)$ K = 294 K. To calculate u , it is best to use SI units throughout. In these units, the molar mass of O_2 is 32.0×10^{-3} kg/mol, and $R = 8.31 \text{ kg}\cdot\text{m}^2/(\text{s}^2\cdot\text{K}\cdot\text{mol})$. Hence,

$$u = \left(\frac{3 \times 8.31 \text{ kg}\cdot\text{m}^2/(\text{s}^2\cdot\text{K}\cdot\text{mol}) \times 294 \text{ K}}{32.0 \times 10^{-3} \text{ kg/mol}} \right)^{\frac{1}{2}} = 479 \text{ m/s}$$

Answer Check When performing calculations that involve this formula, be sure to use the appropriate value of R , $(8.31 \text{ kg}\cdot\text{m}^2)/(\text{s}^2\cdot\text{K}\cdot\text{mol})$, and to express the molar mass in units of kg/mol, and the temperature in kelvins.

(continued)

(continued)

Exercise 5.12

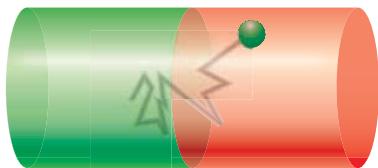
What is the rms speed (in m/s) of a carbon tetrachloride molecule at 22°C?

■ See Problems 5.89, 5.90, 5.91, and 5.92.

Exercise 5.13

At what temperature do hydrogen molecules, H₂, have the same rms speed as nitrogen molecules, N₂, at 455°C? At what temperature do hydrogen molecules have the same average kinetic energy?

■ See Problems 5.93 and 5.94.

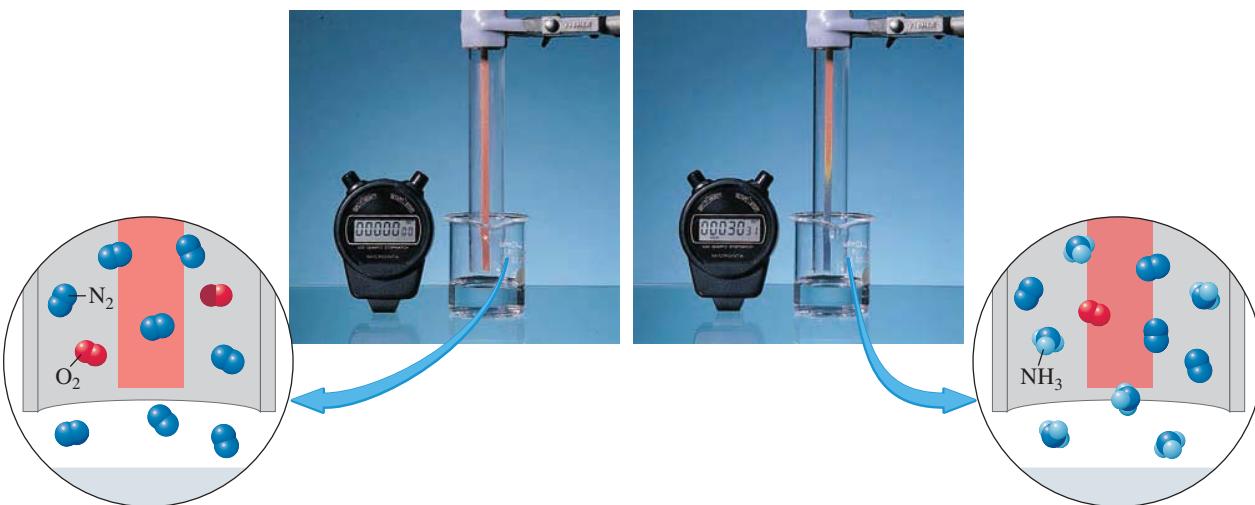
**FIGURE 5.26****Kinetic-theory model of gas diffusion**

A vessel contains two different gases. For clarity, the figure shows the motion of only one molecule. The path of the molecule is chaotic because of the constant collisions with other molecules. After some time, the "green" molecule has by its random motion mixed with the "red" gas. Similar motions of other molecules eventually result in the complete mixing of the two gases.

Diffusion and Effusion

The pleasant odor of apple pie baking in the oven quickly draws people to the kitchen. The spread of an odor is easily explained by kinetic theory. All molecules are in constant, chaotic motion, and eventually a cluster of molecules of a particular substance will spread out to occupy a larger and larger space. Gaseous **diffusion** is *the process whereby a gas spreads out through another gas to occupy the space uniformly*. Figure 5.26 is a kinetic-theory explanation of the diffusion of two gases. An individual molecule moves chaotically as it is buffeted by other molecules. After sufficient time, this constant chaotic motion of molecules results in a complete mixing of the gases. Figure 5.27 demonstrates the diffusion of ammonia gas through air.

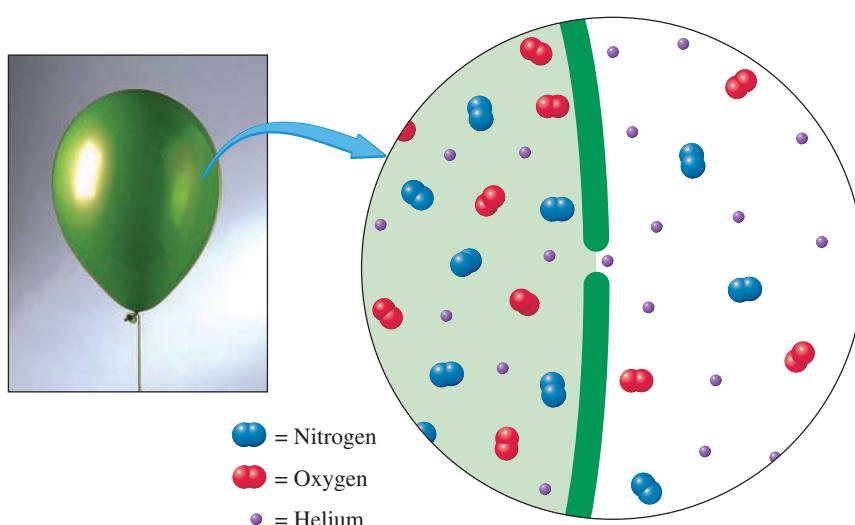
When you think about the kinetic-theory calculations of molecular speed, you might ask why diffusion is not even much faster than it is. Why does it take minutes for the gas to diffuse throughout a room when the molecules are moving at perhaps a thousand miles per hour? This was, in fact, one of the first criticisms of kinetic theory. The answer is simply that a molecule never travels very far in one direction (at ordinary pressures) before it collides with another molecule and moves off in another direction. If you could trace out the path of an individual molecule, it would be a zigzagging trail. For a molecule to cross a room, it has to travel many times the straight-line distance.

**FIGURE 5.27****Gaseous diffusion**

Left: Concentrated aqueous ammonia in the beaker evolves ammonia gas into the glass tube, which contains a strip of wet indicator paper. In the molecular view there are only nitrogen and oxygen molecules (air) surrounding the indicator paper. *Right:* The indicator changes color as the ammonia gas diffuses upward through the air in the tube. The molecular view depicts the appearance of the NH₃ molecules in the tube due to diffusion.

FIGURE 5.28**Model of gaseous effusion**

According to kinetic theory, gas molecules are in constant random motion. When a molecule in the container happens to hit the small opening, it passes (or effuses) to the outside. The rate of effusion depends on the speed of the molecules—the faster the molecules move, the more likely they are to encounter the opening and pass from the inside of the box to the outside.



Although the rate of diffusion certainly depends in part on the average molecular speed, the effect of molecular collisions makes the theoretical picture a bit complicated. *Effusion*, like diffusion, is a process involving the flow of a gas but is theoretically much simpler.

If you place a container of gas in a vacuum and then make a very small hole in the container, the gas molecules escape through the hole at the same speed they had in the container (Figure 5.28). *The process in which a gas flows through a small hole in a container is called effusion.* It was first studied by Thomas Graham, who discovered in 1846 that the rate of effusion of a gas is inversely proportional to the square root of its density. Today we usually state **Graham's law of effusion** in terms of molecular mass: *the rate of effusion of gas molecules from a particular hole is inversely proportional to the square root of the molecular mass of the gas at constant temperature and pressure.*

Let us consider a kinetic-theory analysis of an effusion experiment. Suppose the hole in the container is made small enough so that the gas molecules continue to move randomly (rather than moving together as they would in a wind). When a molecule happens to encounter the hole, it leaves the container. The collection of molecules leaving the container by chance encounters with the hole constitutes the effusing gas. All you have to consider for effusion is the rate at which molecules encounter the hole in the container.

The rate of effusion of molecules from a container depends on three factors: the cross-sectional area of the hole (the larger it is, the more likely molecules are to escape); the number of molecules per unit volume (the more crowded the molecules are, the more likely they are to encounter the hole); and the average molecular speed (the faster the molecules are moving, the sooner they will find the hole and escape).

If you compare the effusion of different gases from the same container, at the same temperature and pressure, the first two factors will be the same. The average molecular speeds will be different, however.

Because the average molecular speed essentially equals $\sqrt{3RT/M_m}$, where M_m is the molar mass, the rate of effusion is proportional to $\sqrt{M_m}$. That is, the rate of effusion is inversely proportional to the square root of the molar mass (or molecular weight), as Graham's law states. The derivation of Graham's law from kinetic theory was considered a triumph of the theory and greatly strengthened confidence in its validity.

Graham's law of effusion:

$$\text{Rate of effusion of molecules} \propto \frac{1}{\sqrt{M_m}} \quad (\text{for the same container at constant } T \text{ and } P)$$

FIGURE 5.29**The hydrogen fountain**

The demonstrator places a beaker containing hydrogen gas over the porous clay container. Hydrogen effuses into the porous container faster than air effuses out. As a result, the pressure inside the porous container and the flask connected to it increases, forcing colored water out the side tube as a stream.



The hydrogen fountain, shown in Figure 5.29, is dependent on the differences in rates of effusion of gases. (Can you explain why a helium-filled balloon loses pressure after a few hours?)

Example 5.13**Calculating the Ratio of Effusion Rates of Gases**

Calculate the ratio of effusion rates of molecules of carbon dioxide, CO_2 , and sulfur dioxide, SO_2 , from the same container and at the same temperature and pressure.

Problem Strategy Here we need to compare the rates of effusion of two gases by taking their rates of effusion. We can use Graham's law of effusion for the two gases to set up a relationship

$$\frac{\text{Rate of effusion of } \text{CO}_2}{\text{Rate of effusion of } \text{SO}_2} = \frac{\frac{1}{\sqrt{M_m(\text{CO}_2)}}}{\frac{1}{\sqrt{M_m(\text{SO}_2)}}}$$

where $M_m(\text{SO}_2)$ is the molar mass of SO_2 (64.1 g/mol) and $M_m(\text{CO}_2)$ is the molar mass of CO_2 (44.0 g/mol). This equation can be simplified to

$$\frac{\text{Rate of effusion of } \text{CO}_2}{\text{Rate of effusion of } \text{SO}_2} = \sqrt{\frac{M_m(\text{SO}_2)}{M_m(\text{CO}_2)}}$$

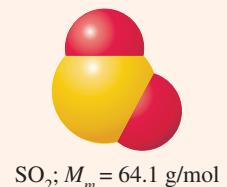
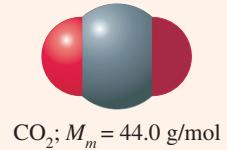
(Note that the two rates of effusion are inversely proportional to the square roots of the molar masses.)

Solution Substituting these molar masses into the formula gives

$$\frac{\text{Rate of effusion of } \text{CO}_2}{\text{Rate of effusion of } \text{SO}_2} = \sqrt{\frac{64.1 \text{ g/mol}}{44.0 \text{ g/mol}}} = 1.21$$

In other words, carbon dioxide effuses 1.21 times faster than sulfur dioxide (because CO_2 molecules move 1.21 times faster on average than SO_2 molecules).

Answer Check Analyze your answer to make sure that the gas with the lower molar mass has the greater rate of effusion. In this case, the CO_2 would be expected to have the greater effusion rate, so we should expect the effusion rate ratio of CO_2 to SO_2 to be greater than 1.



(continued)

(continued)

Exercise 5.14 If it takes 3.52 s for 10.0 mL of helium to effuse through a hole in a container at a particular temperature and pressure, how long would it take for 10.0 mL of oxygen, O₂, to effuse from the same container at the same temperature and pressure? (Note that the rate of effusion can be given in terms of volume of gas effused per second.)

■ See Problems 5.95, 5.96, 5.97, and 5.98.

Exercise 5.15 If it takes 4.67 times as long for a particular gas to effuse as it takes hydrogen under the same conditions, what is the molecular mass of the gas? (Note that the rate of effusion is inversely proportional to the time it takes for a gas to effuse.)

■ See Problems 5.99 and 5.100.

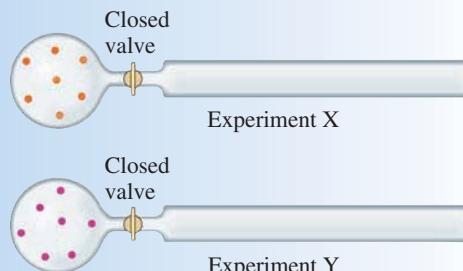
Graham's law has practical application in the preparation of fuel rods for nuclear fission reactors. Such reactors depend on the fact that the uranium-235 nucleus undergoes fission (splits) when bombarded with neutrons. When the nucleus splits, several neutrons are emitted and a large amount of energy is liberated. These neutrons bombard more uranium-235 nuclei, and the process continues with the evolution of more energy. However, natural uranium consists of 99.27% uranium-238 (which does not undergo fission) and only 0.72% uranium-235 (which does undergo fission). A uranium fuel rod must contain about 3% uranium-235 to sustain the nuclear reaction.

To increase the percentage of uranium-235 in a sample of uranium (a process called *enrichment*), one first prepares uranium hexafluoride, UF₆, a white, crystalline solid that is easily vaporized. < Uranium hexafluoride vapor is allowed to pass through a series of porous membranes. Each membrane has many small holes through which the vapor can effuse. Because the UF₆ molecules with the lighter isotope of uranium travel about 0.4% faster than the UF₆ molecules with the heavier isotope, the gas that passes through first is somewhat richer in uranium-235. When this vapor passes through another membrane, the uranium-235 vapor becomes further concentrated. It takes many effusion stages to reach the necessary enrichment.

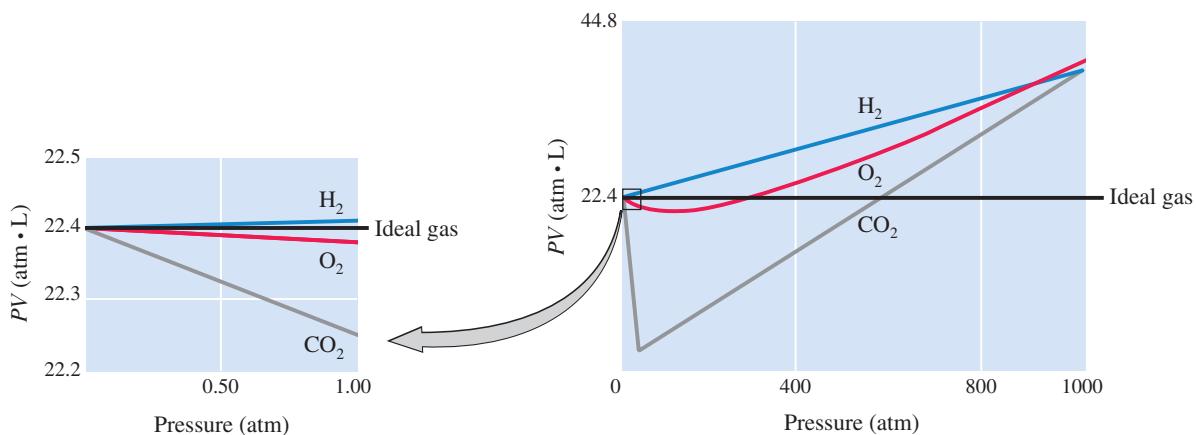
Uranium hexafluoride vapor has a density of 13.0 g/L at 57°C (the temperature at which the solid sublimes). This is more than 12 times as dense as air at the same temperature.

Concept Check 5.5

Consider the experimental apparatus shown. In this setup, each round flask contains a gas, and the long tube contains no gas (that is, it is a vacuum).



- We use 1.0 mol of He for experiment X and 1.0 mol of Ar for experiment Y. If both valves are opened at the same time, which gas would you expect to reach the end of the long tube first?
- If you wanted the Ar to reach the end of the long tube at the same time as the He, what experimental condition (that is, you cannot change the equipment) could you change to make this happen?

**FIGURE 5.30****Pressure–volume product of gases at different pressures**

Right: The pressure–volume product of one mole of various gases at 0°C and at different pressures.

Left: Values at low pressure. For an ideal gas, the pressure–volume product is constant.

5.8**Real Gases**

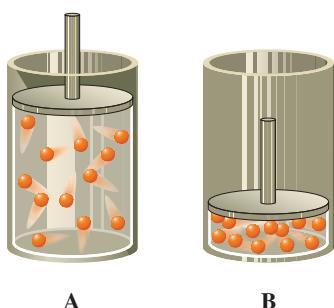
In Section 5.2, we found that, contrary to Boyle's law, the pressure–volume product for O_2 at 0°C was not quite constant, particularly at high pressures (see PV column in Table 5.3). Experiments show that the ideal gas law describes the behavior of real gases quite well at low pressures and moderate temperatures, but not at high pressures and low temperatures.

Figure 5.30 shows the behavior of the pressure–volume product at various pressures for several gases. The gases deviate noticeably from Boyle's law (ideal gas) behavior at high pressures. Also, the deviations differ for each kind of gas. We can explain why this is so by examining the postulates of kinetic theory, from which the ideal gas law can be derived.

Postulate 1 of kinetic theory says that the volume of space occupied by molecules is negligible compared with the total gas volume. To derive the ideal gas law from kinetic theory, we must assume that each molecule is free to move throughout the entire gas volume, V . At low pressures, where the volume of individual molecules is negligible compared with the total volume available (Figure 5.31A), the ideal gas law is a good approximation. At higher pressures, where the volume of individual molecules becomes important (Figure 5.31B), the space through which a molecule can move is significantly different from V .

Postulate 3 says that the forces of attraction between molecules (intermolecular forces) in a gas are very weak or negligible. This is a good approximation at low pressures, where molecules tend to be far apart, because these forces diminish rapidly as the distance between molecules increases. Intermolecular forces become significant at higher pressures, though, because the molecules tend to be close together. Because of these intermolecular forces, the actual pressure of a gas is less than that predicted by ideal gas behavior. As a molecule begins to collide with a wall surface, neighboring molecules pull this colliding molecule slightly away from the wall, giving a reduced pressure (Figure 5.32).

The Dutch physicist J. D. van der Waals (1837–1923) was the first to account for these deviations of a real gas from ideal gas behavior. The **van der Waals equation** is

**FIGURE 5.31****Effect of molecular volume at high pressure**

(A) At low pressures, the volume of molecules is a small fraction of the total volume and can be neglected, as in the ideal gas law. (B) At high pressures, the volume of molecules is a significant fraction of the total volume and cannot be neglected. The ideal gas law is no longer a good approximation.

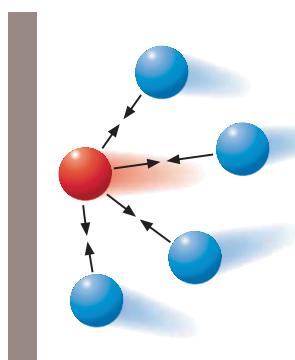


FIGURE 5.32 ▲
Effect of intermolecular attractions on gas pressure

Gas pressure on a wall is due to molecules colliding with it. Here a molecule (shown in red) about to collide with the wall is attracted away from the wall by the weak attractive forces of neighboring molecules (intermolecular forces). As a result, the pressure exerted by the gas is less than that expected in the absence of those forces.

an equation similar to the ideal gas law, but includes two constants, a and b , to account for deviations from ideal behavior.

$$\left(P + \frac{n^2a}{V^2} \right) (V - nb) = nRT$$

The constants a and b are chosen to fit experiment as closely as possible. Table 5.7 gives values of van der Waals constants for several gases.

You can obtain the van der Waals equation from the ideal gas law, $PV = nRT$, by making the following replacements:

Ideal Gas Equation

V

P

van der Waals Equation

becomes $V - nb$

becomes $P + n^2a/V^2$

To obtain these substitutions, van der Waals reasoned as follows. The volume available for a molecule to move in equals the gas volume, V , minus the volume occupied by molecules. So he replaced V in the ideal gas law with $V - nb$, where nb represents the volume occupied by n moles of molecules. Then he noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighboring molecules, n/V . However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration, n/V . Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas law by a factor proportional to n^2/V^2 . Letting a be the proportionality constant, we can write

$$P(\text{actual}) = P(\text{ideal}) - n^2a/V^2$$

or

$$P(\text{ideal}) = P(\text{actual}) + n^2a/V^2$$

In other words, you replace P in the ideal gas law by $P + n^2a/V^2$.

The next example illustrates the use of the van der Waals equation to calculate the pressure exerted by a gas under given conditions.

TABLE 5.7 | **van der Waals Constants for Some Gases**

Gas	a L ² ·atm/mol ²	b L/mol
CO ₂	3.658	0.04286
C ₂ H ₆	5.570	0.06499
C ₂ H ₅ OH	12.56	0.08710
He	0.0346	0.0238
H ₂	0.2453	0.02651
O ₂	1.382	0.03186
SO ₂	6.865	0.05679
H ₂ O	5.537	0.03049

From Lide, David R., Ed., in *CRC Handbook of Chemistry and Physics*, 74th ed., pp. 6–48. Copyright CRC Press Inc., Boca Raton, Florida, 1993. With the permission of CRC Press, Inc.

Example 5.14

Using the van der Waals Equation

If sulfur dioxide were an ideal gas, the pressure at 0.0°C exerted by 1.000 mole occupying 22.41 L would be 1.000 atm (22.41 L is the molar volume of an ideal gas at STP). Use the van der Waals equation to estimate the pressure of this volume of 1.000 mol SO₂ at 0.0°C. See Table 5.7 for values of *a* and *b*.

Problem Strategy You first rearrange the van der Waals equation to give *P* in terms of the other variables.

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

Now you substitute *R* = 0.08206 L·atm/(K·mol), *T* = 273.2 K, *V* = 22.41 L, *a* = 6.865 L²·atm/mol², and *b* = 0.05679 L/mol.

Solution

$$\begin{aligned} P &= \frac{1.000 \text{ mol} \times 0.08206 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 273.2 \text{ K}}{22.41 \text{ L} - (1.000 \text{ mol} \times 0.05679 \text{ L/mol})} - \\ &\quad \frac{(1.000 \text{ mol})^2 \times 6.865 \text{ L}^2 \cdot \text{atm}/\text{mol}^2}{(22.41 \text{ L})^2} \\ &= 1.003 \text{ atm} - 0.014 \text{ atm} = \mathbf{0.989 \text{ atm}} \end{aligned}$$

Note that the first term, *nRT*/*(V - nb)*, gives the pressure corrected for molecular volume. This pressure, 1.003 atm, is slightly higher than the ideal value, 1.000 atm, because the volume through which a molecule is free to move, *V - nb*, is smaller than what is assumed for an ideal gas (*V*). Therefore, the concentration of molecules in this volume is greater, and the number of collisions per unit surface area is expected to be greater. However, the last term, *n*²*a*/*V*², corrects for intermolecular forces, which reduce the force of the collisions, and this reduces the pressure to 0.989 atm.

Answer Check Make sure that you used the appropriate value for the ideal gas constant and that the units of volume and pressure match those given for the constants *a* and *b*.

Exercise 5.16 Use the van der Waals equation to calculate the pressure of 1.000 mol ethane, C₂H₆, that has a volume of 22.41 L at 0.0°C. Compare the result with the value predicted by the ideal gas law.

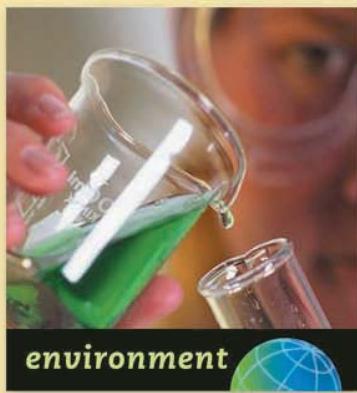
■ See Problems 5.101 and 5.102.

Concept Check 5.6

A 1.00-L container is filled with an ideal gas and the recorded pressure is 350 atm. We then put the same amount of a real gas into the container and measure the pressure.

- If the real gas molecules occupy a relatively small volume and have large intermolecular attractions, how would you expect the pressures of the two gases to compare?
- If the real gas molecules occupy a relatively large volume and there are negligible intermolecular attractions, how would you expect the pressures of the two gases to compare?
- If the real gas molecules occupy a relatively large volume and have large intermolecular attractions, how would you expect the pressures of the two gases to compare?

A Chemist Looks at . . .



Yes, I know, I shouldn't have left that chocolate bar on the seat of my car, which I parked on a sunny street near the university. You and I know that the interior of such a car can become quite hot. Have you ever wondered why? If the sun's heat energy can get into the car through its window glass, why can't it leave equally well?

Parked cars are similar to greenhouses, which people have used for centuries to protect plants from cold weather. The Swedish chemist Svante Arrhenius, whom you may remember from the previous chapter (for his theory of ionic solutions), realized that carbon dioxide in the atmosphere acts like the glass in a greenhouse. His calculations, published in 1898, were the first to show how sensitive the temperature of the earth might be to the

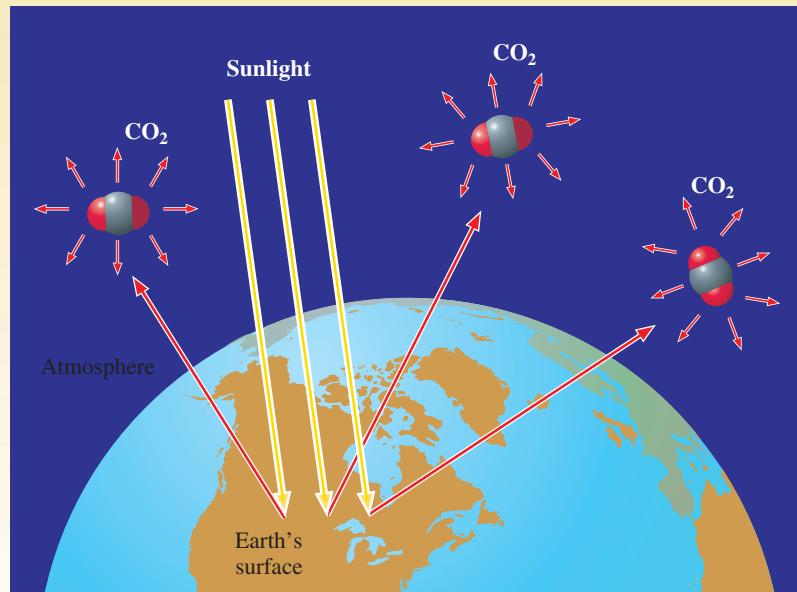
percentage of carbon dioxide in the atmosphere. Arrhenius's reference to the earth's atmospheric envelope, with its carbon dioxide, as a "hothouse" has evolved into our present-day term *greenhouse effect*.

Here is the explanation of the greenhouse effect. The principal gases in the atmosphere are oxygen, O₂, and nitrogen, N₂. These gases are transparent to visible light from the sun, and when this light reaches the surface of the earth, it is absorbed and converted to heat. This heat causes atoms in the earth's surface to vibrate, which then radiate the heat energy as infrared radiation, or heat rays (Figure 5.33). Neither oxygen nor nitrogen absorb infrared radiation, so if the earth's atmosphere contained only these gases, the infrared radiation, or heat rays, would simply escape into outer space; there would be no greenhouse effect. However, other gases in the atmosphere, especially carbon dioxide, do absorb infrared radiation, and it is this absorption that warms the atmosphere and eventually also the earth's surface, giving us a greenhouse effect. The

FIGURE 5.33 ►

Greenhouse effect of certain gases in the atmosphere

The atmosphere is transparent to sunlight, except for radiation in the far ultraviolet. When sunlight reaches the earth's surface, it is absorbed. The heated surface then radiates the energy back as infrared radiation. The major components of the atmosphere, O₂ and N₂, are transparent to this radiation, but gases such as CO₂, H₂O, CH₄, and chlorofluorocarbons, do absorb infrared rays. These substances in the atmosphere then reradiate the infrared rays, with the result that a significant fraction of the radiation returns to earth. In effect, these gases trap the radiation, acting like the glass on a greenhouse.



greater the percentage of carbon dioxide in the atmosphere, the warmer the earth should be. (Glass, acting like carbon dioxide, allows visible light to pass into a greenhouse, but absorbs infrared radiation, effectively trapping the heat.)

The greenhouse effect has become associated with the concept of *global warming*. Records kept since the nineteenth century clearly show that the amount of carbon dioxide in the atmosphere has increased dramatically, from about 284 ppm (parts per million) in 1830 to about

370 ppm in 2000 (Figure 5.34). (Parts per million is equivalent to mole percent $\times 10^{-4}$.) Scientists believe that our burning of fossil fuels (coal, oil, and natural gas) is responsible for this change. Moreover, temperature measurements made at the surface of the earth during the past 100 years indicate an average temperature increase of between 0.4°C and 0.8°C . Thus, many climate scientists believe that human activities are at least partially responsible for global warming, and hence, they predict drastic changes in climate.



FIGURE 5.34 ▲

Concentrations of carbon dioxide in the atmosphere (average annual values)

Concentrations of carbon dioxide in the atmosphere have been increasing steadily since about 1830. The blue curve is derived from ice core samples (containing air bubbles) obtained from Antarctica. The purple curve is derived from direct measurements of atmospheric carbon dioxide collected since 1958 at Mauna Loa, Hawaii. (Source of blue curve: D. M. Etheridge, L. P. Steele, R. L. Langenfelds, R. J. Francey, J. M. Barnola, and V. I. Morgan. 1998. Historical CO₂ records from the Law Dome DE08, DE08-2, and DSS ice cores. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. Source of purple curve: C. D. Keeling and T. P. Whorf. 2005. Atmospheric CO₂ records from sites in the SIO air sampling network. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A.)

■ See Problems 5.107 and 5.108.

A Checklist for Review

Important Terms

pressure (5.1)
pascal (Pa) (5.1)
barometer (5.1)
manometer (5.1)
millimeters of mercury (mmHg or torr) (5.1)
atmosphere (atm) (5.1)
bar (5.1)
Boyle's law (5.2)
Charles's law (5.2)

Avogadro's law (5.2)
molar gas volume (V_m) (5.2)
standard temperature and pressure (STP) (5.2)
molar gas constant (R) (5.3)
ideal gas law (5.3)
partial pressure (5.5)
Dalton's law of partial pressures (5.5)
mole fraction (5.5)

kinetic-molecular theory of gases (kinetic theory) (5.6)
root-mean-square (rms) molecular speed (5.7)
diffusion (5.7)
effusion (5.7)
Graham's law of effusion (5.7)
van der Waals equation (5.8)

Key Equations

$$PV = \text{constant} \quad (\text{constant } n, T)$$

$$\frac{V}{T} = \text{constant} \quad (\text{constant } n, P)$$

V_n = specific constant
 (depending on T, P ; independent of gas)

$$PV = nRT$$

$$PM_m = dRT$$

$$P = P_A + P_B + P_C + \dots$$

$$\text{Mole fraction of } A = \frac{n_A}{n} = \frac{P_A}{P}$$

$$u = \sqrt{\frac{3RT}{M_m}} = \left(\frac{3RT}{M_m}\right)^{\frac{1}{2}}$$

$$\text{Rate of effusion } \} \quad \frac{1}{\sqrt{M_m}}$$

(same container at constant T, P)

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Summary of Facts and Concepts

The **pressure** of a gas equals the force exerted per unit area of surface. It is measured by a **manometer** in units of **pascals**, **millimeters of mercury**, or **atmospheres**.

Gases at low to moderate pressures and moderate temperatures follow the same simple relationships, or gas laws. Thus, for a given amount of gas at constant temperature, the volume varies inversely with pressure (**Boyle's law**). Also, for a given amount of gas at constant pressure, the volume is directly proportional to the absolute temperature (**Charles's law**). These two laws, together with **Avogadro's law** (equal volumes of any two gases at the same temperature and pressure contain the same number of molecules), can be formulated as one equation, $PV = nRT$ (**ideal gas law**). This equation gives the relationship among P , V , n , and T for a gas. It also relates these quantities for each component in a gas mixture. The total gas pressure, P , equals the sum of the partial pressures of each component (**law of partial pressures**).

The ideal gas law can be explained by the **kinetic-molecular theory**. We define an ideal gas as consisting of molecules with negligible volume that are in constant random motion. In the ideal gas model, there are no intermolecular forces between molecules, and the average kinetic energy of molecules is proportional to the absolute temperature. From kinetic theory, one can show that the **rms molecular speed** equals $\sqrt{3RT/M_m}$. Given this result, one can derive **Graham's law of effusion**: the rate of effusion of gas molecules under identical conditions is inversely proportional to the square root of the molecular mass.

Real gases deviate from the ideal gas law at high pressure and low temperature. From kinetic theory, we expect these deviations, because real molecules do have volume and intermolecular forces do exist. These two factors are partially accounted for in the **van der Waals equation**.

Media Summary

Visit the **student website** at college.hmco.com/pic/ebbing9e to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:



Prepare for Class

■ Video Lessons Mini lectures from chemistry experts

- Properties of Gases
- Boyle's Law
- Charles's Law
- The Combined Gas Law
- Avogadro's Law
- CIA Demonstration: The Potato Cannon
- The Ideal Gas Law
- Applications of the Ideal Gas Law
- Partial Pressure and Dalton's Law
- The Kinetic-Molecular Theory of Gases
- Molecular Speeds
- Effusion and Diffusion
- Comparing Real and Ideal Gases



Improve Your Grade

■ Visualizations Molecular-level animations and lab demonstration videos

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- Boyle's Law: A Molecular-Level View
- Collapsing Can

Access these resources using the passkey available free with new texts or for purchase separately.

Liquid Nitrogen and Balloons

- Charles's Law: A Graphical View
- Charles's Law: A Molecular-Level View
- The Ideal Gas Law: $PV = nRT$
- Visualizing Molecular Motion: Single Molecule
- Visualizing Molecular Motion: Many Molecules
- Kinetic–Molecular Theory/Heat Transfer
- Diffusion of Gases
- Gaseous Ammonia and Hydrochloric Acid
- Effusion of a Gas

■ Tutorials Animated examples and interactive activities

- The Ideal Gas Law

■ Flashcards Key terms and definitions

- Online Flashcards

■ Self-Assessment Questions Additional questions with full worked-out solutions

- 6 Self-Assessment Questions



ACE the Test

Multiple-choice quizzes

3 ACE Practice Tests

Learning Objectives

5.1 Gas Pressure and Its Measurement

- Define *pressure* and its units.
- Convert units of pressure. **Example 5.1**

5.2 Empirical Gas Laws

- Express *Boyle's law* in words and as an equation.
- Use *Boyle's law*. **Example 5.2**
- Express *Charles's law* in words and as an equation.
- Use *Charles's law*. **Example 5.3**
- Express the *combined gas law* as an equation.
- Use the *combined gas law*. **Example 5.4**
- State *Avogadro's law*.
- Define *standard temperature and pressure (STP)*.

5.3 The Ideal Gas Law

- State what makes a gas an *ideal gas*.
- Learn the *ideal gas law* equation.
- Derive the empirical gas laws from the ideal gas law. **Example 5.5**
- Use the ideal gas law. **Example 5.6**
- Calculate gas density. **Example 5.7**
- Determine the molecular mass of a vapor. **Example 5.8**
- Use an equation to calculate gas density.

5.4 Stoichiometry Problems Involving Gas Volumes

- Solving stoichiometry problems involving gas volumes. **Example 5.9**

5.5 Gas Mixture; Law of Partial Pressures

- Learn the equation for *Dalton's law of partial pressures*.
- Define the *mole fraction* of a gas.
- Calculate the partial pressure and mole fractions of a gas in a mixture. **Example 5.10**
- Describe how gases are collected over water and how to determine the *vapor pressure* of water.
- Calculate the amount of gas collected over water. **Example 5.11**

5.6 Kinetic Theory of an Ideal Gas

- List the five postulates of the *kinetic theory*.
- Provide a qualitative description of the gas laws based on the kinetic theory.

5.7 Molecular Speeds; Diffusion and Effusion

- Describe how the *root-mean-square (rms) molecular speed* of gas molecules varies with temperature.
- Describe the molecular-speed distribution of gas molecules at different temperatures.

- Calculate the rms speed of gas molecules.

Example 5.12

- Define *effusion* and *diffusion*.

- Describe how individual gas molecules move undergoing diffusion.

- Calculate the ratio of effusion rates of gases.

Example 5.13

5.8 Real Gases

- Explain how and why a *real gas* is different from an ideal gas.

- Use the van der Waals equation. **Example 5.14**

Self-Assessment and Review Questions

5.1 Define *pressure*. From the definition, obtain the SI unit of pressure in terms of SI base units.

5.2 For what purpose is a manometer used? How does it work?

5.3 What variables determine the height of the liquid in a manometer?

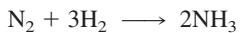
5.4 Starting with Boyle's law (stated as an equation), obtain an equation for the final volume occupied by a gas from the initial volume when the pressure is changed at constant temperature.

5.5 The volume occupied by a gas depends linearly on degrees Celsius at constant pressure, but it is not directly proportional to degrees Celsius. However, it is directly proportional to kelvins. What is the difference between a linear relationship and a direct proportion?

5.6 Explain how you would set up an absolute temperature scale based on the Fahrenheit scale, knowing that absolute zero is -273.15°C .

5.7 Starting with Charles's law (stated as an equation), obtain an equation for the final volume of a gas from its initial volume when the temperature is changed at constant pressure.

5.8 State Avogadro's law in words. How does this law explain the law of combining volumes? Use the gas reaction



as an example in your explanation.

5.9 What are the standard conditions for comparing gas volumes?

5.10 What does the term *molar gas volume* mean? What is the molar gas volume (in liters) at STP for an ideal gas?

5.11 Starting from Boyles's, Charles's, and Avogadro's laws, obtain the ideal gas law, $PV = nRT$.

5.12 What variables are needed to describe a gas that obeys the ideal gas law? What are the SI units for each variable?

5.13 What is the value of R in units of $\text{L} \cdot \text{mmHg}/(\text{K} \cdot \text{mol})$?

5.14 The ideal gas law relates four variables. An empirical gas law relates two variables, assuming the other two are constant. How many empirical gas laws can be obtained? Give statements of each.

5.15 Give the postulates of kinetic theory and state any evidence that supports them.

5.16 Explain Boyle's law in terms of the kinetic theory.

5.17 What is the origin of gas pressure, according to kinetic theory?

5.18 How does the rms molecular speed depend on absolute temperature? on molar volume?

5.19 Explain why a gas appears to diffuse more slowly than average molecular speeds might suggest.

5.20 What is effusion? Why does a gas whose molecules have smaller mass effuse faster than one whose molecules have larger mass?

5.21 Under what conditions does the behavior of a real gas begin to differ significantly from the ideal gas law?

5.22 What is the physical meaning of the a and b constants in the van der Waals equation?

5.23 Which of the following is *not* part of the kinetic molecular theory?

- The greater the volume occupied by a given amount of gas, the higher the intermolecular forces.
- The average kinetic energy is proportional to the absolute temperature.
- Gas particles are in constant motion.
- Total kinetic energy is conserved during collision.
- Gas molecules have no volume.

5.24 A sample of nitrogen gas is placed into a container at 200 K. If the temperature of the container is reduced by 100°C and the measured pressure decreases by 50%, how does the volume of the container change?

- The container volume increases by less than 50%.
- The container volume increases by more than 50%.
- The container volume doesn't change.
- The container volume increases by 50%.
- The container volume decreases by 50%.

5.25 At standard temperature and pressure, a 1.00-mol sample of argon gas is vented into a 22.4-L rigid box that already contains 1.00 mol of nitrogen gas. We would expect the argon gas to

- decrease the total gas pressure in the box by 50%.
- occupy the entire 22.4-L volume of the box.
- increase the total gas pressure in the box by less than 50%.
- spread out into the box, but the actual volume occupied by the gas cannot be known without pressure information.
- occupy only a volume of 11.2 L of the box, since there is already 1.0 mol of nitrogen present in the container.

5.26 A 1-liter container is filled with 2.0 mol Ar, 2.0 mol H₂, and 4.0 mol Kr. Which of the following statements about these gases is *false*?

- The Kr is the densest of the three gases.
- The mole fraction of Ar in the flask is 0.25.
- The total pressure in the flask is four times the pressure of the Ar.
- The Ar atoms hit the walls of the flask with the greatest force of the three gases.
- H₂ has the highest rms velocity of the three gases.

Concept Explorations

5.27 Gas Laws and Kinetic Theory of Gases I

Shown below are two identical containers labeled A and B. Container A contains a molecule of an ideal gas, and container B contains two molecules of an ideal gas. Both containers are at the same temperature.

- a. How do the pressures in the two containers compare? Be sure to explain your answer.

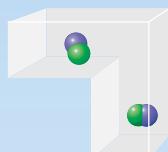


A

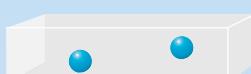


B

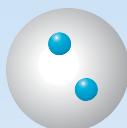
- b. Shown below are four different containers (C, D, E, and F), each with the same volume and at the same temperature. How do the pressures of the gases in the containers compare?



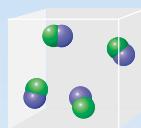
C



D

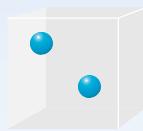


E



F

- c. Container H below has twice the volume of container G. How will the pressure in the containers compare? Explain your reasoning.



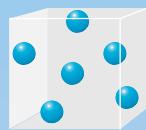
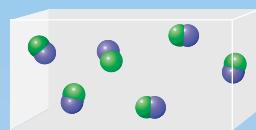
G



H

- d. How will the pressure of containers G and H compare if you add two more gas molecules to container H?
e. Consider containers J and L below. Container L has twice the volume of container J. Container J is at a temperature of

100 K, and container L is at 200 K. How does the pressure in container J compare with that in container L? Include an explanation as part of your answer.

T = 100 K
JT = 200 K
L

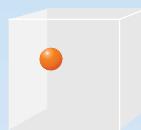
5.28 Gas Laws and Kinetic Theory of Gases II

Consider the box below that contains a single atom of an ideal gas.

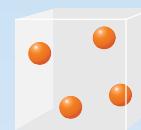
- a. Assuming that this gas atom is moving, describe how it creates pressure inside the container.



- b. Now consider the two containers below, each at the same temperature. If we were to measure the gas pressure in each container, how would they compare? Explain your answer.



A

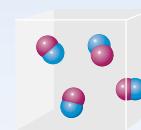


B

- c. Consider the two containers below, labeled C and D, one with an ideal gas atom and one with ideal gas molecules, each at the same temperature. The gas molecule has more mass than the gas atom. How do the pressures of the two containers compare? Why?



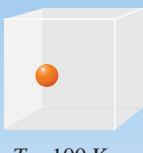
C



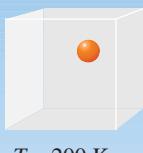
D

- d. For the containers C and D above, which would have the higher root-mean-square (rms) molecular speed? How does the difference in rms speeds support or contradict the answer you obtained above when you compared the pressures?

- e. Consider containers E and F below. How do the pressures in these containers compare? Be sure to explain your answer.

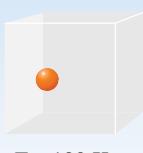


E

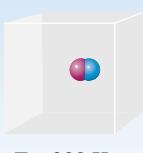


F

- f. Consider containers G and H below, one with a gas atom and one with a gas molecule. As before, the gas molecule has more mass than the gas atom. Explain how the pressures in these containers compare.



G

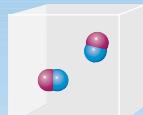


H

- g. Now think about the containers below, I and J. How do the pressures in these containers compare? Be sure to justify your answer.



I

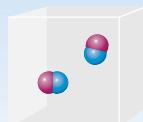


J

- h. Finally, how do the pressures in containers K and L compare?



K



L

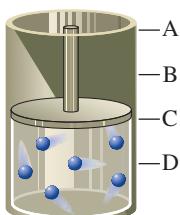
Conceptual Problems

- 5.29** Using the concepts developed in this chapter, explain the following observations.

- Automobile tires are flatter on cold days.
- You are not supposed to dispose of aerosol cans in a fire.
- The lid of a water bottle pops off when the bottle sits in the sun.
- A balloon pops when you squeeze it.

- 5.30** You have three identical flasks, each containing equal amounts of N₂, O₂, and He. The volume of the N₂ flask is doubled, the O₂ flask volume is halved, and the He flask volume is reduced to one-third of the original volume. Rank the flasks from highest to lowest pressure both before and after the volume is changed and indicate by what factor the pressure has changed.

- 5.31** Consider the following gas container equipped with a movable piston.



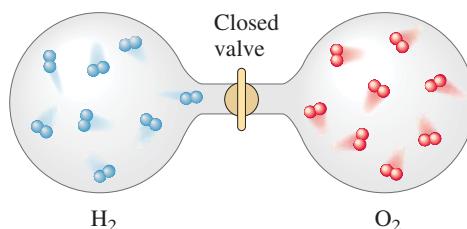
- By what factor (increase by 1, decrease by 1.5, etc.) would you change the pressure if you wanted the volume to change from volume C to volume D?
- If the piston were moved from volume C to volume A, by what factor would the pressure change?
- By what factor would you change the temperature in order to change from volume C to volume B?

- d.** If you increased the number of moles of gas in the container by a factor of 2, by what factors would the pressure and the volume change?

- 5.32** A 3.00-L flask containing 2.0 mol of O₂ and 1.0 mol of N₂ is in a room that is at 22.0°C.

- How much (what fraction) of the total pressure in the flask is due to the N₂?
- The flask is cooled and the pressure drops. What happens, if anything, to the mole fraction of the O₂ at the lower temperature?
- 1.0 L of liquid water is introduced into the flask containing both gases. The pressure is then measured about 45 minutes later. Would you expect the measured pressure to be higher or lower?
- Given the information in this problem and the conditions in part c, would it be possible to calculate the pressure in the flask after the introduction of the water? If it is not possible with the given information, what further information would you need to accomplish this task?

- 5.33** Consider the following setup, which shows identical containers connected by a tube with a valve that is presently closed. The container on the left has 1.0 mol of H₂ gas; the container on the right has 1.0 mol of O₂.



Note: Acceptable answers to some of these questions might be “both” or “neither one.”

- a. Which container has the greatest density of gas?
 - b. Which container has molecules that are moving at a faster average molecular speed?
 - c. Which container has more molecules?
 - d. If the valve is opened, will the pressure in each of the containers change? If it does, how will it change (increase, decrease, or no change)?
 - e. 2.0 mol of Ar is added to the system with the valve open. What fraction of the total pressure will be due to the H₂?
- 5.34** Two identical He-filled balloons, each with a volume of 20 L, are allowed to rise into the atmosphere. One rises to an altitude of 3000 m while the other rises to 6000 m.
- a. Assuming that the balloons are at the same temperature, which balloon has the greater volume?

Practice Problems

Note: In these problems, the final zeros given in temperatures and pressures (for example, 20°C, 760 mmHg) are significant figures.

Units of Pressure

- 5.37** A gas in a closed-tube manometer (Figure 5.4) has a measured pressure of 0.047 atm. Calculate the pressure in mmHg.
- 5.38** The barometric pressure measured outside an airplane at 9 km (30,000 ft) was 259 mmHg. Calculate the pressure in kPa.

Empirical Gas Laws

- 5.39** Suppose you had a 3.15-L sample of neon gas at 21°C and a pressure of 0.951 atm. What would be the volume of this gas if the pressure were increased to 1.292 atm while the temperature remained constant?
- 5.40** You fill a balloon with helium gas to a volume of 2.68 L at 23°C and 789 mmHg. Now you release the balloon. What would be the volume of helium if its pressure changed to 632 mmHg but the temperature were unchanged?

- 5.41** You have a cylinder of argon gas at 19.8 atm pressure at 19°C. The volume of argon in the cylinder is 50.0 L. What would be the volume of this gas if you allowed it to expand to the pressure of the surrounding air (0.974 atm)? Assume the temperature remains constant.

- 5.42** A diving bell is a container open at the bottom. As the bell descends, the water level inside changes so that the pressure inside equals the pressure outside. Initially, the volume of air is 8.58 m³ at 1.020 atm and 20°C. What is the volume at 1.212 atm and 20°C?

- 5.43** A McLeod gauge measures low gas pressures by compressing a known volume of the gas at constant temperature. If 315 cm³ of gas is compressed to a volume of 0.0457 cm³ under a pressure of 2.51 kPa, what was the original gas pressure?

- 5.44** If 456 dm³ of krypton at 101 kPa and 21°C is compressed into a 27.0-dm³ tank at the same temperature, what is the pressure of krypton in the tank?

- 5.45** A sample of nitrogen gas at 18°C and 760 mmHg has a volume of 3.92 mL. What is the volume at 0°C and 1 atm of pressure?

- b. What information would you need in order to calculate the volume of each of the balloons at their respective heights?

- 5.35** You have a balloon that contains O₂. What could you do to the balloon in order to double the volume? Be specific in your answers; for example, you could increase the number of moles of O₂ by a factor of 2.
- 5.36** Three 25.0-L flasks are placed next to each other on a shelf in a chemistry stockroom. The first flask contains He at a pressure of 1.0 atm, the second contains Xe at 1.50 atm, and the third contains F₂ and has a label that says 2.0 mol F₂. Consider the following questions about these flasks.

- a. Which flask has the greatest number of moles of gas?
- b. If you wanted each of the flasks to be at the same pressure as the He flask, what general things could you do to the other two containers to make this happen?

- 5.46** A mole of gas at 0°C and 760 mmHg occupies 22.41 L. What is the volume at 20°C and 760 mmHg?

- 5.47** Helium gas, He, at 22°C and 1.00 atm occupied a vessel whose volume was 2.54 L. What volume would this gas occupy if it were cooled to liquid-nitrogen temperature (-197°C)?

- 5.48** An experiment called for 4.83 L of sulfur dioxide, SO₂, at 0°C and 1.00 atm. What would be the volume of this gas at 25°C and 1.00 atm?

- 5.49** A vessel containing 39.5 cm³ of helium gas at 25°C and 106 kPa was inverted and placed in cold ethanol. As the gas contracted, ethanol was forced into the vessel to maintain the same pressure of helium. If this required 7.7 cm³ of ethanol, what was the final temperature of the helium?

- 5.50** A sample of 62.3 cm³ of argon gas at 18°C was contained at a pressure of 155 kPa in a J-shaped tube with mercury, as in Figure 5.5. Later the temperature changed. When the mercury level was adjusted to give the same pressure of argon, the gas volume changed to 61.2 cm³. What was the final temperature of the argon?

- 5.51** A bacterial culture isolated from sewage produced 35.5 mL of methane, CH₄, at 31°C and 753 mmHg. What is the volume of this methane at standard temperature and pressure (0°C, 760 mmHg)?

- 5.52** Pantothenic acid is a B vitamin. Using the Dumas method, you find that a sample weighing 71.6 mg gives 3.84 mL of nitrogen gas at 23°C and 785 mmHg. What is the volume of nitrogen at STP?

- 5.53** In the presence of a platinum catalyst, ammonia, NH₃, burns in oxygen, O₂, to give nitric oxide, NO, and water vapor. How many volumes of nitric oxide are obtained from one volume of ammonia, assuming each gas is at the same temperature and pressure?

- 5.54** Methanol, CH₃OH, can be produced in industrial plants by reacting carbon dioxide with hydrogen in the presence of a catalyst. Water is the other product. How many volumes of hydrogen are required for each volume of carbon dioxide when each gas is at the same temperature and pressure?

Ideal Gas Law

5.55 Starting from the ideal gas law, prove that the volume of a mole of gas is inversely proportional to the pressure at constant temperature (Boyle's law).

5.56 Starting from the ideal gas law, prove that the volume of a mole of gas is directly proportional to the absolute temperature at constant pressure (Charles's law).

5.57 A cylinder of oxygen gas contains 91.3 g O₂. If the volume of the cylinder is 8.58 L, what is the pressure of the O₂ if the gas temperature is 21°C?

5.58 In an experiment, you fill a heavy-walled 5.00-L flask with methane gas, CH₄. If the flask contains 7.13 g of methane at 19°C, what is the gas pressure?

5.59 An experiment calls for 3.50 mol of chlorine, Cl₂. What volume will this be if the gas volume is measured at 34°C and 4.00 atm?

5.60 According to your calculations, a reaction should yield 5.67 g of oxygen, O₂. What do you expect the volume to be at 23°C and 0.985 atm?

5.61 The maximum safe pressure that a certain 4.00-L vessel can hold is 3.50 atm. If the vessel contains 0.410 mol of gas, what is the maximum temperature (in degrees Celsius) to which this vessel can be subjected?

5.62 A 2.50-L flask was used to collect a 5.65-g sample of propane gas, C₃H₈. After the sample was collected, the gas pressure was found to be 741 mmHg. What was the temperature of the propane in the flask?

5.63 What is the density of ammonia gas, NH₃, at 31°C and 751 mmHg? Obtain the density in grams per liter.

5.64 Calculate the density of hydrogen sulfide gas, H₂S, at 56°C and 967 mmHg. Obtain the density in grams per liter.

5.65 Butane, C₄H₁₀, is an easily liquefied gaseous fuel. Calculate the density of butane gas at 0.897 atm and 24°C. Give the answer in grams per liter.

5.66 Chloroform, CHCl₃, is a volatile (easily vaporized) liquid solvent. Calculate the density of chloroform vapor at 98°C and 797 mmHg. Give the answer in grams per liter.

5.67 A chemist vaporized a liquid compound and determined its density. If the density of the vapor at 90°C and 753 mmHg is 1.585 g/L, what is the molecular mass of the compound?

5.68 You vaporize a liquid substance at 100°C and 755 mmHg. The volume of 0.548 g of vapor is 237 mL. What is the molecular mass of the substance?

5.69 A 2.56-g sample of a colorless liquid was vaporized in a 250-mL flask at 121°C and 786 mmHg. What is the molecular mass of this substance?

5.70 A 2.30-g sample of white solid was vaporized in a 345-mL vessel. If the vapor has a pressure of 985 mmHg at 148°C, what is the molecular mass of the solid?

5.71 Ammonium chloride, NH₄Cl, is a white solid. When heated to 325°C, it gives a vapor that is a mixture of ammonia and hydrogen chloride.



Suppose someone contends that the vapor consists of NH₄Cl molecules rather than a mixture of NH₃ and HCl. Could you decide between these alternative views on the basis of gas-density measurements? Explain.

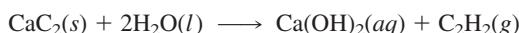
5.72 Phosphorus pentachloride, PCl₅, is a white solid that sublimes (vaporizes without melting) at about 100°C. At higher temperatures, the PCl₅ vapor decomposes to give phosphorus trichloride, PCl₃, and chlorine, Cl₂.



How could gas-density measurements help to establish that PCl₅ vapor is decomposing?

Stoichiometry with Gas Volumes

5.73 Calcium carbide reacts with water to produce acetylene gas, C₂H₂.



Calculate the volume (in liters) of acetylene produced at 26°C and 684 mmHg from 0.050 mol CaC₂ and excess H₂O.

5.74 Magnesium metal reacts with hydrochloric acid to produce hydrogen gas, H₂.



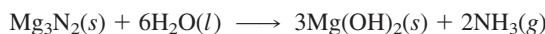
Calculate the volume (in liters) of hydrogen produced at 33°C and 665 mmHg from 0.0840 mol Mg and excess HCl.

5.75 Lithium hydroxide, LiOH, is used in spacecraft to recondition the air by absorbing the carbon dioxide exhaled by astronauts. The reaction is



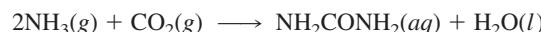
What volume of carbon dioxide gas at 218°C and 781 mmHg could be absorbed by 327 g of lithium hydroxide?

5.76 Magnesium burns in air to produce magnesium oxide, MgO, and magnesium nitride, Mg₃N₂. Magnesium nitride reacts with water to give ammonia.



What volume of ammonia gas at 24°C and 753 mmHg will be produced from 4.56 g of magnesium nitride?

5.77 Urea, NH₂CONH₂, is a nitrogen fertilizer that is manufactured from ammonia and carbon dioxide.



What volume of ammonia at 25°C and 3.00 atm is needed to produce 908 g (2 lb) of urea?

5.78 Nitric acid is produced from nitric oxide, NO, which in turn is prepared from ammonia by the Ostwald process:



What volume of oxygen at 35°C and 2.15 atm is needed to produce 50.0 g of nitric oxide?

5.79 Ammonium sulfate is used as a nitrogen and sulfur fertilizer. It is produced by reacting ammonia with sulfuric acid. Write the balanced equation for the reaction of gaseous ammonia with sulfuric acid solution. What volume (in liters) of ammonia at 15°C and 1.15 atm is required to produce 150.0 g of ammonium sulfate?

5.80 Sodium hydrogen carbonate is also known as baking soda. When this compound is heated, it decomposes to sodium carbonate, carbon dioxide, and water vapor. Write the balanced equation for this reaction. What volume (in liters) of carbon dioxide gas at 77°C and 756 mmHg will be produced from 26.8 g of sodium hydrogen carbonate?

Gas Mixtures

5.81 Calculate the total pressure (in atm) of a mixture of 0.0200 mol of helium, He, and 0.0100 mol of hydrogen, H₂, in a 2.50-L flask at 10°C. Assume ideal gas behavior.

5.82 Calculate the total pressure (in atm) of a mixture of 0.0300 mol of helium, He, and 0.0200 mol of oxygen, O₂, in a 4.00-L flask at 20°C. Assume ideal gas behavior.

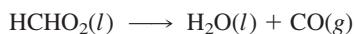
5.83 A 200.0-mL flask contains 1.03 mg O₂ and 0.56 mg He at 15°C. Calculate the partial pressures of oxygen and of helium in the flask. What is the total pressure?

5.84 The atmosphere in a sealed diving bell contained oxygen and helium. If the gas mixture has 0.200 atm of oxygen and a total pressure of 3.00 atm, calculate the mass of helium in 10.0 L of the gas mixture at 20°C.

5.85 The gas from a certain volcano had the following composition in mole percent (that is, mole fraction $\times 100$): 65.0% CO₂, 25.0% H₂, 5.4% HCl, 2.8% HF, 1.7% SO₂, and 0.1% H₂S. What would be the partial pressure of each of these gases if the total pressure of volcanic gas were 760 mmHg?

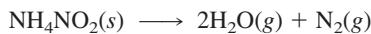
5.86 In a series of experiments, the U.S. Navy developed an undersea habitat. In one experiment, the mole percent composition of the atmosphere in the undersea habitat was 79.0% He, 17.0% N₂, and 4.0% O₂. What will the partial pressure of each gas be when the habitat is 58.8 m below sea level, where the pressure is 6.91 atm?

5.87 Formic acid, HCHO₂, is a convenient source of small quantities of carbon monoxide. When warmed with sulfuric acid, formic acid decomposes to give CO gas.



If 3.85 L of carbon monoxide was collected over water at 25°C and 689 mmHg, how many grams of formic acid were consumed?

5.88 An aqueous solution of ammonium nitrite, NH₄NO₂, decomposes when heated to give off nitrogen, N₂.



This reaction may be used to prepare pure nitrogen. How many grams of ammonium nitrite must have reacted if 3.75 dm³ of nitrogen gas was collected over water at 26°C and 97.8 kPa?

Molecular Speeds; Effusion

5.89 Calculate the rms speeds of N₂ molecules at 25°C and at 125°C. Sketch approximate curves of the molecular speed distributions of N₂ at 25°C and at 125°C.

5.90 Calculate the rms speed of Br₂ molecules at 23°C and 1.00 atm. What is the rms speed of Br₂ at 23°C and 1.50 atm?

5.91 Uranium hexafluoride, UF₆, is a white solid that sublimes (vaporizes without melting) at 57°C under normal atmospheric

pressure. The compound is used to separate uranium isotopes by effusion. What is the rms speed (in m/s) of a uranium hexafluoride molecule at 57°C?

5.92 For a spacecraft or a molecule to leave the moon, it must reach the escape velocity (speed) of the moon, which is 2.37 km/s. The average daytime temperature of the moon's surface is 365 K. What is the rms speed (in m/s) of a hydrogen molecule at this temperature? How does this compare with the escape velocity?

5.93 At what temperature would CO₂ molecules have an rms speed equal to that of H₂ molecules at 25°C?

5.94 At what temperature does the rms speed of O₂ molecules equal 400. m/s?

5.95 What is the ratio of rates of effusion of N₂ and O₂ under the same conditions?

5.96 Obtain the ratio of rates of effusion of H₂ and H₂Se under the same conditions.

5.97 If 0.10 mol of I₂ vapor can effuse from an opening in a heated vessel in 39 s, how long will it take 0.10 mol H₂ to effuse under the same conditions?

5.98 If it takes 10.6 hours for 1.00 L of nitrogen, N₂, to effuse through the pores in a balloon, how long would it take for 1.00 L of helium, He, to effuse under the same conditions?

5.99 If 4.83 mL of an unknown gas effuses through a hole in a plate in the same time it takes 9.23 mL of argon, Ar, to effuse through the same hole under the same conditions, what is the molecular mass of the unknown gas?

5.100 A given volume of nitrogen, N₂, required 68.3 s to effuse from a hole in a chamber. Under the same conditions, another gas required 85.6 s for the same volume to effuse. What is the molecular mass this gas?

van der Waals Equation

5.101 Calculate the pressure of ethanol vapor, C₂H₅OH(g), at 82.0°C if 1.000 mol C₂H₅OH(g) occupies 30.00 L. Use the van der Waals equation (see Table 5.7 for data). Compare with the result from the ideal gas law.

5.102 Calculate the pressure of water vapor at 120.0°C if 1.000 mol of water vapor occupies 32.50 L. Use the van der Waals equation (see Table 5.7 for data). Compare with the result from the ideal gas law.

5.103 Calculate the molar volume of ethane at 1.00 atm and 0°C and at 10.0 atm and 0°C, using the van der Waals equation. The van der Waals constants are given in Table 5.7. To simplify, note that the term n^2a/V^2 is small compared with P . Hence, it may be approximated with negligible error by substituting nRT/P from the ideal gas law for V in this term. Then the van der Waals equation can be solved for the volume. Compare the results with the values predicted by the ideal gas law.

5.104 Calculate the molar volume of oxygen at 1.00 atm and 0°C and at 10.0 atm and 0°C, using the van der Waals equation. The van der Waals constants are given in Table 5.7. (See the note on solving the equation given in Problem 5.103.) Compare the results with the values predicted by the ideal gas law. Also compare with the values obtained from Table 5.3.

General Problems

5.105 A glass tumbler containing 243 cm^3 of air at $1.00 \times 10^2\text{ kPa}$ (the barometric pressure) and 20°C is turned upside down and immersed in a body of water to a depth of 20.5 m. The air in the glass is compressed by the weight of water above it. Calculate the volume of air in the glass, assuming the temperature and barometric pressure have not changed.

5.106 The density of air at 20°C and 1.00 atm is 1.205 g/L . If this air were compressed at the same temperature to equal the pressure at 40.0 m below sea level, what would be its density? Assume the barometric pressure is constant at 1.00 atm . The density of seawater is 1.025 g/cm^3 .

5.107 A flask contains 201 mL of argon at 21°C and 738 mmHg . What is the volume of gas, corrected to STP?

5.108 A steel bottle contains 12.0 L of a gas at 11.0 atm and 20°C . What is the volume of gas at STP?

5.109 A balloon containing 5.0 dm^3 of gas at 14°C and 100.0 kPa rises to an altitude of 2000. m, where the temperature is 20°C . The pressure of gas in the balloon is now 79.0 kPa . What is the volume of gas in the balloon?

5.110 A volume of air is taken from the earth's surface, at 15°C and 1.00 atm , to the stratosphere, where the temperature is -21°C and the pressure is $1.00 \times 10^{-3}\text{ atm}$. By what factor is the volume increased?

5.111 A radioactive metal atom decays (goes to another kind of atom) by emitting an alpha particle (He^{2+} ion). The alpha particles are collected as helium gas. A sample of helium with a volume of 12.05 mL was obtained at 765 mmHg and 23°C . How many atoms decayed during the period of the experiment?

5.112 The combustion method used to analyze for carbon and hydrogen can be adapted to give percentage N by collecting the nitrogen from combustion of the compound as N_2 . A sample of a compound weighing 8.75 mg gave 1.59 mL N_2 at 25°C and 749 mmHg . What is the percentage N in the compound?

5.113 Dry air at STP has a density of 1.2929 g/L . Calculate the average molecular weight of air from the density.

5.114 A hydrocarbon gas has a density of 1.22 g/L at 20°C and 1.00 atm . An analysis gives 80.0% C and 20.0% H. What is the molecular formula?

5.115 A person exhales about $5.8 \times 10^2\text{ L}$ of carbon dioxide per day (at STP). The carbon dioxide exhaled by an astronaut is absorbed from the air of a space capsule by reaction with lithium hydroxide, LiOH .



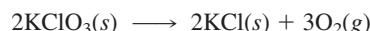
How many grams of lithium hydroxide are required per astronaut per day?

5.116 Pyruvic acid, $\text{HC}_3\text{H}_3\text{O}_3$, is involved in cell metabolism. It can be assayed for (that is, the amount of it determined) by using a yeast enzyme. The enzyme makes the following reaction go to completion:



If a sample containing pyruvic acid gives 21.2 mL of carbon dioxide gas, CO_2 , at 349 mmHg and 30°C , how many grams of pyruvic acid are there in the sample?

5.117 Liquid oxygen was first prepared by heating potassium chlorate, KClO_3 , in a closed vessel to obtain oxygen at high pressure. The oxygen was cooled until it liquefied.



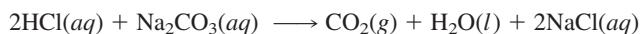
If $170.\text{ g}$ of potassium chlorate reacts in a 2.50-L vessel, which was initially evacuated, what pressure of oxygen will be attained when the temperature is finally cooled to 25°C ? Use the preceding chemical equation and ignore the volume of solid product.

5.118 Raoul Pictet, the Swiss physicist who first liquefied oxygen, attempted to liquefy hydrogen. He heated potassium formate, KCHO_2 , with KOH in a closed 2.50-L vessel.



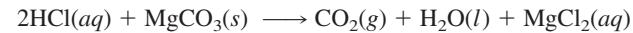
If 50.0 g of potassium formate reacts in a 2.50-L vessel, which was initially evacuated, what pressure of hydrogen will be attained when the temperature is finally cooled to 25°C ? Use the preceding chemical equation and ignore the volume of solid product.

5.119 A 24.9-mL volume of hydrochloric acid reacts completely with 55.0 mL of aqueous Na_2CO_3 . The reaction is



The volume of CO_2 formed is 141 mL at 27°C and 727 mmHg . What is the molarity of the HCl solution?

5.120 An 18.6-mL volume of hydrochloric acid reacts completely with a solid sample of MgCO_3 . The reaction is



The volume of CO_2 formed is 159 mL at 23°C and 731 mmHg . What is the molarity of the HCl solution?

5.121 A 41.41-mL sample of a 0.1250 M acid reacts with an excess of Na_2CO_3 to form 150.0 mL CO_2 at 646 mmHg and 27°C . If the acid is either HCl or H_2SO_4 , which is it?

5.122 A 48.90-mL sample of a 0.2040 M acid reacts with an excess of Na_2CO_3 to form 125.0 mL CO_2 at 722 mmHg and 17°C . If the acid is either HCl or H_2SO_4 , which is it?

5.123 If the rms speed of NH_3 molecules is found to be 0.605 km/s , what is the temperature (in degrees Celsius)?

5.124 If the rms speed of He atoms in the exosphere (highest region of the atmosphere) is $3.53 \times 10^3\text{ m/s}$, what is the temperature (in kelvins)?

5.125 Calculate the ratio of rates of effusion of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$, where ^{235}U and ^{238}U are isotopes of uranium. The atomic masses are ^{235}U , 235.04 amu ; ^{238}U , 238.05 amu ; ^{19}F (the only naturally occurring isotope), 18.998 amu . Carry five significant figures in the calculation.

5.126 Hydrogen has two stable isotopes, ^1H and ^2H , with atomic masses of 1.0078 amu and 2.0141 amu , respectively. Ordinary hydrogen gas, H_2 , is a mixture consisting mostly of $^1\text{H}_2$ and $^1\text{H}^2\text{H}$. Calculate the ratio of rates of effusion of $^1\text{H}_2$ and $^1\text{H}^2\text{H}$ under the same conditions.

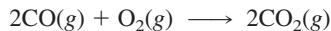
- 5.127** A 1.000-g sample of an unknown gas at 0°C gives the following data:

P (atm)	V (L)
0.2500	3.1908
0.5000	1.5928
0.7500	1.0601
1.0000	0.7930

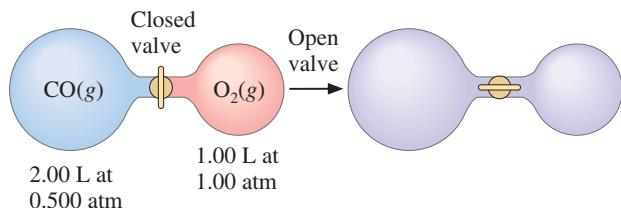
Use these data to calculate the value of the molar mass at each of the given pressures from the ideal gas law (we will call this the “apparent molar mass” at this pressure). Plot the apparent molar masses against pressure and extrapolate to find the molar mass at zero pressure. Because the ideal gas law is most accurate at low pressures, this extrapolation will give an accurate value for the molar mass. What is the accurate molar mass?

- 5.128** Plot the data given in Table 5.3 for oxygen at 0°C to obtain an accurate molar mass for O₂. To do this, calculate a value of the molar mass at each of the given pressures from the ideal gas law (we will call this the “apparent molar mass” at this pressure). On a graph show the apparent molar mass versus the pressure and extrapolate to find the molar mass at zero pressure. Because the ideal gas law is most accurate at low pressures, this extrapolation will give an accurate value for the molar mass. What is the accurate molar mass?

- 5.129** Carbon monoxide, CO, and oxygen, O₂, react according to



Assuming that the reaction takes place and goes to completion, determine what substances remain and what their partial pressures are after the valve is opened in the apparatus represented in the accompanying figure. Also assume that the temperature is fixed at 300 K.



- 5.130** Suppose the apparatus shown in the figure accompanying Problem 5.129 contains H₂ at 0.500 atm in the left vessel separated from O₂ at 1.00 atm in the other vessel. The valve is then opened. If H₂ and O₂ react to give H₂O when the temperature is fixed at 300 K, what substances remain and what are their partial pressures after reaction?

5.131 How does nitrogen monoxide, NO, function in the body to regulate blood pressure?

5.132 How does nitroglycerine alleviate the pain of an angina attack?

5.133 What famous chemist first predicted the greenhouse effect of carbon dioxide gas?

5.134 Explain the greenhouse effect.

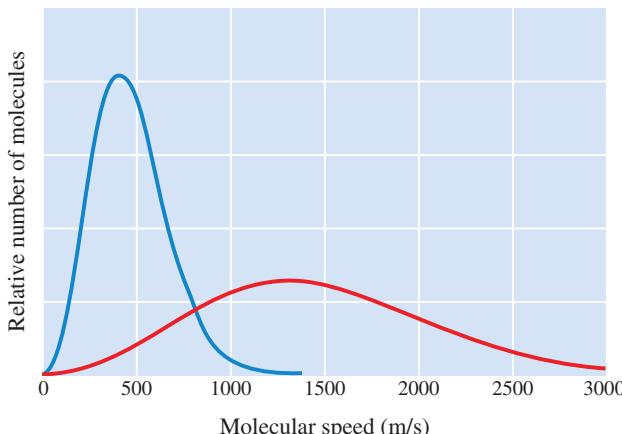
Strategy Problems

- 5.135** A 24.6-mL volume of a hydrochloric acid solution reacts completely with a solid sample of magnesium carbonate, producing 183 mL of CO₂ that is collected over water at 24.0°C and 738 torr total pressure. The reaction is



What is the molarity of the HCl solution?

- 5.136** The graph below represents the distribution of molecular speeds of hydrogen and neon at 200 K.



- Match each curve to the appropriate gas.
- Calculate the rms speed (in m/s) for each of the gases at 200 K.
- Which of the gases would you expect to have the greater effusion rate at 200 K? Justify your answer.
- Calculate the temperature at which the rms speed of the hydrogen gas would equal the rms speed of the neon at 200 K.

- 5.137** A submersible balloon is sent to the bottom of the ocean. On shore, the balloon had a capacity of 162 L when it was filled at 21.0°C and standard pressure. When it reaches the ocean floor, which is at 5.92°C, the balloon occupies 18.8 L of space. What is the pressure on the ocean floor?

- 5.138** A given mass of gas occupies a volume of 435 mL at 25°C and 740 mmHg. What will be the new volume at STP?

- 5.139** A container is filled with 16.0 g of O₂ and 14.0 g of N₂.

- What is the volume of the container at STP?
- What is the partial pressure of the O₂ gas?
- What are the mole fraction and the mole percent of the N₂ in the mixture?

- 5.140** Sulfur-containing compounds give skunks their potent smell. One of the principal smelly compounds in skunk spray is (E)-2-butene-1-thiol, C₄H₇S.

- What is the root-mean-square (rms) molecular speed of a gas molecule of this compound at 25°C?

b. Using the value from part a, calculate how long it would take a molecule of C_4H_7S to reach your nose if you were 150 m from the skunk.

c. Does the calculation that you performed in part b provide an accurate estimate for the length of time it would take for the molecule to travel 150 m, or is there something that was overlooked in performing the calculation?

5.141 Sulfur hexafluoride, SF_6 , is an extremely dense gas. How does its density compare with the density of air? Use a molar mass for air of 29.0 g/mol.

5.142 A rigid 1.0-L container at 75°C is fitted with a gas pressure gauge. A 1.0-mol sample of ideal gas is introduced into the container.

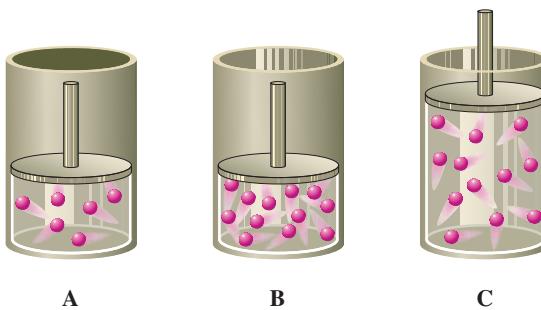
- What would the pressure gauge in the container be reading in mmHg?
- Describe the interactions in the container that are causing the pressure.
- Say the temperature in the container were increased to 150°C. Describe the effect this would have on the pressure, and, in terms of kinetic theory, explain why this change occurred.

5.143 The reaction $8H_2(g) + S_8(l) \longrightarrow 8H_2S(g)$ is run at 125°C and a constant pressure of 12.0 atm. Assuming complete reaction,

what mass of S_8 would be required to produce 6.00×10^2 mL of H_2S gas under these conditions?

5.144 Shown below are three containers of an ideal gas (A, B, and C), each equipped with a movable piston (assume that atmospheric pressure is 1.0 atm).

- How do the pressures in these containers compare?
- Are all the gases at the same temperature? If not, compare the temperatures.
- If you cooled each of the containers in an ice-water bath to 0.0°C, describe how the volumes and pressures of the gases in these containers would compare.



Cumulative-Skills Problems

5.145 A sample of natural gas is 85.2% methane, CH_4 , and 14.8% ethane, C_2H_6 , by mass. What is density of this mixture at 18°C and 771 mmHg?

5.146 A sample of a breathing mixture for divers contained 34.3% helium, He; 51.7% nitrogen, N_2 ; and 14.0% oxygen, O_2 (by mass). What is the density of this mixture at 22°C and 755 mmHg?

5.147 A sample of sodium peroxide, Na_2O_2 , was reacted with an excess of water.



All of the sodium peroxide reacted, and the oxygen was collected over water at 21°C. The barometric pressure was 771 mmHg. The apparatus was similar to that shown in Figure 5.20. However, the level of water inside the tube was 25.0 cm above the level of water outside the tube. If the volume of gas in the tube is 31.0 mL, how many grams of sodium peroxide were in the sample?

5.148 A sample of zinc metal was reacted with an excess of hydrochloric acid.



All of the zinc reacted, and the hydrogen gas was collected over water at 17°C; the barometric pressure was 751 mmHg. The apparatus was similar to that shown in Figure 5.20, but the level of water inside the tube was 31.0 cm above the level outside the tube. If the volume of gas in the tube is 22.1 mL, how many grams of zinc were there in the sample?

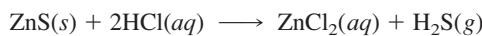
5.149 A mixture contained calcium carbonate, $CaCO_3$, and magnesium carbonate, $MgCO_3$. A sample of this mixture

weighing 7.85 g was reacted with excess hydrochloric acid. The reactions are



If the sample reacted completely and produced 1.94 L of carbon dioxide, CO_2 , at 25°C and 785 mmHg, what were the percentages of $CaCO_3$ and $MgCO_3$ in the mixture?

5.150 A mixture contained zinc sulfide, ZnS , and lead sulfide, PbS . A sample of the mixture weighing 6.12 g was reacted with an excess of hydrochloric acid. The reactions are



If the sample reacted completely and produced 1.049 L of hydrogen sulfide, H_2S , at 23°C and 745 mmHg, what were the percentages of ZnS and PbS in the mixture?

5.151 A mixture of N_2 and Ne contains equal moles of each gas and has a total mass of 10.0 g. What is the density of this gas mixture at 500 K and 15.00 atm? Assume ideal gas behavior.

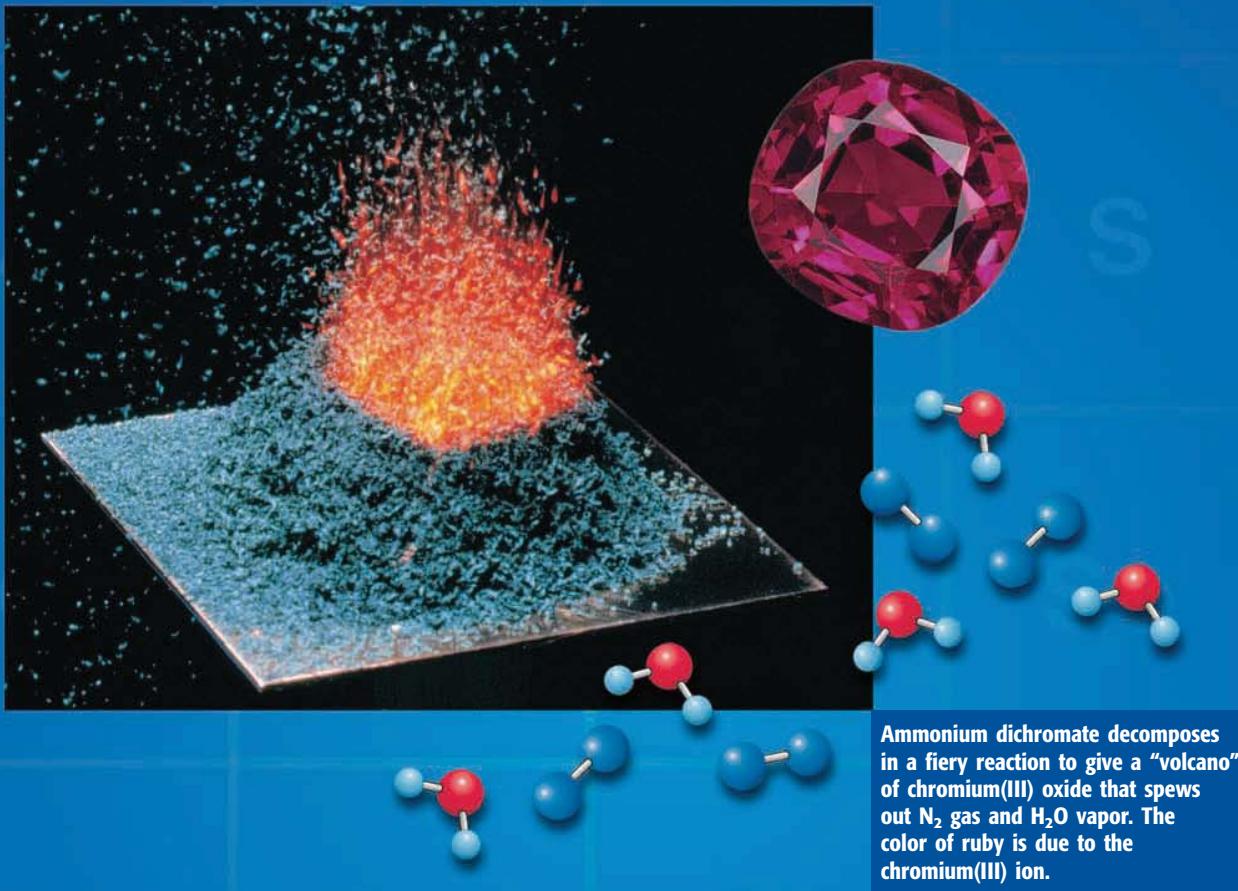
5.152 A mixture of Ne and Ar gases at 350 K contains twice as many moles of Ne as of Ar and has a total mass of 50.0 g. If the density of the mixture is 4.00 g/L, what is the partial pressure of Ne ?

5.153 An ideal gas with a density of 3.00 g/L has a pressure of 675 mmHg at 25°C. What is the root-mean-square speed of the molecules of this gas?

5.154 The root-mean-square speed of the molecules of an ideal gas at 25°C and a pressure of 2.50 atm is 5.00×10^2 m/s. What is the density of this gas?

6

Thermochemistry



Contents and Concepts

Understanding Heats of Reaction

- 6.1 Energy and Its Units
- 6.2 Heat of Reaction
- 6.3 Enthalpy and Enthalpy Change
- 6.4 Thermochemical Equations
- 6.5 Applying Stoichiometry to Heats of Reaction
- 6.6 Measuring Heats of Reaction

The first part of the chapter lays the groundwork for understanding what we mean by heats of reaction.

Using Heats of Reaction

- 6.7 Hess’s Law
- 6.8 Standard Enthalpies of Formation
- 6.9 Fuels—Foods, Commercial Fuels, and Rocket Fuels

Now that we understand the basic properties of heats of reaction and how to measure them, we can explore how to use them.

Nearly all chemical reactions involve either the release or the absorption of heat, a form of energy. The burning of coal and gasoline are dramatic examples of chemical reactions in which a great deal of heat is released. Such reactions are important sources of warmth and energy. Chemical reactions that absorb heat are usually less dramatic. The reaction of barium hydroxide with an ammonium salt is an exception. If crystals of barium hydroxide octahydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, are mixed with crystals of ammonium nitrate, NH_4NO_3 , in a flask, the solids form first a slush, then a liquid. Because the reaction mixture absorbs heat from the surroundings, the flask feels cool. It soon becomes so cold that if it is set in a puddle of water on a board, the water freezes; the board can then be inverted with the flask frozen to it (Figure 6.1).

In this chapter, we will be concerned with the quantity of heat released or absorbed in a chemical reaction. We will address several questions: How do you measure the quantity of heat released or absorbed by a chemical reaction? To what extent can you relate the

■ See pages 252–253 for
the Media Summary.

quantity of heat involved in a given reaction to the quantities of heat in other reactions? And how can you use this information?

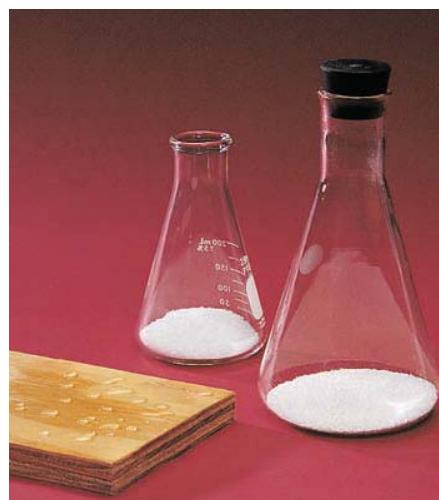


FIGURE 6.1

A reaction that absorbs heat

Two crystalline substances, barium hydroxide octahydrate and an ammonium salt, are mixed thoroughly in a flask. Then the flask, which feels quite cold to the touch, is set in a puddle of water on a board. In a couple of minutes, the flask and board are frozen solidly together. The board can then be inverted with the flask frozen to it.

Understanding Heats of Reaction

Thermodynamics is the science of the relationships between heat and other forms of energy. *Thermochemistry* is one area of thermodynamics. It concerns the study of the quantity of heat absorbed or evolved (given off) by chemical reactions. An example of a heat-evolving reaction is the burning of fuel. There may be practical reasons why you want to know the quantity of heat evolved during the burning of a fuel: you could calculate the cost of the fuel per unit of heat energy produced; you could calculate the quantity of heat obtained per unit mass of rocket fuel; and so forth. But there are also theoretical reasons for wanting to know the quantity of heat involved in a reaction. For example, knowing such values, you are able to calculate the amount of energy needed to break a particular kind of chemical bond and so learn something about the strength of that bond. Heat measurements also provide data needed to determine whether a particular chemical reaction occurs and, if so, to what extent. <

We have just used the terms *energy* and *heat*, assuming you have some idea of what they mean. But to proceed, you will need precise definitions of these and other terms. In the following section, we will define energy and its different forms and introduce units of energy.

These questions concern chemical equilibrium and will be discussed in Chapter 18.

6.1

Energy and Its Units

We can define **energy** briefly as *the potential or capacity to move matter*. According to this definition, energy is not a material thing but rather a property of matter. Energy exists in different forms that can be interconverted. You can see the relationship of a given form of energy to the motion of matter by following its interconversions into different forms.

Consider the interconversions of energy in a steam-driven electrical generator. A fuel is burned to heat water and generate steam. The steam expands against a piston (or turbine), which is connected to a drive shaft that turns an electrical coil in a magnetic field. Electricity is generated in the coil. The fuel contains chemical energy, which is converted to heat. Part of the heat is then converted to motion of the drive

shaft, and this motion is converted to electrical energy. The electrical energy could be used to run a motor, transforming the electrical energy back to the energy of motion. Or you could send the electricity into a lightbulb, converting electrical energy to heat energy and light energy. Photovoltaic cells can convert light back to electricity, which could be used to run a motor that can move matter (Figure 6.2). These examples show that energy can exist in different forms, including heat, light, and electrical energy, and these different forms can be interconverted. You also see their relationship to the energy of motion.

In this chapter, we will be especially concerned with the energy of substances, or chemical energy, and its transformation during chemical reaction into heat energy. To prepare for this, we will first explore the quantitative meaning of the energy of motion (*kinetic energy*). Then we will look at the concepts of *potential energy* and of the *internal energy* of substances, which is defined in terms of the kinetic and potential energies of the particles making up the substance.



FIGURE 6.2

Conversion of light energy to kinetic energy

Solar-powered vehicles use panels of photovoltaic cells.

Kinetic Energy; Units of Energy

Kinetic energy is *the energy associated with an object by virtue of its motion*. An object of mass m and speed or velocity v has kinetic energy E_k equal to

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

This formula shows that the kinetic energy of an object depends on both its mass and its speed. A heavy object can move more slowly than a light object and still have the same kinetic energy. <

Consider the kinetic energy of a person whose mass is 59.0 kg and whose speed is 26.8 m/s. (This is equivalent to a person with a mass of 130 lb traveling in an automobile going 60 miles per hour.) You substitute the mass and speed into the formula.

$$E_k = \frac{1}{2} \times (59.0 \text{ kg}) \times (26.8 \text{ m/s})^2 = 2.12 \times 10^4 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

Note that the unit of energy comes out of the calculation. Because you substituted SI units of mass and speed, you obtain the SI unit of energy. *The SI unit of energy, $\text{kg}\cdot\text{m}^2/\text{s}^2$, is given the name **joule (J)** (pronounced “jewl”) after the English physicist James Prescott Joule (1818–1889), who studied the energy concept.* You see that a person weighing 130 lb and traveling 60 miles per hour has a kinetic energy equal to $2.12 \times 10^4 \text{ J}$, or 21.2 kJ (21.2 kilojoules).

The joule is an extremely small unit. To appreciate its size, note that the *watt* is a measure of the quantity of energy used per unit time and equals 1 joule per second. A 100-watt bulb, for example, uses 100 joules of energy every second. A kilowatt-hour, the unit by which electric energy is sold, equals 3600 kilowatt-seconds

In the previous chapter, we used the symbol u for average molecular speed. Here v is the speed of an individual object or particle.

(there are 3600 seconds in 1 hour), or 3.6 million joules. A household might use something like 1000 kilowatt-hours (3.6 billion joules) of electricity in a month.

The **calorie (cal)** is a *non-SI unit of energy commonly used by chemists, originally defined as the amount of energy required to raise the temperature of one gram of water by one degree Celsius*. This is only an approximate definition, however, because we now know that the energy needed to heat water depends slightly on the temperature of the water. In 1925 the calorie was defined in terms of the joule:

$$1 \text{ cal} = 4.184 \text{ J} \quad (\text{exact definition})$$

A person weighing 130 lb and traveling 60 miles per hour has a kinetic energy of

$$2.12 \times 10^4 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 5.07 \times 10^3 \text{ cal (5.07 kcal)}$$

Example 6.1

Calculating Kinetic Energy

A good pitcher can throw a baseball so that it travels between 60 and 90 miles per hour (although speeds in excess of 100 miles per hour have been recorded). A regulation baseball weighing 143 g (0.143 kg) travels 75 miles per hour (33.5 m/s). What is the kinetic energy of this baseball in joules? in calories?

Problem Strategy Kinetic energy is defined by the formula $E_k = \frac{1}{2}mv^2$. You simply substitute into this formula, making certain that m and v are expressed in the same system of units.

Solution Substitute into the defining equation for the kinetic energy, using SI units.

$$E_k = \frac{1}{2} \times 0.143 \text{ kg} \times (33.5 \text{ m/s})^2 = 80.2 \text{ J}$$

Using the conversion factor 1 cal/4.184 J we obtain

$$80.2 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 19.2 \text{ cal}$$

Answer Check Make sure that the values for m and v are in the same units; SI units are generally appropriate. The SI unit of mass is kg, and the SI unit of speed is m/s. The answer then comes out in SI units (joules in this case).

Exercise 6.1

An electron, whose mass is 9.11×10^{-31} kg, is accelerated by a positive charge to a speed of 5.0×10^6 m/s. What is the kinetic energy of the electron in joules? in calories?

■ See Problems 6.43, 6.44, 6.45, and 6.46.

Potential Energy

Potential energy is the energy an object has by virtue of its position in a field of force. For example, water at the top of a dam has potential energy (in addition to whatever kinetic energy it may possess), because the water is at a relatively high position in the gravitational force field of the earth. You can calculate this potential energy of the water from the formula $E_p = mgh$. Here E_p is the potential energy of a quantity of water at the top of the dam, m is the mass of the water, g is the constant acceleration of gravity, and h is the height of the water measured from some standard level. The choice of this standard level is arbitrary, because only differences of potential energy are important in any physical situation. It is convenient to choose the standard level to be the surface of the earth. As a quantity of water falls over the dam, its potential energy decreases from mgh at the top of the dam to zero at the earth's surface.

**FIGURE 6.3****Potential energy and kinetic energy**

Water at the top of the dam has potential energy. As the water falls over the dam, this potential energy is converted to kinetic energy.

The potential energy of the water at the top of the dam is converted to kinetic energy when the water falls to a lower level. As the water falls, it moves more quickly. The potential energy decreases and the kinetic energy increases. Figure 6.3 shows the potential energy of water being converted to kinetic energy as the water falls over a dam.

Internal Energy

Consider the total energy of a quantity of water as it moves over the dam. This water as a whole has kinetic energy and potential energy. However, we know that water is made up of molecules, which are made up of smaller particles, electrons and nuclei. Each of these particles also has kinetic energy and potential energy. *The sum of the kinetic and potential energies of the particles making up a substance* is referred to as the **internal energy**, U , of the substance. Therefore, the total energy, E_{tot} , of a quantity of water equals the sum of its kinetic and potential energies as a whole ($E_k + E_p$) plus its internal energy.

$$E_{tot} = E_k + E_p + U$$

Normally when you study a substance in the laboratory, the substance is at rest in a vessel. Its kinetic energy as a whole is zero. Moreover, its potential energy as a whole is constant, and you can take it to be zero. In this case, the total energy of the substance equals its internal energy, U .

Law of Conservation of Energy

We have discussed situations in which one form of energy can be converted into another form of energy. For example, when water falls over a dam, potential energy is converted into kinetic energy. Some of the kinetic energy of the water may also be converted into random molecular motion—that is, into internal energy of the water. The total energy, E_{tot} , of the water, however, remains constant, equal to the sum of the kinetic energy, E_k , the potential energy, E_p , and the internal energy, U , of the water.

This result can be stated more generally as the **law of conservation of energy**: *energy may be converted from one form to another, but the total quantity of energy remains constant.*

Concept Check 6.1

A solar-powered water pump has photovoltaic cells that protrude from top panels. These cells collect energy from sunlight, storing it momentarily in a battery, which later runs an electric motor that pumps water up to a storage tank on a hill. What energy conversions are involved in using sunlight to pump water into the storage tank?

6.2**Heat of Reaction**

In the chapter opening, we mentioned chemical reactions (such as the burning of coal) that evolve, or release, heat. We also described a reaction that absorbs heat. Both types of reaction involve a *heat of reaction*. To understand this concept, you need to know what is meant by a thermodynamic *system* and its *surroundings* and to have a precise definition of the term *heat*.

Suppose that you are interested in studying the change of a thermodynamic property (such as internal energy) during a physical or chemical change. *The substance or*

**FIGURE 6.4****Illustration of a thermodynamic system**

The *system* consists of the portion of the universe that we choose to study; in this case, it is a solution of $\text{Ba}(\text{OH})_2$ and NH_4NO_3 . Everything else, including the reaction vessel, constitutes the *surroundings*.

mixture of substances under study in which a change occurs is called the **thermodynamic system** (or simply **system**). The **surroundings** are everything in the vicinity of the thermodynamic system (Figure 6.4).

Definition of Heat

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the thermodynamic system and its surroundings. As long as a system and its surroundings are in thermal contact (that is, they are not thermally insulated from one another), energy (heat) flows between them to establish temperature equality, or *thermal equilibrium*. Heat flows from a region of higher temperature to one of lower temperature; once the temperatures become equal, heat flow stops. Note that once heat flows into a system, it appears in the system as an increase in its internal energy. You would not say that the system has heat, because heat is only an energy flow.

We can explain this flow of energy between two regions of different temperatures in terms of kinetic-molecular theory. Imagine two vessels in contact, each containing oxygen gas and the one on the left being hotter (Figure 6.5). According to kinetic theory, the average speed of molecules in the hotter gas is greater than that of molecules in the colder gas. But as the molecules in their random motions collide with the vessel walls, they lose energy to or gain energy from the walls. The faster molecules tend to slow down, while the slower molecules tend to speed up. Eventually, the average speeds of the molecules in the two vessels (and therefore the temperatures of the two gases) become equal. The net result is that energy is transferred through the vessel walls from the hot gas to the cold gas; that is, heat has flowed from the hotter vessel to the cooler one.

Heat and temperature are sometimes confused. The distinction is clear in the kinetic picture of a gas. According to kinetic theory, the absolute temperature of a gas is directly proportional to the average kinetic energy of the molecules. When you add heat to a gas, you increase its internal energy—and therefore its total kinetic energy. This increase in kinetic energy will be distributed over the molecules in the sample. Therefore, the increase in average kinetic energy per molecule (and thus the increase in temperature) depends on the size of the gas sample. A given quantity of heat will raise the temperature of a sample more if the sample is small.

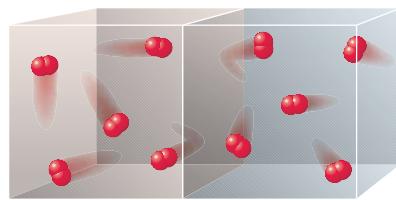
Heat is denoted by the symbol q . The algebraic sign of q is chosen to be positive if heat is absorbed by the system and negative if heat is evolved. The sign of q can be remembered this way: when heat is absorbed by a system, energy is *added* to it; q is assigned a positive quantity. On the other hand, when heat is evolved by a system, energy is *subtracted* from it; q is assigned a negative number.

Heat of Reaction

Consider a system in which a chemical reaction occurs. Before the reaction, the system and surroundings are at the same temperature, say 25°C . When the reaction starts, however, the temperature changes.

Suppose the temperature of the system falls. In that case, heat flows from the surroundings into the system. When the reaction stops, heat continues to flow until the system returns to the temperature of its surroundings (25°C). Heat has flowed into the system; that is, the system has absorbed heat and q is positive.

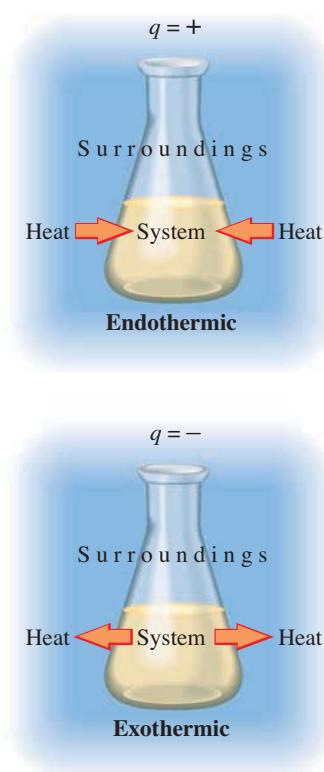
Suppose, on the other hand, that the temperature of the system rises. In this case, heat flows from the system to the surroundings. When the reaction stops, heat continues to flow until the system returns to the temperature of its surroundings (25°C). In this case, heat has flowed out of the system; that is, the system has evolved heat and q is negative.

**FIGURE 6.5****A kinetic-theory explanation of heat**

The vessel on the left contains oxygen molecules at a higher temperature than the oxygen molecules on the right. Molecules collide with the vessel walls, thereby losing or gaining energy. The faster molecules tend to slow down, and the slower molecules tend to speed up. The net result is that energy is transferred through the vessel walls from the hot gas to the cold gas. We call this energy transfer *heat*.

FIGURE 6.6 ▶**An exothermic process**

Left: The test tube contains anhydrous copper(II) sulfate (white crystals) and a thermometer that registers 26.1°C. The graduated cylinder contains water. *Right:* Water from the graduated cylinder has been added to the test tube, where the copper(II) sulfate forms hydrated copper(II) ion (blue color). The thermometer now registers 90.2°C, because the hydration process is exothermic.



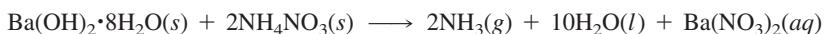
The **heat of reaction** (at a given temperature) is *the value of q required to return a system to the given temperature at the completion of the reaction*.

Chemical reactions or physical changes are classified as exothermic or endothermic. An **exothermic process** is *a chemical reaction or a physical change in which heat is evolved* (q is negative); see Figure 6.6. An **endothermic process** is *a chemical reaction or a physical change in which heat is absorbed* (q is positive). Experimentally, you note that in the exothermic reaction, the reaction flask initially warms; in the endothermic reaction, the reaction flask initially cools. We can summarize as follows:

Type of Reaction	Experimental Effect Noted	Result on System	Sign of q
Endothermic	Reaction vessel cools (heat is absorbed)	Energy added	+
Exothermic	Reaction vessel warms (heat is evolved)	Energy subtracted	-

Suppose that in an experiment 1 mol of methane burns in oxygen and evolves 890 kJ of heat: $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$. The reaction is exothermic. Therefore the heat of reaction, q , is -890 kJ .

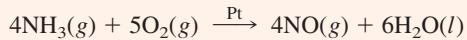
Or consider the reaction described in the chapter opening, in which crystals of barium hydroxide octahydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, react with crystals of ammonium nitrate, NH_4NO_3 ,



When 1 mol $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reacts with 2 mol NH_4NO_3 , the reaction mixture absorbs 170.8 kJ of heat. The reaction is endothermic. Therefore the heat of reaction, q , is $+170.8 \text{ kJ}$.

Exercise 6.2

Ammonia burns in the presence of a platinum catalyst to give nitric oxide, NO.



In an experiment, 4 mol NH_3 is burned and evolves 1170 kJ of heat. Is the reaction endothermic or exothermic? What is the value of q ?

■ See Problems 6.47, 6.48, 6.49, and 6.50.

6.3

Enthalpy and Enthalpy Change

The heat absorbed or evolved by a reaction depends on the conditions under which the reaction occurs. Usually, a reaction takes place in a vessel open to the atmosphere and therefore at the constant pressure of the atmosphere. We will assume that this is the case and write the heat of reaction as q_p , the subscript p indicating that the process occurs at constant pressure.

Enthalpy

There is a property of substances called enthalpy (en'-thal-py) that is related to the heat of reaction q_p . **Enthalpy** (denoted H) is *an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.* (An extensive property is a property that depends on the amount of substance. Other examples of extensive properties are mass and volume.)

Enthalpy is a state function. A **state function** is *a property of a system that depends only on its present state, which is determined by variables such as temperature and pressure, and is independent of any previous history of the system.* This means that a change in enthalpy does not depend on how the change was made, but only on the initial state and final state of the system. An analogy may clarify the point. Suppose you are hiking in mountainous terrain. You start walking from campsite A, which is at an altitude of 1200 ft above sea level according to your pocket altimeter, and you take the curving, graded path upward to campsite B (Figure 6.7). Alternatively, you could have taken a more direct, but more difficult, route to campsite B. The distances traveled are different; the distance by the graded path is longer than by the more direct route. However, the altitude (height above sea level) of campsite B is independent of how you got there (independent of any history). If you find the altitude of campsite B to be 4800 ft after arriving by the graded path, the altitude will be 4800 ft by any other path (assuming your altimeter is accurate, of course). Moreover, the difference in altitude of the two campsites is independent of the route you take from one to the other. Altitude is analogous to a state function, whereas distance traveled is not.

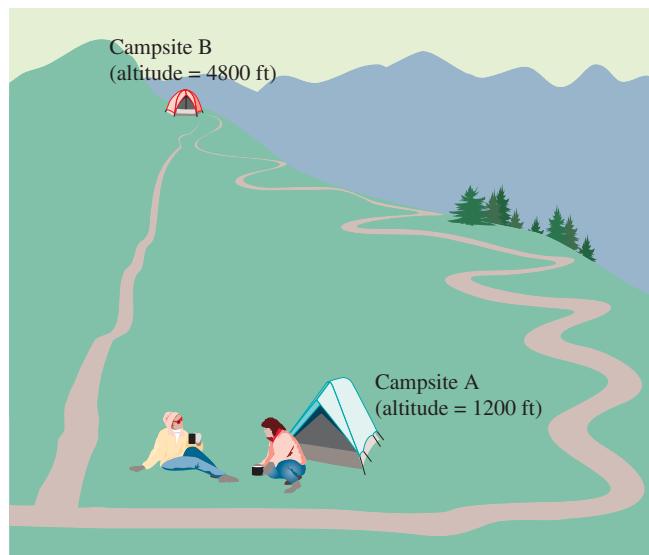
Enthalpy of Reaction

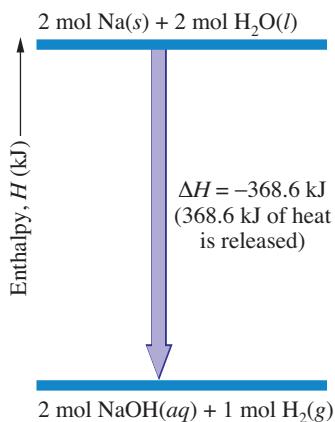
Consider a chemical reaction system. At first, the enthalpy of the system is that of the reactants. But as the reaction proceeds, the enthalpy changes and finally becomes

FIGURE 6.7

An analogy to illustrate a state function

The two campsites differ by 3600 ft in altitude. This difference in altitude is independent of the path taken between the campsites. The distance traveled and the things encountered along the way, however, do depend on the path taken. Altitude here is analogous to a thermodynamic state function.



**FIGURE 6.8****An enthalpy diagram**

When 2 mol Na(s) and 2 mol H₂O(l) react to give 2 mol NaOH(aq) and 1 mol H₂(g), 368.6 kJ of heat is released, and the enthalpy of the system decreases by 368.6 kJ.

equal to that of the products. *The change in enthalpy for a reaction at a given temperature and pressure* (called the **enthalpy of reaction**) is obtained by subtracting the enthalpy of the reactants from the enthalpy of the products. We will use the symbol Δ (meaning “change in”) and write the change in enthalpy as ΔH . You apply the Δ notation by taking the final value and subtracting the initial value. Thus $\Delta H = H_{\text{final}} - H_{\text{initial}}$. Since you start from reactants and end with products, the enthalpy of reaction is

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

Because H is a state function, the value of ΔH is independent of the details of the reaction. It depends only on the initial state (the reactants) and the final state (the products).

The key relation in this chapter is that between enthalpy change and heat of reaction:

$$\Delta H = q_p$$

The enthalpy of reaction equals the heat of reaction at constant pressure.

To illustrate the concepts we have introduced, consider the reaction at 25°C of sodium metal and water, carried out in a beaker open to the atmosphere at 1.00 atm pressure.



The metal and water react vigorously and heat evolves. Experiment shows that 2 mol of sodium metal reacts with 2 mol of water to evolve 368.6 kJ of heat. Because heat evolves, the reaction is exothermic, and you write $q_p = -368.6 \text{ kJ}$. Therefore, the enthalpy of reaction, or change of enthalpy for the reaction, is $\Delta H = -368.6 \text{ kJ}$. Figure 6.8 shows an *enthalpy diagram* for this reaction.

Enthalpy and Internal Energy

In the preceding discussion, we noted that the enthalpy change equals the heat of reaction at constant pressure. This will be sufficient for the purpose of this chapter, which is to introduce the concepts of heat of reaction and enthalpy change. Later we will look at thermodynamics in more detail. Still, it is useful at this point to note briefly the relationship of enthalpy to internal energy.

The enthalpy, H , is defined precisely as the internal energy, U , plus pressure, P , times volume, V .

$$H = U + PV$$

To obtain some understanding of this equation, consider a reaction system at constant pressure P . We will label the initial quantities (those for reactants) with a subscript i and the final quantities (those for products) with a subscript f . Then

$$\Delta H = H_f - H_i = (U_f + PV_f) - (U_i + PV_i)$$

Collecting the internal-energy terms and the pressure-volume terms, you can rewrite this as

$$\Delta H = (U_f - U_i) + P(V_f - V_i) = \Delta U + P\Delta V$$

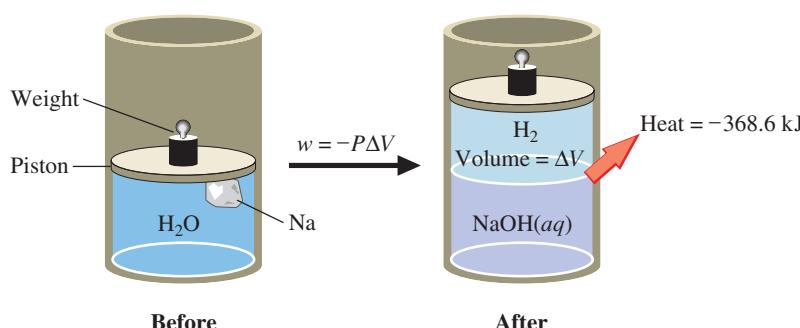
We write ΔU for $U_f - U_i$ and ΔV for $V_f - V_i$ and rearrange this as follows:

$$\Delta U = \Delta H - P\Delta V$$

The last term in this equation ($-P\Delta V$) is the energy required by the system to change volume against the constant pressure of the atmosphere. (The minus sign means that energy is required to increase the volume of the system.) This required energy is called the *pressure-volume work*. Thus, the equation says that the internal energy of the

FIGURE 6.9**Pressure-volume work**

In this experiment, we replace the pressure of the atmosphere by a piston-and-weight assembly of equal pressure. As sodium metal reacts with water, the hydrogen gas evolved pushes the piston and weight upward (compare *before* and *after*). It requires work to raise the piston and weight upward in a gravitational field.



system changes in two ways. It changes because energy leaves or enters the system as heat (ΔH), and it changes because the system increases or decreases in volume against the constant pressure of the atmosphere (which requires energy $-P\Delta V$).

Consider a specific reaction. When 2 mol of sodium metal and 2 mol of water react in a beaker, 1 mol of hydrogen gas forms and heat evolves. If you measured this heat, you would find it to be -368.6 kJ , indicating that 368.6 kJ of energy has left the system in the form of heat.

Because hydrogen gas forms during the reaction, the volume of the system increases. To expand, the system must push back the atmosphere, and this requires energy equal to the pressure–volume work. It may be easier to see this pressure–volume work if you replace the constant pressure of the atmosphere by an equivalent pressure from a piston-and-weight assembly, as in Figure 6.9. When hydrogen gas is released during the reaction, it pushes upward on the piston and raises the weight. It requires energy to lift a weight upward in a gravitational field. If you calculate this pressure–volume work at 25°C and 1.00 atm pressure, you find that it is $-P\Delta V = -2.5 \text{ kJ}$.

In the sodium–water reaction, the internal energy changes by -368.6 kJ because heat evolves and changes by -2.5 kJ because pressure–volume work is done. The total change of internal energy is

$$\Delta U = \Delta H - P\Delta V = -368.6 \text{ kJ} - 2.5 \text{ kJ} = -371.1 \text{ kJ}$$

As you can see, ΔU does not differ a great deal from ΔH . This is the case in most reactions, so the heat of reaction at constant pressure is approximately equal to the change of internal energy.

6.4

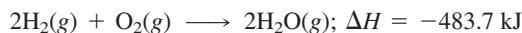
Thermochemical Equations

We will often find it convenient to write the enthalpy of reaction, ΔH , with the chemical equation. A **thermochemical equation** is *the chemical equation for a reaction (including phase labels) in which the equation is given a molar interpretation, and the enthalpy of reaction for these molar amounts is written directly after the equation*. For the reaction of sodium and water, you would write



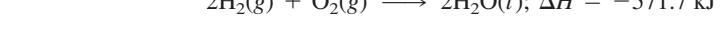
This equation says that 2 mol of sodium reacts with 2 mol of water to produce 2 mol of sodium hydroxide and 1 mol of hydrogen gas, and 368.6 kJ of heat evolves.

Note that the thermochemical equation includes phase labels. This is because the enthalpy change, ΔH , depends on the phase of the substances. Consider the reaction of hydrogen and oxygen to produce water. If the product is water vapor, 2 mol of H_2 burn to release 483.7 kJ of heat.



On the other hand, if the product is liquid water, the heat released is 571.7 kJ.

| It takes 44.0 kJ of heat to vaporize 1 mol of liquid water at 25°C.



In this case, additional heat is released when water vapor condenses to liquid. <

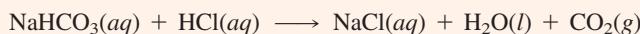
Example 6.2

Writing Thermochemical Equations

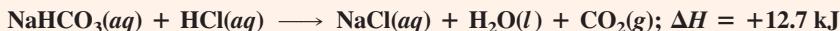
Aqueous sodium hydrogen carbonate solution (baking soda solution) reacts with hydrochloric acid to produce aqueous sodium chloride, water, and carbon dioxide gas. The reaction absorbs 12.7 kJ of heat at constant pressure for each mole of sodium hydrogen carbonate. Write the thermochemical equation for the reaction.

Problem Strategy Remember that the thermochemical equation is the balanced equation for the reaction, given a molar interpretation, with the enthalpy of reaction written directly after it. You need to translate the names of substances given in the problem statement into their formulas and then balance the equation. (This is an acid–base reaction; refer to Section 4.4 for a discussion.) The problem statement gives you the quantity of heat absorbed (heat is added to the system), so the enthalpy change is a positive quantity. Note too that this is the heat absorbed for each mole of sodium hydrogen carbonate.

Solution You first write the balanced chemical equation.



The equation is for 1 mol NaHCO_3 , with the absorption of 12.7 kJ of heat. The corresponding ΔH is +12.7 kJ. The thermochemical equation is



Answer Check Check that the formulas of the substances in the equation are correct and that the equation is balanced. Also check that the enthalpy of reaction has the correct sign and that its value is for the correct amount of reactant given in the problem statement (1 mol NaHCO_3).

Exercise 6.3 A propellant for rockets is obtained by mixing the liquids hydrazine, N_2H_4 , and dinitrogen tetroxide, N_2O_4 . These compounds react to give gaseous nitrogen, N_2 , and water vapor, evolving 1049 kJ of heat at constant pressure when 1 mol N_2O_4 reacts. Write the thermochemical equation for this reaction.

| See Problems 6.51 and 6.52.

The following are two important rules for manipulating thermochemical equations:

- When a thermochemical equation is multiplied by any factor, the value of ΔH for the new equation is obtained by multiplying the value of ΔH in the original equation by that same factor.
- When a chemical equation is reversed, the value of ΔH is reversed in sign.

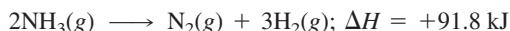
Consider the thermochemical equation for the synthesis of ammonia.



Suppose you want the thermochemical equation to show what happens when twice as many moles of nitrogen and hydrogen react to produce ammonia. Because double the amounts of substances are present, the enthalpy of reaction is doubled (enthalpy is an extensive quantity). Doubling the previous equation, you obtain



Suppose you reverse the first equation we wrote for the synthesis of ammonia. Then the reaction is the dissociation of 2 mol of ammonia into its elements. The thermochemical equation is

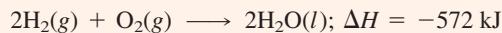


If you use the molar interpretation of a chemical equation, there is nothing unreasonable about using such coefficients as $\frac{1}{2}$ and $\frac{3}{2}$.

Example 6.3

Manipulating Thermochemical Equations

When 2 mol $\text{H}_2(g)$ and 1 mol $\text{O}_2(g)$ react to give liquid water, 572 kJ of heat evolves.



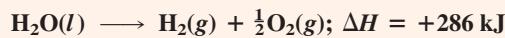
Write this equation for 1 mol of liquid water. Give the reverse equation, in which 1 mol of liquid water dissociates into hydrogen and oxygen.

Problem Strategy Recall the rules for manipulating thermochemical equations. When you multiply an equation by a factor, you also multiply ΔH by the same factor. When you reverse an equation, you multiply ΔH by -1 .

Solution You multiply the coefficients and ΔH by $\frac{1}{2}$:



Reversing the equation, you get



Answer Check If you multiply an equation by a factor, check that every formula and ΔH have been multiplied by that factor.

Exercise 6.4

- a. Write the thermochemical equation for the reaction described in Exercise 6.3 for the case involving 1 mol N_2H_4 . b. Write the thermochemical equation for the reverse of the reaction described in Exercise 6.3.

■ See Problems 6.53, 6.54, 6.55, and 6.56.

Concept Check 6.2

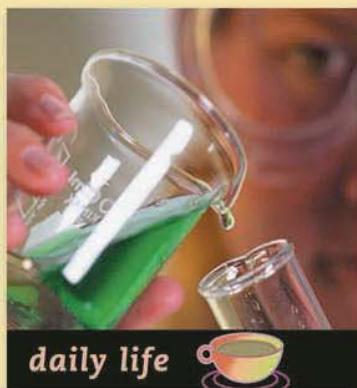
Natural gas consists primarily of methane, CH_4 . It is used in a process called *steam reforming* to prepare a gaseous mixture of carbon monoxide and hydrogen for industrial use.



The reverse reaction, the reaction of carbon monoxide and hydrogen, has been explored as a way to prepare methane (synthetic natural gas). Which of the following are exothermic? Of these, which one is the most exothermic?

- $\text{CH}_4(g) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + 3\text{H}_2(g)$
- $2\text{CH}_4(g) + 2\text{H}_2\text{O}(g) \longrightarrow 2\text{CO}(g) + 6\text{H}_2(g)$
- $\text{CO}(g) + 3\text{H}_2(g) \longrightarrow \text{CH}_4(g) + \text{H}_2\text{O}(g)$
- $2\text{CO}(g) + 6\text{H}_2(g) \longrightarrow 2\text{CH}_4(g) + 2\text{H}_2\text{O}(g)$

A Chemist Looks at . . .



Lucifers and Other Matches

Samuel Jones, an Englishman, patented one of the first kinds of matches in 1828. It consisted of a glass bead containing sulfuric acid surrounded by a coating of sugar with an oxidizing agent. You

ignited the match by

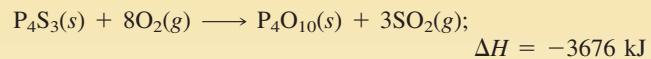
breaking the bead using a pair of pliers or, if you were more daring, your teeth. This action released the acid, which ignited an exothermic reaction in the surrounding combustible materials.

Later Jones began to market a friction match discovered, but not patented, by John Walker. Walker, who had been experimenting with explosives, discovered this match one day when he tried to remove a small glob of a dried mixture of antimony sulfide and potassium chlorate from a stick. He rubbed the stick on the floor and was surprised when it burst into flame. Jones called his matches "Lucifers." They were well named; when lighted, they gave off a shower of sparks and smoky fumes with the acrid odor of sulfur dioxide. Jones had every box inscribed with the warning "Persons whose lungs are delicate should by no means use Lucifers."

A few years later, a Frenchman, Charles Sauria, invented the white phosphorus match, which became an immediate success. When rubbed on a rough surface, the match lighted easily, without hazardous sparks, and smelled better than Lucifers. The match head contained white phosphorus, an oxidizing agent, and glue. White phosphorus is a yellowish-white, waxy substance, often sold in the form of sticks looking something like fat crayons. Unlike crayons, though, white phosphorus ignites spontaneously in air (so it is generally stored under water).

The glue in the match mixture had two purposes: it protected the white phosphorus from air, and it held the match mixture firmly together. The white phosphorus match had one serious drawback. White phosphorus is quite poisonous. Workers in match factories often began to show the agonizing symptoms of "phossy jaw," from white phosphorus poisoning, in which the jawbone disintegrates. The manufacture of white phosphorus matches was outlawed in the early 1900s.

The head of the "strike-anywhere" match, which you can buy today at any grocery store, contains the relatively nontoxic tetraphosphorus trisulfide, P_4S_3 , and potassium chlorate, $KClO_3$ (Figure 6.10). By rubbing the match head against a surface, you create enough heat by friction to ignite the match material. Tetraphosphorus trisulfide then burns in air in a very exothermic reaction.



Safety matches have a head containing mostly an oxidizing agent and require a striking surface containing nonpoisonous red phosphorus.



FIGURE 6.10

Strike-anywhere matches

Left: The head of the match contains tetraphosphorus trisulfide and potassium chlorate.
Right: The substances in the match head react when frictional heat ignites the mixture.

■ See Problems 6.121 and 6.122.

6.5

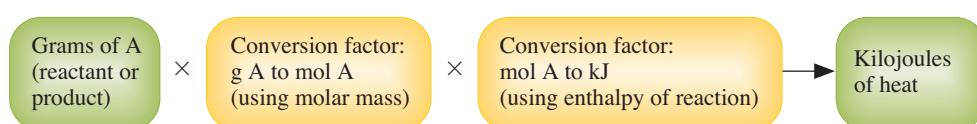
Applying Stoichiometry to Heats of Reaction

As you might expect, the quantity of heat obtained from a reaction will depend on the amount of reactants. We can extend the method used to solve stoichiometry problems, described in Chapter 3, to problems involving the quantity of heat.

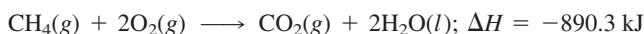
Consider the reaction of methane, CH_4 (the principal constituent of natural gas), burning in oxygen at constant pressure. How much heat could you obtain from 10.0 g of methane, assuming you had an excess of oxygen? You can answer this question if

FIGURE 6.11**Calculating the heat obtained from a reaction**

Convert the grams of a reactant or product to moles (using the molar mass). Then convert these moles to kilojoules of heat (using the enthalpy of reaction).



you know the enthalpy change for the reaction of 1 mol of methane. The thermochemical equation is



The calculation involves the following conversions:

Grams of CH_4 \longrightarrow moles of CH_4 \longrightarrow kilojoules of heat

$$10.0 \frac{\text{g CH}_4}{\text{mol CH}_4} \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \times \frac{-890.3 \text{ kJ}}{1 \text{ mol CH}_4} = -556 \text{ kJ}$$

Figure 6.11 illustrates the general calculation. <

If you wanted the result in kilocalories, you could convert this answer as follows:

$$556 \text{ kJ} \times \frac{1 \text{ kcal}}{4.184 \text{ kJ}} = 133 \text{ kcal}$$

Example 6.4**Calculating the Heat of Reaction from the Stoichiometry**

How much heat is evolved when 9.07×10^5 g of ammonia is produced according to the following equation? (Assume that the reaction occurs at constant pressure.)



Problem Strategy The calculation involves converting grams of NH_3 to moles of NH_3 and then to kilojoules of heat.

Grams of NH_3 \longrightarrow moles of NH_3 \longrightarrow kilojoules of heat

You obtain the conversion factor for the second step from the thermochemical equation, which says that the production of 2 mol NH_3 is accompanied by $q_p = -91.8 \text{ kJ}$.

Solution $9.07 \times 10^5 \frac{\text{g NH}_3}{\text{mol NH}_3} \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} \times \frac{-91.8 \text{ kJ}}{2 \text{ mol NH}_3} = -2.45 \times 10^6 \text{ kJ}$

Thus, 2.45×10^6 kJ of heat evolves.

Answer Check Make sure that the units in the calculation cancel to give the units of heat. Also note the sign of ΔH to decide whether heat is evolved or absorbed.

Exercise 6.5 How much heat evolves when 10.0 g of hydrazine reacts according to the reaction described in Exercise 6.3?

■ See Problems 6.57, 6.58, 6.59, and 6.60.

6.6**Measuring Heats of Reaction**

So far we have introduced the concept of heat of reaction and have related it to the enthalpy change. We also showed how to display the enthalpy change in a thermochemical equation, and from this equation how to calculate the heat of reaction for any given amount of substance. Now that you have a firm idea of what heats of reaction are, how would you measure them?

First, we need to look at the heat required to raise the temperature of a substance, because a thermochemical measurement is based on the relationship between heat and temperature change. The heat required to raise the temperature of a substance is called its *heat capacity*.

Heat Capacity and Specific Heat

Heat is required to raise the temperature of a given amount of substance, and the quantity of heat depends on the temperature change. The **heat capacity** (C) of a sample of substance is *the quantity of heat needed to raise the temperature of the sample of substance one degree Celsius (or one kelvin)*. Changing the temperature of the sample from an initial temperature t_i to a final temperature t_f requires heat equal to

$$q = C\Delta t$$

The heat capacity will depend on whether the process is constant-pressure or constant-volume. We will assume a constant-pressure process unless otherwise stated.

where Δt is the change of temperature and equals $t_f - t_i$.

Suppose a piece of iron requires 6.70 J of heat to raise the temperature by one degree Celsius. Its heat capacity is therefore 6.70 J/ $^{\circ}\text{C}$. The quantity of heat required to raise the temperature of the piece of iron from 25.0 $^{\circ}\text{C}$ to 35.0 $^{\circ}\text{C}$ is

$$q = C\Delta t = (6.70 \text{ J}/^{\circ}\text{C}) \times (35.0^{\circ}\text{C} - 25.0^{\circ}\text{C}) = 67.0 \text{ J}$$

Heat capacity is directly proportional to the amount of substance. Often heat capacities are listed for molar amounts of substances. The *molar heat capacity* of a substance is its heat capacity for one mole of substance.

Heat capacities are also compared for one-gram amounts of substances. The **specific heat capacity** (or simply **specific heat**) is *the quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (or one kelvin) at constant pressure*. To find the heat q required to raise the temperature of a sample, you multiply the specific heat of the substance, s , by the mass in grams, m , and the temperature change, Δt .

$$q = s \times m \times \Delta t$$

The specific heats and molar heat capacities of a few substances are listed in Table 6.1. Values depend somewhat on temperature, and those listed are for 25 $^{\circ}\text{C}$. Water has a specific heat of 4.18 J/(g \cdot $^{\circ}\text{C}$)—that is, 4.18 joules per gram per degree Celsius. In terms of calories, the specific heat of water is 1.00 cal/(g \cdot $^{\circ}\text{C}$). Example 6.5 illustrates the use of the preceding equation.

TABLE 6.1

Specific Heats and Molar Heat Capacities of Some Substances*

Substance	Specific Heat J/(g \cdot $^{\circ}\text{C}$)	Molar Heat Capacity J/(mol \cdot $^{\circ}\text{C}$)
Aluminum, Al	0.901	24.3
Copper, Cu	0.384	24.4
Ethanol, C ₂ H ₅ OH	2.43	112.2
Iron, Fe	0.449	25.1
Water, H ₂ O	4.18	75.3

*Values are for 25 $^{\circ}\text{C}$.

Example 6.5

Relating Heat and Specific Heat

Calculate the heat absorbed by 15.0 g of water to raise its temperature from 20.0 $^{\circ}\text{C}$ to 50.0 $^{\circ}\text{C}$ (at constant pressure). The specific heat of water is 4.18 J/(g \cdot $^{\circ}\text{C}$).

Problem Strategy Note that specific heat is the heat needed to raise the temperature of one gram of substance one degree Celsius. To get the total heat, multiply specific heat by the grams of substance and by the change in degrees Celsius.

(continued)

(continued)

Solution You substitute into the equation

$$q = s \times m \times \Delta t$$

The temperature change is

$$\Delta t = t_f - t_i = 50.0^\circ\text{C} - 20.0^\circ\text{C} = +30.0^\circ\text{C}$$

Therefore,

$$q = 4.18 \text{ J/(g}\cdot^\circ\text{C)} \times 15.0 \text{ g} \times (+30.0^\circ\text{C}) = \mathbf{1.88 \times 10^3 \text{ J}}$$

Answer Check Be sure to put units on quantities in your calculation and to note whether units cancel to give units of heat.

Exercise 6.6 Iron metal has a specific heat of 0.449 J/(g·°C). How much heat is transferred to a 5.00-g piece of iron, initially at 20.0°C, when it is placed in a pot of boiling water? Assume that the temperature of the water is 100.0°C and that the water remains at this temperature, which is the final temperature of the iron.

■ See Problems 6.63 and 6.64.

Measurement of Heat of Reaction

You measure the heat of reaction in a **calorimeter**, a device used to measure the heat absorbed or evolved during a physical or chemical change. The device can be as simple as the apparatus sketched in Figure 6.12, which consists of an insulated container (for example, a pair of polystyrene coffee cups) with a thermometer. More elaborate calorimeters are employed when precise measurements are needed for research, although the basic idea remains the same—to measure temperature changes under controlled circumstances and relate these temperature changes to heat.

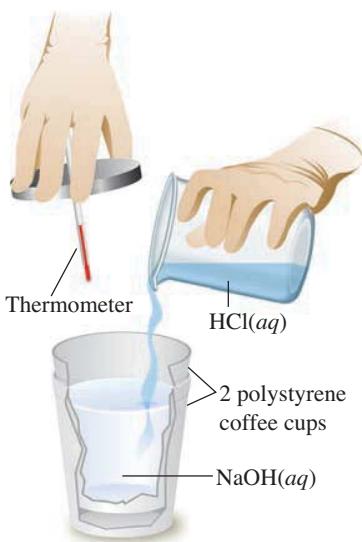
The coffee-cup calorimeter shown in Figure 6.12 is a constant-pressure calorimeter. The heat of the reaction is calculated from the temperature change caused by the reaction, and since this is a constant-pressure process, the heat can be directly related to the enthalpy change, ΔH . Research versions of a constant-pressure calorimeter are available, and these are used when gases are not involved.

For reactions involving gases, a **bomb calorimeter** is generally used (Figure 6.13). Consider the heat of combustion of graphite, the form of carbon used in the “lead” of a pencil. To measure the heat released when graphite burns in oxygen, a sample of graphite is placed in a small cup in the calorimeter. The graphite is surrounded by oxygen, and the graphite and oxygen are sealed in a steel vessel, or bomb. An electrical circuit is activated to start the burning of the graphite. The bomb is surrounded by water in an insulated container, and the heat of reaction is calculated from the temperature change of the calorimeter caused by the reaction.

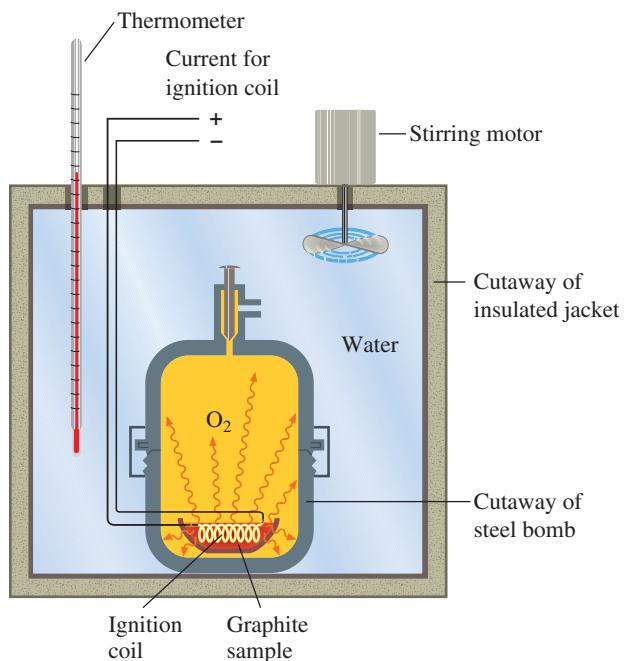
Because the reaction in a bomb calorimeter occurs in a closed vessel, the pressure does not generally remain constant. Rather the volume remains constant, and under these conditions the heat of reaction does not in general equal ΔH ; a small correction is usually needed. However, this correction is negligible when the reaction does not involve gases or when the number of moles of reactant gas equals the number of moles of product gas, as in the combustion of graphite to carbon dioxide. <

The next example describes the calculations needed to obtain ΔH from calorimetric measurements.

At the end of Section 6.3, we noted that $\Delta H = \Delta U + P\Delta V$. The heat at constant volume equals ΔU . To obtain ΔH , you must add a correction, $P\Delta V$. The change in volume is significant only if there are changes in gas volumes. From the ideal gas law, the molar volume of a gas is RT/P . If the moles of gas that have reacted is n_i and the moles of gas produced is n_f , then $P\Delta V$ equals essentially $RT \times (n_f - n_i)$, or $RT\Delta n$, where Δn refers to the change of moles of gas. To obtain the correction in joules, we use $R = 8.31 \text{ J/(K}\cdot\text{mol)}$. Thus, RT at 25°C (298 K) is $8.31 \text{ J/(K}\cdot\text{mol)} \times 298 \text{ K} = 2.48 \times 10^3 \text{ J/mol}$. The final result is $\Delta H = \Delta U + (2.48 \text{ kJ}) \times \Delta n$.

**FIGURE 6.12****A simple coffee-cup calorimeter**

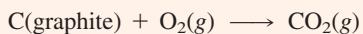
This calorimeter is made of two nested polystyrene coffee cups. The outer cup helps to insulate the reaction mixture from its surroundings. After the reactants are added to the inner cup, the calorimeter is covered to reduce heat loss by evaporation and convection. The heat of reaction is determined by noting the temperature rise or fall.

**FIGURE 6.13****A bomb calorimeter**

This type of calorimeter can be used to determine the heat of combustion of a substance. The figure shows a sample of graphite being burned in oxygen within a vessel called the bomb. An electric current passing through the ignition coil starts the graphite burning. The temperature of the water surrounding the bomb rises as heat flows from the exothermic reaction of graphite and oxygen. Example 6.6 illustrates the calculations involved in determining the heat of combustion in such an experiment.

Example 6.6Calculating ΔH from Calorimetric Data

Suppose 0.562 g of graphite is placed in a calorimeter with an excess of oxygen at 25.00°C and 1 atm pressure (Figure 6.13). Excess O₂ ensures that all carbon burns to form CO₂. The graphite is ignited, and it burns according to the equation



On reaction, the calorimeter temperature rises from 25.00°C to 25.89°C. The heat capacity of the calorimeter and its contents was determined in a separate experiment to be 20.7 kJ/°C. What is the heat of reaction at 25.00°C and 1 atm pressure? Express the answer as a thermochemical equation.

Problem Strategy First, you need to obtain the heat absorbed by the calorimeter when the sample burns, using the calorimeter's temperature rise and its heat capacity. Note that the heat released by reaction of the sample (a negative quantity) equals the heat absorbed by the calorimeter (a positive quantity), except for this sign change. Then, you need to convert this heat to the heat released per mole to obtain ΔH .

Step 1: To obtain heat absorbed by the calorimeter, you reason as follows. The heat released by the reaction is absorbed by the calorimeter and its contents. Let q_{rxn} be the quantity of heat from the reaction mixture, and let C_{cal} be the heat capacity of the calorimeter and contents. The quantity of heat absorbed by the calorimeter is $C_{cal}\Delta t$. This will have the same magnitude as q_{rxn} , but the opposite sign: $q_{rxn} = -C_{cal}\Delta t$.

(continued)

(continued)

Substituting values of C_{cal} and Δt , you obtain the heat q_{rxn} from the sample of C (0.562 g). The factor ($q_{rxn}/0.562$ g C) converts



Step 2: What is the heat released from 1 mol C (equal to ΔH)? Convert this amount of C (mathematically) to grams C. Then convert this to kJ heat, using the conversion factor you obtained in Step 1 ($q_{rxn}/0.562$ g C). The conversion steps are



Solution

Step 1: The heat from the graphite sample is

$$\begin{aligned} q_{rxn} &= -C_{cal}\Delta t = -20.7 \text{ kJ/}^{\circ}\text{C} \times (25.89^{\circ}\text{C} - 25.00^{\circ}\text{C}) \\ &= -20.7 \text{ kJ/}^{\circ}\text{C} \times 0.89^{\circ}\text{C} = -18.4 \text{ kJ} \end{aligned}$$

An extra figure is retained in q_{rxn} for further computation. The negative sign indicates the reaction is exothermic, as expected for a combustion. The factor to convert grams C to kJ heat is $-18.4 \text{ kJ}/0.562 \text{ g C}$.

Step 2: The conversion of 1 mol C to kJ heat for 1 mol (ΔH) is

$$1 \text{ mol C} \times \frac{12 \text{ g C}}{1 \text{ mol C}} \times \frac{-18.4 \text{ kJ}}{0.562 \text{ g C}} = -3.9 \times 10^2 \text{ kJ}$$

(The final answer has been rounded to two significant figures.) When 1 mol of carbon burns, 3.9×10^2 kJ of heat is released. You can summarize the results by the thermochemical equation:



Answer Check Go over your calculations carefully. Check that the units within each step cancel properly. Also check that you have the right sign for ΔH ; an exothermic reaction will have a negative sign.

Exercise 6.7 Suppose 33 mL of 1.20 M HCl is added to 42 mL of a solution containing excess sodium hydroxide, NaOH, in a coffee-cup calorimeter. The solution temperature, originally 25.0°C , rises to 31.8°C . Give the enthalpy change, ΔH , for the reaction



Express the answer as a thermochemical equation. For simplicity, assume that the heat capacity and the density of the final solution in the cup are those of water. (In more accurate work, these values must be determined.) Also assume that the total volume of the solution equals the sum of the volumes of HCl(aq) and NaOH(aq).

■ See Problems 6.67, 6.68, 6.69, and 6.70.

Using Heats of Reaction

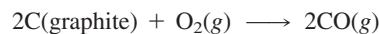
In the first part of this chapter, we looked at the basic properties of the heat of reaction and how to measure it. Now we want to find how heats of reaction can be used. We will see that the ΔH for one reaction can be obtained from the ΔH 's of other reactions. This means that we can tabulate a small number of values and use them to calculate others.

6.7

Hess's Law

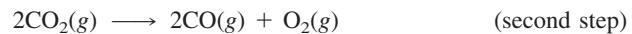
Enthalpy, you may recall, is a state function (Section 6.3). This means that the enthalpy change for a chemical reaction is independent of the path by which the products are obtained. In 1840, the Russian chemist Germain Henri Hess, a professor at the University of St. Petersburg, discovered this result by experiment. **Hess's law of heat summation** states that *for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps.* In other words, no matter how you go from given reactants to products (whether in one step or several), the enthalpy change for the overall chemical change is the same.

To understand Hess's law fully and to see how you can use it, consider a simple example. Suppose you would like to find the enthalpy change for the combustion of graphite (carbon) to carbon monoxide.

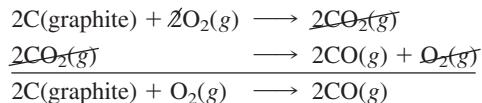


The direct determination of this enthalpy change is very difficult, because once carbon monoxide forms it reacts further with oxygen to yield carbon dioxide. If you do the experiment in an excess of oxygen, you obtain only carbon dioxide, and the enthalpy change is the heat of complete combustion of graphite. On the other hand, if you do the experiment in a limited quantity of oxygen, you obtain a mixture of carbon monoxide and carbon dioxide, and the heat of reaction is a value appropriate for a mixture of these products. How can you obtain the enthalpy change for the preparation of pure carbon monoxide from graphite and oxygen?

The answer is to apply Hess's law. To do this, imagine that the combustion of graphite to carbon monoxide takes place in two separate steps:



In the first step, you burn 2 mol of graphite in 2 mol of oxygen to produce 2 mol of carbon dioxide. In the second step, you decompose this carbon dioxide to give 2 mol of carbon monoxide and 1 mol of oxygen. The net result is the combustion of 2 mol of graphite in 1 mol of oxygen to give 2 mol of carbon monoxide. You can obtain this result by adding the two steps, canceling out 2 mol CO₂ and 1 mol O₂ on both sides of the equation.



According to Hess's law, the enthalpy change for the overall equation (which is the equation you want) equals the sum of the enthalpy changes for the two steps. Now you need to determine the enthalpy changes for the separate steps.

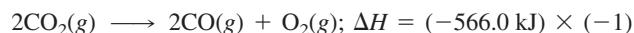
You can determine the enthalpy change for the first step by simply burning graphite in an excess of oxygen, as described in Example 6.6. The result is ΔH = -393.5 kJ per mole of CO₂ formed. For 2 mol CO₂, you multiply by 2.



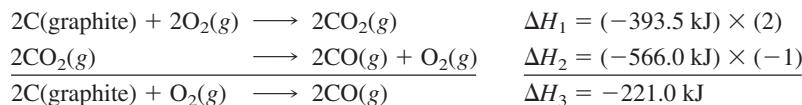
The second step, the decomposition of carbon dioxide, is not an easy experiment. However, the reverse of this decomposition is simply the combustion of carbon monoxide. You could determine the ΔH for that combustion by burning carbon monoxide in an excess of oxygen. The experiment is similar to the one for the combustion of graphite to carbon dioxide.



From the properties of thermochemical equations (Section 6.4), you know that the enthalpy change for the reverse reaction is simply (-1) times the original reaction.

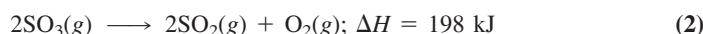
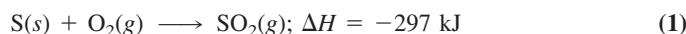


If you now add these two steps and add their enthalpy changes, you obtain the chemical equation and the enthalpy change for the combustion of carbon monoxide, which is what you wanted.

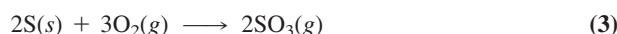


You see that the combustion of 2 mol of graphite to give 2 mol of carbon monoxide has an enthalpy change of -221.0 kJ . Figure 6.14 gives an enthalpy diagram showing the relationship among the enthalpy changes for this calculation.

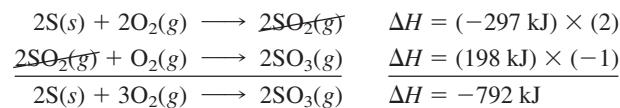
This calculation illustrates how you can use Hess's law to obtain the enthalpy change for a reaction that is difficult to determine by direct experiment. Hess's law is more generally useful, however, in that it allows you to calculate the enthalpy change for one reaction from the values for others, whatever their source. Suppose you are given the following data: <



How could you use these data to obtain the enthalpy change for the following equation?



You need to multiply Equations 1 and 2 by factors (perhaps reversing one or both equations) so that when you add them together you obtain Equation 3. You can usually guess what you need to do to the first two equations to obtain the third one. Note that Equation 3 has a coefficient of 2 for $\text{S}(\text{s})$. This suggests that you should multiply Equation 1 by 2 (and multiply the ΔH by 2). Note also that $\text{SO}_3(\text{g})$ in Equation 3 is on the right-hand side. This suggests that you should reverse Equation 2 (and multiply the ΔH by -1). Here is the calculation:

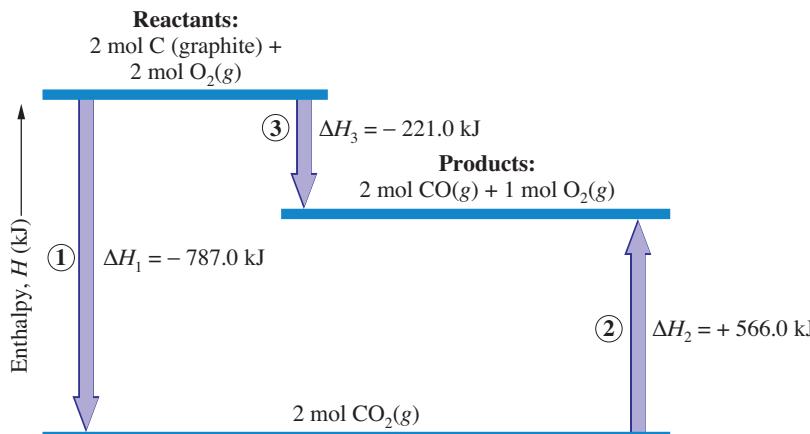


The next example gives another illustration of how Hess's law can be used to calculate the enthalpy change for a reaction from the enthalpy values for other reactions. In

FIGURE 6.14

Enthalpy diagram illustrating Hess's law

The diagram shows two different ways to go from graphite and oxygen (reactants) to carbon monoxide (products). Going by way of reactions 1 and 2 is equivalent to the direct reaction 3.



In this case, the problem involves three equations from which we obtain a fourth. Although this problem is somewhat more complicated than the one we just did, the basic procedure is the same: Compare the coefficients in the equations. See what factors you need to multiply the equations whose ΔH 's you know to obtain the equation you want. Check your results to be sure that the equations (and the ΔH 's) add up properly.

Example 6.7

Applying Hess's Law

What is the enthalpy of reaction, ΔH , for the formation of tungsten carbide, WC, from the elements? (Tungsten carbide is very hard and is used to make cutting tools and rock drills.)



The enthalpy change for this reaction is difficult to measure directly, because the reaction occurs at 1400°C. However, the heats of combustion of the elements and of tungsten carbide can be measured easily:



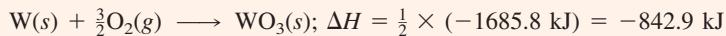
Problem Strategy Note that Equations 1, 2, and 3 involve the reactants and products for the desired reaction (as well as their enthalpy changes). You apply Hess's law to these equations, perhaps reversing an equation or multiplying it by a factor, so that when you add all of them together, you obtain the desired equation.

First, look to see whether any equation needs to be reversed to get a reactant or product on the correct side. If you do reverse an equation, remember to change the sign of its ΔH . Second, to obtain the multiplicative factor for each equation, compare that equation with the desired one. For instance, note that Equation 1 has 2W(s) on the left side, whereas the desired equation has W(s) on the left. Therefore, you divide Equation 1 (and its ΔH) by 2, or multiply by the factor $\frac{1}{2}$.

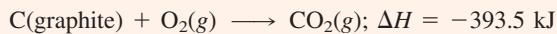
Solution Do any equations need to be reversed? Note that you want to end up with W(s) and C(graphite) on the left side and with WC(s) on the right side of the final equation (the formation of WC from its elements). Equation 1 has W(s) on the left, as required after the addition of the equations. Similarly, Equation 2 has C(graphite) on the left, as required. However, Equation 3 has WC(s) on the left, but it should be on the right. Therefore, you reverse Equation 3 (and multiply its ΔH by -1).



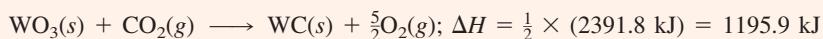
To obtain the multiplicative factor for each equation, you compare Equations 1, 2, and 3', in turn, with the desired equation. We did this earlier (at the end of the Problem Strategy) for Equation 1. Multiplying it by $\frac{1}{2}$, you obtain



Compare Equation 2 with the desired equation. Both have C(graphite) on the left side; therefore, you leave Equation 2 as it is.



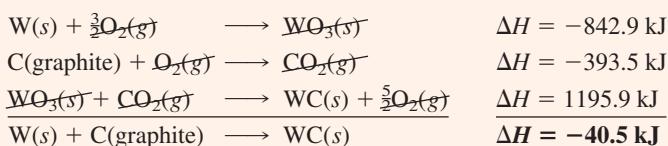
Now, compare Equation 3' with the desired equation. Equation 3' has 2WC(s) on the right side, whereas the desired equation has WC(s) on the right side. Therefore, you multiply Equation 3' (and its ΔH) by $\frac{1}{2}$.



(continued)

(continued)

Now add these last three equations and their corresponding ΔH 's.



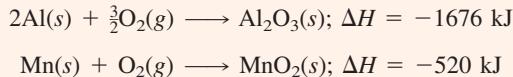
Answer Check Check that when you add the three equations substances that do not appear in the final one cancel correctly. For example, note that $\frac{3}{2}\text{O}_2(g)$ and $\text{O}_2(g)$ on the left sides of the equations cancel $\frac{5}{2}\text{O}_2(g)$ on the right side. Then check that the final equation is the one asked for.

Exercise 6.8

Manganese metal can be obtained by reaction of manganese dioxide with aluminum.



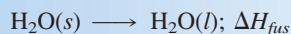
What is ΔH for this reaction? Use the following data:



■ See Problems 6.71, 6.72, 6.73, and 6.74.

Concept Check 6.3

The heat of fusion (also called heat of melting), ΔH_{fus} , of ice is the enthalpy change for



Similarly, the heat of vaporization, ΔH_{vap} , of liquid water is the enthalpy change for



How is the heat of sublimation, ΔH_{sub} , the enthalpy change for the reaction



related to ΔH_{fus} and ΔH_{vap} ?

6.8

Standard Enthalpies of Formation

Because Hess's law relates the enthalpy changes of some reactions to the enthalpy changes of others, we only need to tabulate the enthalpy changes of certain types of reactions. We also generally list enthalpy changes only for certain standard thermodynamic conditions (which are not identical to the standard conditions for gases, STP).

The term **standard state** refers to the *standard thermodynamic conditions chosen for substances when listing or comparing thermodynamic data: 1 atm pressure and the specified temperature (usually 25°C)*. These standard conditions are indicated by a superscript degree sign ($^\circ$). The enthalpy change for a reaction in which reactants in their standard states yield products in their standard states is denoted ΔH° ("delta H degree," but often read as "delta H zero"). The quantity ΔH° is called the *standard enthalpy of reaction*.

The International Union of Pure and Applied Chemistry (IUPAC) recommends that the standard pressure be 1 bar ($1 \times 10^5 \text{ Pa}$). Thermodynamic tables are becoming available for 1 bar pressure, and in the future such tables will probably replace those for 1 atm.

FIGURE 6.15**Allotropes of sulfur**

Left: An evaporating dish contains rhombic sulfur, the stable form of the element at room temperature. *Right:* When this sulfur is melted, then cooled, it forms long needles of monoclinic sulfur, another allotrope. At room temperature, monoclinic sulfur will slowly change back to rhombic sulfur. Both forms contain the molecule S_8 , depicted by the model.



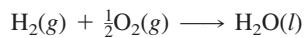
As we will show, it is sufficient to tabulate just the enthalpy changes for formation reactions—that is, for reactions in which compounds are formed from their elements. To specify the formation reaction precisely, however, we must specify the exact form of each element.

Some elements exist in the same physical state (gas, liquid, or solid) in two or more distinct forms. For example, oxygen in any of the physical states occurs both as dioxygen (commonly called simply oxygen), with O_2 molecules, and as ozone, with O_3 molecules. Dioxygen gas is odorless; ozone gas has a characteristic pungent odor. Solid carbon has two principal crystalline forms: graphite and diamond. Graphite is a soft, black, crystalline substance; diamond is a hard, usually colorless crystal. The elements oxygen and carbon are said to exist in different allotropic forms. An **allotrope** is *one of two or more distinct forms of an element in the same physical state* (Figure 6.15).

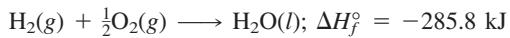
The **reference form** of an element for the purpose of specifying the formation reaction is usually the *stablest form (physical state and allotrope) of the element under standard thermodynamic conditions*. The reference form of oxygen at 25°C is $O_2(g)$; the reference form of carbon at 25°C is graphite. <

Table 6.2 lists standard enthalpies of formation of substances and ions (a longer table is given in Appendix C). The **standard enthalpy of formation** (also called the **standard heat of formation**) of a substance, denoted ΔH_f° , is *the enthalpy change for the formation of one mole of the substance in its standard state from its elements in their reference form and in their standard states*.

To understand this definition, consider the standard enthalpy of formation of liquid water. Note that the stablest forms of hydrogen and oxygen at 1 atm and 25°C are $H_2(g)$ and $O_2(g)$, respectively. These are therefore the reference forms of the elements. You write the formation reaction for 1 mol of liquid water as follows:



The standard enthalpy change for this reaction is -285.8 kJ per mole of H_2O . Therefore, the thermochemical equation is



The values of standard enthalpies of formation listed in Table 6.2 and in other tables are determined by direct measurement in some cases and by applying Hess's law in others. Oxides, such as water, can often be determined by direct calorimetric measurement of the combustion reaction. If you look back at Example 6.7, you will see an illustration of how Hess's law can be used to obtain the enthalpy of formation of tungsten carbide, WC.

Note that the standard enthalpy of formation of an element will depend on the form of the element. For example, the ΔH_f° for diamond equals the enthalpy change

Although the reference form is usually the stablest allotrope of an element, the choice is essentially arbitrary as long as one is consistent.

TABLE 6.2**Standard Enthalpies of Formation (at 25°C)***

Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)
$e^-(g)$	0	$\text{CH}_3\text{CHO}(g)$	-166.1	$\text{NO}_2(g)$	33.10
Bromine		$\text{CH}_3\text{CHO}(l)$	-191.8	$\text{HNO}_3(aq)$	-207.4
$\text{Br}(g)$	111.9	Chlorine		Oxygen	
$\text{Br}^-(aq)$	-121.5	$\text{Cl}(g)$	121.3	$\text{O}(g)$	249.2
$\text{Br}^-(g)$	-219.0	$\text{Cl}^-(aq)$	-167.2	$\text{O}_2(g)$	0
$\text{Br}_2(g)$	30.91	$\text{Cl}^-(g)$	-234.0	$\text{O}_3(g)$	142.7
$\text{Br}_2(l)$	0	$\text{Cl}_2(g)$	0	$\text{OH}^-(aq)$	-230.0
$\text{HBr}(g)$	-36.44	$\text{HCl}(g)$	-92.31	$\text{H}_2\text{O}(g)$	-241.8
Calcium		Fluorine		$\text{H}_2\text{O}(l)$	-285.8
$\text{Ca}(s)$	0	$\text{F}(g)$	79.39	Silicon	
$\text{Ca}^{2+}(aq)$	-542.8	$\text{F}^-(g)$	-255.1	$\text{Si}(s)$	0
$\text{CaCO}_3(s,$ calcite)	-1206.9	$\text{F}^-(aq)$	-332.6	$\text{SiCl}_4(l)$	-687.0
$\text{CaO}(s)$	-635.1	$\text{F}_2(g)$	0	$\text{SiF}_4(g)$	-1614.9
Carbon		$\text{HF}(g)$	-272.5	$\text{SiO}_2(s,$ quartz)	-910.9
$\text{C}(g)$	716.7	Hydrogen		Silver	
$\text{C}(s,$ diamond)	1.897	$\text{H}(g)$	218.0	$\text{Ag}(s)$	0
$\text{C}(s,$ graphite)	0	$\text{H}^+(aq)$	0	$\text{Ag}^+(aq)$	105.6
$\text{CCl}_4(g)$	-95.98	$\text{H}^+(g)$	1536.2	$\text{AgBr}(s)$	-100.4
$\text{CCl}_4(l)$	-135.4	$\text{H}_2(g)$	0	$\text{AgCl}(s)$	-127.1
$\text{CO}(g)$	-110.5	Iodine		$\text{AgF}(s)$	-204.6
$\text{CO}_2(g)$	-393.5	$\text{I}(g)$	106.8	$\text{AgI}(s)$	-61.84
$\text{CO}_3^{2-}(aq)$	-677.1	$\text{I}^-(aq)$	-55.19	Sodium	
$\text{CS}_2(g)$	116.9	$\text{I}^-(g)$	-194.6	$\text{Na}(g)$	107.3
$\text{CS}_2(l)$	89.70	$\text{I}_2(s)$	0	$\text{Na}(s)$	0
$\text{HCN}(g)$	135.1	$\text{HI}(g)$	26.36	$\text{Na}^+(aq)$	-240.1
$\text{HCN}(l)$	108.9	Lead		$\text{Na}^+(g)$	609.3
$\text{HCO}_3^-(aq)$	-692.0	$\text{Pb}(s)$	0	$\text{Na}_2\text{CO}_3(s)$	-1130.8
Hydrocarbons		$\text{Pb}^{2+}(aq)$	-1.7	$\text{NaCl}(s)$	-411.1
$\text{CH}_4(g)$	-74.87	$\text{PbO}(s)$	-219.4	$\text{NaHCO}_3(s)$	-950.8
$\text{C}_2\text{H}_4(g)$	52.47	$\text{PbS}(s)$	-98.32	Sulfur	
$\text{C}_2\text{H}_6(g)$	-84.68	Nitrogen		$\text{S}(g)$	277.0
$\text{C}_6\text{H}_6(l)$	49.0	$\text{N}(g)$	472.7	$\text{S}(s,$ monoclinic)	0.360
Alcohols		$\text{N}_2(g)$	0	$\text{S}(s,$ rhombic)	0
$\text{CH}_3\text{OH}(l)$	-238.7	$\text{NH}_3(g)$	-45.90	$\text{S}_2(g)$	128.6
$\text{C}_2\text{H}_5\text{OH}(l)$	-277.7	$\text{NH}_4^+(aq)$	-132.5	$\text{SO}_2(g)$	-296.8
Aldehydes		$\text{NO}(g)$	90.29	$\text{H}_2\text{S}(g)$	-20.50
$\text{HCHO}(g)$	-117				

*See Appendix C for additional values.

from the stablest form of carbon (graphite) to diamond. The thermochemical equation is



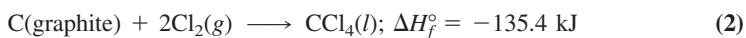
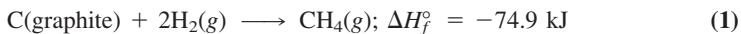
On the other hand, the ΔH_f° for graphite equals zero. Note the values of ΔH_f° for the elements listed in Table 6.2; the reference forms have zero values.

Now let us see how to use standard enthalpies of formation (listed in Table 6.2) to find the standard enthalpy change for a reaction. We will first look at this problem from the point of view of Hess's law. But when we are finished, we will note a pattern in the result, which will allow us to state a simple formula for solving this type of problem.

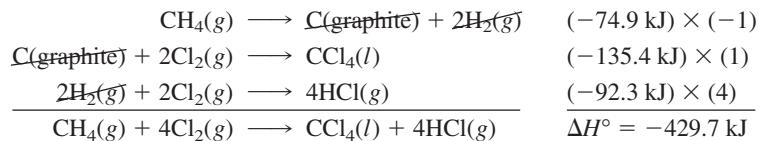
Consider the equation



From Table 6.2 you find the enthalpies of formation for $\text{CH}_4(g)$, $\text{CCl}_4(l)$, and $\text{HCl}(g)$. You can then write the following thermochemical equations:



You now apply Hess's law. Since you want CH_4 to appear on the left, and CCl_4 and 4HCl on the right, you reverse Equation 1 and add Equation 2 and $4 \times$ Equation 3.



The setup of this calculation can be greatly simplified once you closely examine what you are doing. Note that the ΔH_f° for each compound is multiplied by its coefficient in the chemical equation whose ΔH° you are calculating. Moreover, the ΔH_f° for each reactant is multiplied by a negative sign. You can symbolize the enthalpy of formation of a substance by writing the formula in parentheses following ΔH_f° . Then your calculation can be written as follows:

$$\begin{aligned} \Delta H^\circ &= [\Delta H_f^\circ(\text{CCl}_4) + 4 \Delta H_f^\circ(\text{HCl})] - [\Delta H_f^\circ(\text{CH}_4) + 4 \Delta H_f^\circ(\text{Cl}_2)] \\ &= [(-135.4) + 4(-92.3)] \text{ kJ} - [(-74.9) + 4(0)] \text{ kJ} = -429.7 \text{ kJ} \end{aligned}$$

In general, you can calculate the ΔH° for a reaction by the equation

$$\Delta H^\circ = \Sigma n \Delta H_f^\circ(\text{products}) - \Sigma m \Delta H_f^\circ(\text{reactants})$$

Here Σ is the mathematical symbol meaning “the sum of,” and m and n are the coefficients of the substances in the chemical equation.

The next two examples illustrate the calculation of enthalpies of reaction from standard enthalpies of formation.

Example 6.8

Calculating the Heat of Phase Transition from Standard Enthalpies of Formation

Use values of ΔH_f° to calculate the heat of vaporization, $\Delta H_{\text{vap}}^\circ$, of carbon disulfide at 25°C. The vaporization process is

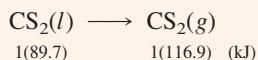


Problem Strategy The vaporization process can be treated like a chemical reaction, with the liquid as the “reactant” and the vapor as the “product.” It is convenient to record the values of ΔH_f° under the formulas in the equation, multiplying them by the coefficients in the equation. You calculate $\Delta H_{\text{vap}}^\circ$ by subtracting values for the “reactant” from values for the “product.”

(continued)

(continued)

Solution Here is the equation for the vaporization, with values of ΔH_f° multiplied by coefficients (here, all 1's).



The calculation is

$$\begin{aligned}\Delta H_{\text{vap}}^\circ &= \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ[\text{CS}_2(g)] - \Delta H_f^\circ[\text{CS}_2(l)] \\ &= (116.9 - 89.7) \text{ kJ} = \mathbf{27.2 \text{ kJ}}\end{aligned}$$

Answer Check Review your arithmetic carefully. Note that vaporization requires adding heat, so the enthalpy change should be positive.

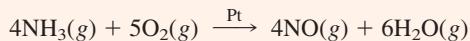
Exercise 6.9 Calculate the heat of vaporization, $\Delta H_{\text{vap}}^\circ$, of water, using standard enthalpies of formation (Table 6.2).

■ See Problems 6.77 and 6.78.

Example 6.9

Calculating the Enthalpy of Reaction from Standard Enthalpies of Formation

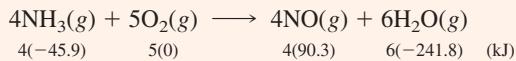
Large quantities of ammonia are used to prepare nitric acid. The first step consists of the catalytic oxidation of ammonia to nitric oxide, NO.



What is the standard enthalpy change for this reaction? Use Table 6.2 for data.

Problem Strategy You record the values of ΔH_f° under the formulas in the equation, multiplying them by the coefficients in the equation. You calculate ΔH° by subtracting values for the reactants from values for the products.

Solution Here is the equation with the ΔH_f° 's recorded beneath it:

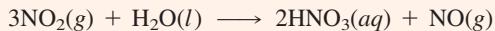


The calculation is

$$\begin{aligned}\Delta H^\circ &= \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants}) \\ &= [4 \Delta H_f^\circ(\text{NO}) + 6 \Delta H_f^\circ(\text{H}_2\text{O})] - [4 \Delta H_f^\circ(\text{NH}_3) + 5 \Delta H_f^\circ(\text{O}_2)] \\ &= [4(90.3) + 6(-241.8)] \text{ kJ} - [4(-45.9) + 5(0)] \text{ kJ} \\ &= \mathbf{-906 \text{ kJ}}\end{aligned}$$

Answer Check Be very careful of arithmetical signs—they are a likely source of mistakes. Also pay particular attention to the state of each substance. Here, for example, you must use the ΔH_f° for $\text{H}_2\text{O}(g)$, not for $\text{H}_2\text{O}(l)$.

Exercise 6.10 Calculate the enthalpy change for the following reaction:



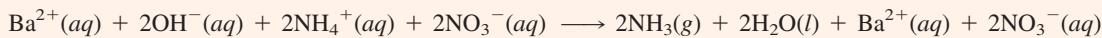
Use standard enthalpies of formation.

■ See Problems 6.79, 6.80, 6.81, and 6.82.

Enthalpies of formation can also be defined for ions. It is not possible to make thermal measurements on individual ions, so we must arbitrarily define the standard enthalpy of formation of one ion as zero. Then values for all other ions can be deduced from calorimetric data. The standard enthalpy of formation of $\text{H}^+(aq)$ is taken as zero. Values of ΔH_f° for some ions are given in Table 6.2.

Exercise 6.11

Calculate the standard enthalpy change for the reaction of an aqueous solution of barium hydroxide, $\text{Ba}(\text{OH})_2$, with an aqueous solution of ammonium nitrate, NH_4NO_3 , at 25°C. (Figure 6.1 illustrated this reaction using solids instead of solutions.) The complete ionic equation is



■ See Problems 6.83 and 6.84.

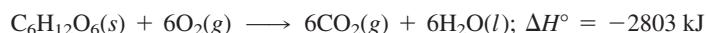
6.9**Fuels—Foods, Commercial Fuels, and Rocket Fuels**

A *fuel* is any substance that is burned or similarly reacted to provide heat and other forms of energy. The earliest use of fuels for heat came with the control of fire, which was achieved about 750,000 years ago. This major advance allowed the human species to migrate from tropical savannas and eventually to inhabit most of the earth. Through cooking, fire also increased the variety of edible food supplies and provided some protection of the food from bacterial decay. During the mid-eighteenth century, the discovery of the steam engine, which converts the chemical energy latent in fuels to mechanical energy, ushered in the Industrial Revolution. Today fuels not only heat our homes and move our cars but are absolutely necessary for every facet of modern technology. For example, fuels generate the electricity required for our modern computing and communications technologies, and they propel the rocket engines that make possible our explorations of outer space. In this section we will look at foods as fuels; at fossil fuels (which include gas, oil, and coal); at coal gasification and liquefaction; and at rocket fuels.

Foods as Fuels

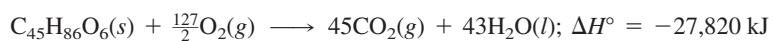
Foods fill three needs of the body: they supply substances for the growth and repair of tissue, they supply substances for the synthesis of compounds used in the regulation of body processes, and they supply energy. About 80% of the energy we need is for heat. The rest is used for muscular action, chemical processes, and other body processes. <

The body generates energy from food by the same overall process as combustion, so the overall enthalpy change is the same as the heat of combustion, which can be determined in a calorimeter. You can get some idea of the energy available from carbohydrate foods by looking at a typical one, glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). The thermochemical equation for the combustion of glucose is



One gram of glucose yields 15.6 kJ (3.73 kcal) of heat when burned.

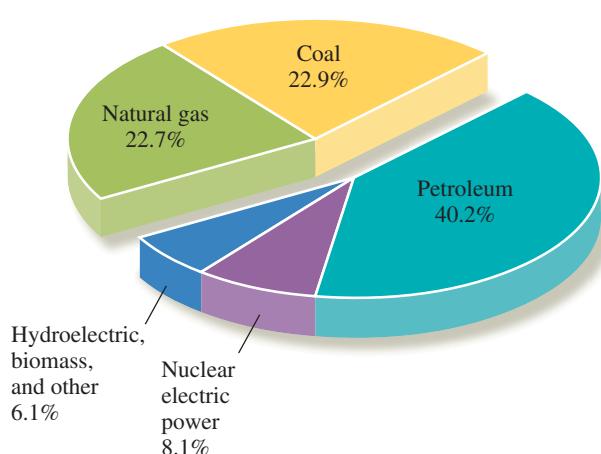
A representative fat is glyceryl trimyristate, $\text{C}_{45}\text{H}_{86}\text{O}_6$. The equation for its combustion is



One gram of this fat yields 38.5 kJ (9.20 kcal) of heat when burned. The average values quoted for carbohydrates and fats are 4.0 kcal/g and 9.0 kcal/g, respectively. < Note

The human body requires about as much energy in a day as does a 100-watt lightbulb.

In the popular literature of nutrition, the kilocalorie is referred to as the Calorie (capital C). Thus, these values are given as 4.0 Calories and 9.0 Calories.

**FIGURE 6.16****Sources of energy consumed in the United States (2005)**Data are from *Monthly Energy Review On-line*, <http://www.eia.doe.gov>.

that fats contain more than twice the fuel value per gram as do carbohydrates. Thus, by storing its fuel as fat, the body can store more fuel for a given mass of body tissue.

Fossil Fuels

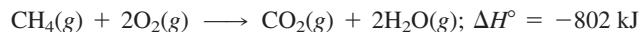
All of the fossil fuels in existence today were created millions of years ago when aquatic plants and animals were buried and compressed by layers of sediment at the bottoms of swamps and seas. Over time this organic matter was converted by bacterial decay and pressure to petroleum (oil), gas, and coal. Figure 6.16 gives the percentages of the total energy consumed in the United States from various sources. Fossil fuels account for over 80% of the total.

Anthracite, or hard coal, the oldest variety of coal, was laid down as long as 250 million years ago and may contain over 80% carbon. Bituminous coal, a younger variety of coal, has between 45% and 65% carbon. Fuel values of coals are rated in Btu's (British thermal units) per pound, which are essentially heats of combustion per pound of coal. A typical value is 13,200 Btu/lb. A Btu equals 1054 J, so 1 Btu/lb equals 2.32 J/g. Therefore, the combustion of coal in oxygen yields about 30.6 kJ/g. You can compare this value with the heat of combustion of pure carbon (graphite).



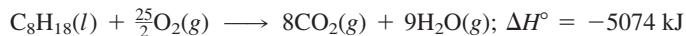
The value given in the equation is for 1 mol (12.0 g) of carbon. Per gram, you get 32.8 kJ/g, which is comparable with the values obtained for coal.

Natural gas and petroleum together account for nearly three-quarters of the fossil fuels consumed per year. They are very convenient fluid fuels, being easily transportable and having no ash. Purified natural gas is primarily methane, CH_4 , but it also contains small amounts of ethane, C_2H_6 ; propane, C_3H_8 ; and butane, C_4H_{10} . We would expect the fuel values of natural gas to be close to that for the heat of combustion of methane:



This value of ΔH° is equivalent to 50.1 kJ per gram of fuel.

Petroleum is a very complicated mixture of compounds. Gasoline, which is obtained from petroleum by chemical and physical processes, contains many different hydrocarbons (compounds of carbon and hydrogen). One such hydrocarbon is octane, C_8H_{18} . The combustion of octane evolves 5074 kJ of heat per mole.



This value of ΔH° is equivalent to 44.4 kJ/g. These combustion values indicate another reason why the fluid fossil fuels are popular: they release more heat per gram than coal does.

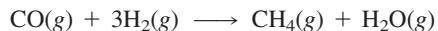
Coal Gasification and Liquefaction

The major problem with petroleum and natural gas as fuels is their relative short supply. It has been estimated that petroleum supplies will be 80% depleted by about the year 2030. Natural-gas supplies may be depleted even sooner.

Coal supplies, on the other hand, are sufficient to last several more centuries. This abundance has spurred much research into developing commercial methods for converting coal to the more easily handled liquid and gaseous fuels. Most of these methods begin by converting coal to carbon monoxide, CO. One way involves the water–gas reaction.



In this reaction, steam is passed over hot coal. Once a mixture of carbon monoxide and hydrogen is obtained, it can be transformed by various reactions into useful products. For example, in the methanation reaction (discussed at length in Chapter 14), this mixture is reacted over a catalyst to give methane.

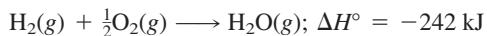


Different catalysts and different reaction conditions result in liquid fuels. An added advantage of coal gasification and coal liquefaction is that sulfur, normally present in fossil fuels, can be removed during the process. The burning of sulfur-containing coal is a major source of air pollution and acid rain.

Rocket Fuels

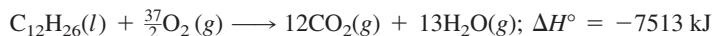
Rockets are self-contained missiles propelled by the ejection of gases from an orifice. Usually these are hot gases propelled from the rocket by the reaction of a fuel with an oxidizer. Rockets are believed to have originated with the Chinese—perhaps before the thirteenth century, which is when they began to appear in Europe. However, it was not until the twentieth century that rocket propulsion began to be studied seriously, and since World War II rockets have become major weapons. Space exploration with satellites propelled by rocket engines began in 1957 with the Russian satellite *Sputnik I*. Today weather and communications satellites are regularly put into orbit about the earth using rocket engines.

One of the factors determining which fuel and oxidizer to use is the mass of the fuel and oxidizer required. We have already seen that natural gas and gasoline have higher fuel values per gram than does coal. The difference is caused by the higher hydrogen content of natural gas and gasoline. Hydrogen is the element of lowest density, and at the same time it reacts exothermically with oxygen to give water. You might expect hydrogen and oxygen to be an ideal fuel–oxidizer combination. The thermochemical equation for the combustion of hydrogen is



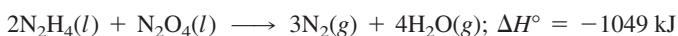
This value of ΔH° is equivalent to 120 kJ/g of fuel (H_2) compared with 50 kJ/g of methane. The second and third stages of the *Saturn V* launch vehicle that sent a three-man Apollo crew to the moon used a hydrogen/oxygen system. The launch vehicle contained liquid hydrogen (boiling at -253°C) and liquid oxygen, or LOX (boiling at -183°C).

The first stage of liftoff used kerosene and oxygen, and an unbelievable 550 metric tons (550×10^3 kg) of kerosene were burned in 2.5 minutes! It is interesting to calculate the average rate of energy production in this 2.5-minute interval. Kerosene is approximately $\text{C}_{12}\text{H}_{26}$. The thermochemical equation is



This value of ΔH° is equivalent to 44.1 kJ/g. Thus, 550×10^6 g of fuel generated 2.43×10^{10} kJ in 150 s (2.5 min). Each second, the average energy produced was 1.62×10^{11} J. This is equivalent to 1.62×10^{11} watts, or 217 million horsepower (1 horsepower equals 745.7 watts, or J/s).

The landing module for the Apollo mission used a fuel made of hydrazine, N_2H_4 , and a derivative of hydrazine. The oxidizer was dinitrogen tetroxide, N_2O_4 . These substances are normally liquids and are therefore easier to store than liquid hydrogen and oxygen. The reaction of the oxidizer with hydrazine is



Solid propellants are also used as rocket fuels. The mixture used in the booster rockets of the space shuttles (Figure 6.17) is a fuel containing aluminum metal powder. An oxidizer of ammonium perchlorate, NH_4ClO_4 , is mixed with the fuel.



FIGURE 6.17

The launching of a space shuttle

The solid fuel for the booster rockets is a mixture of aluminum metal powder and other materials with ammonium perchlorate as the oxidizer. A cloud of aluminum oxide forms as the rockets burn.

A Checklist for Review

Important Terms

energy (6.1)
kinetic energy (6.1)
joule (J) (6.1)
calorie (cal) (6.1)
potential energy (6.1)
internal energy (6.1)
law of conservation of energy (6.1)
thermodynamic system (or system) (6.2)

surroundings (6.2)
heat (6.2)
heat of reaction (6.2)
exothermic process (6.2)
endothermic process (6.2)
enthalpy (6.3)
state function (6.3)
enthalpy of reaction (6.3)
thermochemical equation (6.4)
heat capacity (6.6)

specific heat capacity (specific heat) (6.6)
calorimeter (6.6)
Hess's law of heat summation (6.7)
standard state (6.8)
allotrope (6.8)
reference form (6.8)
standard enthalpy of formation (standard heat of formation) (6.8)

Key Equations

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

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

$$\Delta H = q_p$$

$$q = C \Delta t$$

$$q = s \times m \times \Delta t$$

$$\Delta H^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$$

Summary of Facts and Concepts

Energy exists in various forms, including *kinetic energy* and *potential energy*. The SI unit of energy is the *joule* (1 calorie = 4.184 joules). The *internal energy* of a substance is the sum of the kinetic energies and potential energies of the particles making up the substance. According to the *law of conservation of energy*, the total quantity of energy remains constant.

Reactions absorb or evolve definite quantities of heat under given conditions. At constant pressure, this *heat of reaction* is the *enthalpy of reaction*, ΔH . The chemical equation plus ΔH for molar amounts of reactants is referred to as the *thermochemical equation*. With it, you can calculate the heat

for any amount of substance by *applying stoichiometry to heats of reaction*. One measures the heat of reaction in a *calorimeter*. Direct calorimetric determination of the heat of reaction requires a reaction that goes to completion without other reactions occurring at the same time. Otherwise, the heat or enthalpy of reaction is determined indirectly from other enthalpies of reaction by using *Hess's law of heat summation*. Thermochemical data are conveniently tabulated as *enthalpies of formation*. If you know the values for each substance in an equation, you can easily compute the enthalpy of reaction. As an application of thermochemistry, the last section of the chapter discusses fuels.

Media Summary

Visit the **student website** at college.hmco.com/pic/ebbing9e to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:



Prepare for Class

- **Video Lessons** Mini lectures from chemistry experts
 The Nature of Energy
 Energy, Calories, and Nutrition

- CIA Demonstration: Cool Fire
- Constant-Pressure Calorimetry
- Bomb Calorimetry (Constant Volume)
- Hess's Law
- Enthalpies of Formation



Improve Your Grade

- **Visualizations** Molecular-level animations and lab demonstration videos
Hess's Law
- **Tutorials** Animated examples and interactive activities
Hess's Law
Work, Heat, and Energy Flow
- **Flashcards** Key terms and definitions
Online Flashcards

Access these resources using the passkey available free with new texts or for purchase separately.

Learning Objectives

6.1 Energy and Its Units

- Define *energy*, *kinetic energy*, *potential energy*, and *internal energy*.
- Define the SI unit of energy *joule*, as well as the common unit of energy *calorie*.
- Calculate the kinetic energy of a moving object.
Example 6.1
- State the law of conservation of energy.

6.2 Heat of Reaction

- Define a *thermodynamic system* and its *surroundings*.
- Define *heat* and *heat of reaction*.
- Distinguish between an *exothermic process* and an *endothermic process*.

6.3 Enthalpy and Enthalpy Change

- Define *enthalpy* and *enthalpy of reaction*.
- Explain how the terms *enthalpy of reaction* and *heat of reaction* are related.
- Explain how enthalpy and internal energy are related.

6.4 Thermochemical Equations

- Define a *thermochemical equation*.
- Write a thermochemical equation given pertinent information. *Example 6.2*
- Learn the two rules for manipulating (reversing and multiplying) thermochemical equations.
- Manipulate a thermochemical equation using these rules.
Example 6.3

6.5 Applying Stoichiometry to Heats of Reaction

- Calculate the heat absorbed or evolved from a reaction given its enthalpy of reaction and the mass of a reactant or product.
Example 6.4

6.6 Measuring Heats of Reaction

- Define *heat capacity* and *specific heat*.
- Relate the heat absorbed or evolved to the specific heat, mass, and temperature change.

- **Self-Assessment Questions** Additional questions with full worked-out solutions
6 Self-Assessment Questions



ACE the Test

- Multiple-choice quizzes
3 ACE Practice Tests

- Calculate using this relation between heat and specific heat.
Example 6.5
- Define *calorimeter*.
- Calculate the enthalpy of reaction from calorimetric data (its temperature change and heat capacity). *Example 6.6*

6.7 Hess's Law

- State Hess's law of heat summation.
- Apply Hess's law to obtain the enthalpy change for one reaction from the enthalpy changes of a number of other reactions. *Example 6.7*

6.8 Standard Enthalpies of Formation

- Define *standard state* and *reference form*.
- Define *standard enthalpy of formation*.
- Calculate the heat of a phase transition using standard enthalpies of formation for the different phases.
Example 6.8
- Calculate the heat (enthalpy) of reaction from the standard enthalpies of formation of the substances in the reaction.
Example 6.9

6.9 Fuels—Foods, Commercial Fuels, and Rocket Fuels

- Define *fuel*.
- Describe the three needs of the body that are fulfilled by foods.
- Give the approximate average values quoted (per gram) for the heat values (heats of combustion) for fats and for carbohydrates.
- List the three major fossil fuels.
- Describe the processes of coal gasification and coal liquefaction.
- Describe some fuel–oxidizer systems used in rockets.

Self-Assessment and Review Questions

6.1 Define *energy*, *kinetic energy*, *potential energy*, and *internal energy*.

6.2 Define the joule in terms of SI base units.

6.3 What is the original definition of the calorie? What is the present definition?

6.4 Describe the interconversions of potential and kinetic energy in a moving pendulum. A moving pendulum eventually comes to rest. Has the energy been lost? If not, what has happened to it?

6.5 Suppose heat flows into a vessel containing a gas. As the heat flows into the gas, what happens to the gas molecules? What happens to the internal energy of the gas?

6.6 Define an *exothermic* reaction and an *endothermic* reaction. Give an example of each.

6.7 The internal energy of a substance is a state function. What does this mean?

6.8 Under what condition is the enthalpy change equal to the heat of reaction?

6.9 How does the enthalpy change for an endothermic reaction occurring at constant pressure?

6.10 Why is it important to give the states of the reactants and products when giving an equation for ΔH ?

6.11 If an equation for a reaction is doubled and then reversed, how is the value of ΔH changed?

6.12 Consider the reaction of methane, CH_4 , with oxygen, O_2 , discussed in Section 6.5. How would you set up the calculation if the problem had been to compute the heat if 10.0 g H_2O were produced (instead of 10.0 g CH_4 reacted)?

6.13 Define the heat capacity of a substance. Define the specific heat of a substance.

6.14 Describe a simple calorimeter. What measurements are needed to determine the heat of reaction?

6.15 What property of enthalpy provides the basis of Hess's law? Explain.

6.16 You discover that you cannot carry out a particular reaction for which you would like the enthalpy change. Does this mean that you will be unable to obtain this enthalpy change? Explain.

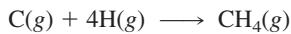
6.17 What is meant by the thermodynamic standard state?

6.18 What is meant by the reference form of an element? What is the standard enthalpy of formation of an element in its reference form?

6.19 What is meant by the standard enthalpy of formation of a substance?

6.20 Write the chemical equation for the formation reaction of $\text{H}_2\text{S}(g)$.

6.21 Is the following reaction the appropriate one to use in determining the enthalpy of formation of methane, $\text{CH}_4(g)$? Why or why not?



6.22 What is a fuel? What are the fossil fuels?

6.23 Give chemical equations for the conversion of carbon in coal to methane, CH_4 .

6.24 List some rocket fuels and corresponding oxidizers. Give thermochemical equations for the exothermic reactions of these fuels with the oxidizers.

6.25 The equation for the combustion of 2 mol of butane can be written



Which of the following produces the *least* heat?

- a. Burning 1 mol of butane.
- b. Reacting 1 mol of oxygen with excess butane.
- c. Burning enough butane to produce 1 mol of carbon dioxide.
- d. Burning enough butane to produce 1 mol of water.
- e. All of the above reactions (a, b, c, and d) produce the same amount of heat.

6.26 A 5.0-g sample of water starting at 60.0°C loses 418 J of energy in the form of heat. What is the *final* temperature of the water after this heat loss?

- a. 20°C
- b. 40°C
- c. 50°C
- d. 60°C
- e. 80°C

6.27 Hypothetical elements A_2 and B_2 react according to the following equation, forming the compound AB .



If solutions $\text{A}_2(aq)$ and $\text{B}_2(aq)$, starting at the same temperature, are mixed in a coffee-cup calorimeter, the reaction that occurs is

- a. exothermic, and the temperature of the resulting solution rises.
- b. endothermic, and the temperature of the resulting solution rises.
- c. endothermic, and the temperature of the resulting solution falls.
- d. exothermic, and the temperature of the resulting solution falls.
- e. exothermic or endothermic, depending on the original and final temperatures.

6.28 Consider the following specific heats of metals.

Metal	Specific Heat
copper	$0.385 \text{ J}/(\text{g}\cdot{}^\circ\text{C})$
magnesium	$1.02 \text{ J}/(\text{g}\cdot{}^\circ\text{C})$
mercury	$0.138 \text{ J}/(\text{g}\cdot{}^\circ\text{C})$
silver	$0.237 \text{ J}/(\text{g}\cdot{}^\circ\text{C})$

Four 25-g samples, one of each metal, and four insulated containers with identical water volumes, all start out at room temperature. Now suppose you add exactly the same quantity of heat to each metal sample. Then you place the hot metal samples in different containers of water (that all have the same volume of water). Which of the answers below is true?

- a. The water with the copper will be the hottest.
- b. The water with the magnesium will be the hottest.
- c. The water with the mercury will be the hottest.
- d. The water with the silver will be the hottest.
- e. The temperature of the water will be the same in all the cups.

Concept Explorations

6.29 Thermal Interactions

Part 1: In an insulated container, you mix 200. g of water at 80°C with 100. g of water at 20°C. After mixing, the temperature of the water is 60°C.

- How much did the temperature of the hot water change?
How much did the temperature of the cold water change?
Compare the magnitudes (positive values) of these changes.
- During the mixing, how did the heat transfer occur: from hot water to cold, or from cold water to hot?
- What quantity of heat was transferred from one sample to the other?
- How does the quantity of heat transferred to or from the hot-water sample compare with the quantity of heat transferred to or from the cold-water sample?
- Knowing these relative quantities of heat, why is the temperature change of the cold water greater than the magnitude of the temperature change of the hot water.
- A sample of hot water is mixed with a sample of cold water that has twice its mass. Predict the temperature change of each of the samples.
- You mix two samples of water, and one increases by 20°C, while the other drops by 60°C. Which of the samples has less mass? How do the masses of the two water samples compare?
- A 7-g sample of hot water is mixed with a 3-g sample of cold water. How do the temperature changes of the two water samples compare?

Part 2: A sample of water is heated from 10°C to 50°C. Can you calculate the amount of heat added to the water sample that

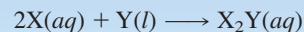
caused this temperature change? If not, what information do you need to perform this calculation?

Part 3: Two samples of water are heated from 20°C to 60°C. One of the samples requires twice as much heat to bring about this temperature change as the other. How do the masses of the two water samples compare? Explain your reasoning.

6.30 Enthalpy

- A 100.-g sample of water is placed in an insulated container and allowed to come to room temperature at 21°C. To heat the water sample to 41°C, how much heat must you add to it?

- Consider the hypothetical reaction,



being run in an insulated container that contains 100. g of solution. If the temperature of the solution changes from 21°C to 31°C, how much heat does the chemical reaction produce? How does this answer compare with that in part a? (You can assume that this solution is so dilute that it has the same heat capacity as pure water.)

- If you wanted the temperature of 100. g of this solution to increase from 21°C to 51°C, how much heat would you have to add to it? (Try to answer this question without using a formula.)
- If you had added 0.02 mol of X and 0.01 mol of Y to form the solution in part b, how many moles of X and Y would you need to bring about the temperature change described in part c.
- Judging on the basis of your answers so far, what is the enthalpy of the reaction $2X(aq) + Y(l) \longrightarrow X_2Y(aq)$?

Conceptual Problems

6.31 A small car is traveling at twice the speed of a larger car, which has twice the mass of the smaller car. Which car has the greater kinetic energy? (Or do they both have the same kinetic energy?)

6.32 The equation for the combustion of butane, C₄H₁₀, is



Which one of the following generates the least heat? Why?

- burning one mole of butane
- reacting one mole of oxygen with excess butane
- producing one mole of carbon dioxide by burning butane
- producing one mole of water by burning butane

6.33 A 250.-g sample of water at 20.0°C is placed in a freezer that is held at a constant temperature of -20.0°C. Considering the water as the “system,” answer the following questions:

- what is the sign of q_{sys} for the water after it is placed in the freezer?
- After a few hours, what will be the state of the water?
- How will the initial enthalpy for the water compare with the final enthalpy of the water after it has spent several hours in the freezer?

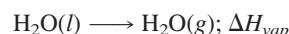
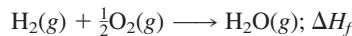
- What will the temperature of the water be after several hours in the freezer?

6.34 A 20.0-g block of iron at 50.0°C and a 20.0 g block of aluminum at 45°C are placed in contact with each other. Assume that heat is only transferred between the two blocks.



- Draw an arrow indicating the heat flow between the blocks.
- What is the sign of q_{sys} for the aluminum when the blocks first come into contact?
- What will you observe when q_{sys} for the iron is zero?
- Estimate the temperature of the Al and Fe blocks when q_{sys} of the iron equals q_{sys} of the aluminum.

6.35 What is the enthalpy change for the preparation of one mole of liquid water from the elements, given the following equations?



6.36 A block of aluminum and a block of iron, both having the same mass, are removed from a freezer and placed outside on a warm day. When the same quantity of heat has flowed into each block, which block will be warmer? Assume that neither block has yet reached the outside temperature. (See Table 6.1 for the specific heats of the metals.)

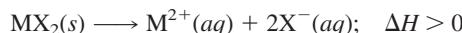
6.37 You have two samples of different metals, metal A and metal B, each having the same mass. You heat both metals to 95°C and then place each one into separate beakers containing the same quantity of water at 25°C.

- You measure the temperatures of the water in the two beakers when each metal has cooled by 10°C and find that the temperature of the water with metal A is higher than the temperature of the water with metal B. Which metal has the greater specific heat? Explain.
- After waiting a period of time, the temperature of the water in each beaker rises to a maximum value. In which beaker does the water rise to the higher value, the one with metal A or the one with metal B? Explain.

6.38 Consider the reactions of silver metal, $\text{Ag}(s)$, with each of the halogens: fluorine, $\text{F}_2(g)$, chlorine, $\text{Cl}_2(g)$, and bromine, $\text{Br}_2(l)$. What chapter data could you use to decide which reaction is most exothermic? Which reaction is that?

6.39 Tetraphosphorus trisulfide, P_4S_3 , burns in excess oxygen to give tetraphosphorus decoxide, P_4O_{10} , and sulfur dioxide, SO_2 . Suppose you have measured the enthalpy change for this reaction. How could you use it to obtain the enthalpy of formation of P_4S_3 ? What other data do you need?

6.40 A soluble salt, MX_2 , is added to water in a beaker. The equation for the dissolving of the salt is:



- Immediately after the salt dissolves, is the solution warmer or colder?
- Indicate the direction of heat flow, in or out of the beaker, while the salt dissolves.
- After the salt dissolves and the water returns to room temperature, what is the value of q for the system?

Practice Problems

Energy and Its Units

6.41 Methane, CH_4 , is a major component of marsh gas. When 0.5000 mol methane burns to produce carbon dioxide and liquid water, -445.1 kJ of heat is released. What is this heat in kilocalories?

6.42 Hydrogen sulfide, H_2S , is produced during decomposition of organic matter. When 0.5500 mol H_2S burns to produce $\text{SO}_2(g)$ and $\text{H}_2\text{O}(l)$, -309.1 kJ of heat is released. What is this heat in kilocalories?

6.43 A car whose mass is $4.85 \times 10^3 \text{ lb}$ is traveling at a speed of 57 miles per hour. What is the kinetic energy of the car in joules? In calories? See Table 1.4 for conversion factors.

6.44 A bullet weighing 245 grains is moving at a speed of $2.52 \times 10^3 \text{ ft/s}$. Calculate the kinetic energy of the bullet in joules and in calories. One grain equals 0.0648 g.

6.45 Chlorine dioxide, ClO_2 , is a reddish yellow gas used in bleaching paper pulp. The average speed of a ClO_2 molecule at 25°C is 306 m/s. What is the kinetic energy (in joules) of a ClO_2 molecule moving at this speed?

6.46 Nitrous oxide, N_2O , has been used as a dental anesthetic. The average speed of an N_2O molecule at 25°C is 379 m/s. Calculate the kinetic energy (in joules) of an N_2O molecule traveling at this speed.

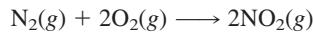
Heat of Reaction

6.47 The process of dissolving ammonium nitrate, NH_4NO_3 , in water is an endothermic process. What is the sign of q ? If you were to add some ammonium nitrate to water in a flask, would you expect the flask to feel warm or cool?

6.48 The decomposition of ozone, O_3 , to oxygen, O_2 , is an exothermic reaction. What is the sign of q ? If you were to touch

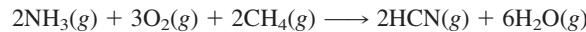
a flask in which ozone is decomposing to oxygen, would you expect the flask to feel warm or cool?

6.49 Nitric acid, a source of many nitrogen compounds, is produced from nitrogen dioxide. An old process for making nitrogen dioxide employed nitrogen and oxygen.



The reaction absorbs 66.2 kJ of heat per 2 mol NO_2 produced. Is the reaction endothermic or exothermic? What is the value of q ?

6.50 Hydrogen cyanide is used in the manufacture of clear plastics such as Lucite and Plexiglas. It is prepared from ammonia and natural gas (CH_4).



The reaction evolves 939 kJ of heat per 2 mol HCN formed. Is the reaction endothermic or exothermic? What is the value of q ?

Thermochemical Equations

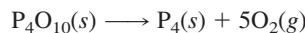
6.51 When 1 mol of iron metal reacts with hydrochloric acid at constant temperature and pressure to produce hydrogen gas and aqueous iron(II) chloride, 89.1 kJ of heat evolves. Write a thermochemical equation for this reaction.

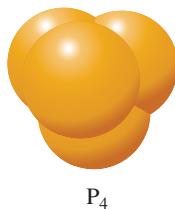
6.52 When 2 mol of potassium chlorate crystals decompose to potassium chloride crystals and oxygen gas at constant temperature and pressure, 78.0 kJ of heat is given off. Write a thermochemical equation for this reaction.

6.53 When white phosphorus burns in air, it produces phosphorus(V) oxide.

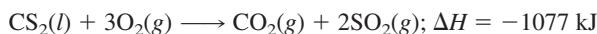


What is ΔH for the following equation?

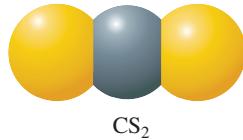




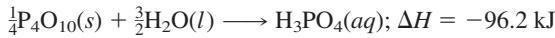
6.54 Carbon disulfide burns in air, producing carbon dioxide and sulfur dioxide.



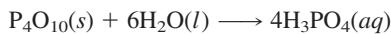
What is ΔH for the following equation?



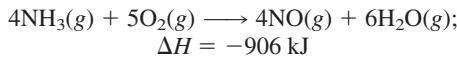
6.55 Phosphoric acid, H₃PO₄, can be prepared by the reaction of phosphorus(V) oxide, P₄O₁₀, with water.



What is ΔH for the reaction involving 1 mol of P₄O₁₀?



6.56 With a platinum catalyst, ammonia will burn in oxygen to give nitric oxide, NO.



What is the enthalpy change for the following reaction?



Stoichiometry of Reaction Heats

6.57 Colorless nitric oxide, NO, combines with oxygen to form nitrogen dioxide, NO₂, a brown gas.



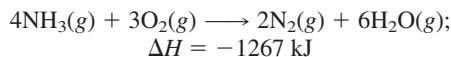
What is the enthalpy change per gram of nitric oxide?

6.58 Hydrogen, H₂, is used as a rocket fuel. The hydrogen is burned in oxygen to produce water vapor.



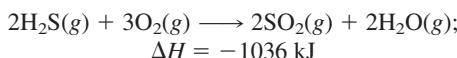
What is the enthalpy change per gram of hydrogen?

6.59 Ammonia burns in the presence of a copper catalyst to form nitrogen gas.



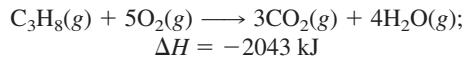
What is the enthalpy change to burn 35.8 g of ammonia?

6.60 Hydrogen sulfide, H₂S, is a foul-smelling gas. It burns to form sulfur dioxide.

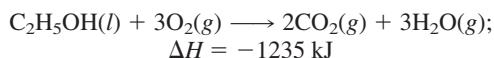


Calculate the enthalpy change to burn 28.5 g of hydrogen sulfide.

6.61 Propane, C₃H₈, is a common fuel gas. Use the following to calculate the grams of propane you would need to provide 369 kJ of heat.



6.62 Ethanol, C₂H₅OH, is mixed with gasoline and sold as gasohol. Use the following to calculate the grams of ethanol needed to provide 358 kJ of heat.



Heat Capacity and Calorimetry

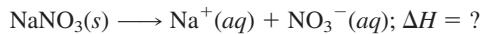
6.63 You wish to heat water to make coffee. How much heat (in joules) must be used to raise the temperature of 0.180 kg of tap water (enough for one cup of coffee) from 19°C to 96°C (near the ideal brewing temperature)? Assume the specific heat is that of pure water, 4.18 J/(g·°C).

6.64 An iron skillet weighing 1.28 kg is heated on a stove to 178°C. Suppose the skillet is cooled to room temperature, 21°C. How much heat energy (in joules) must be removed to effect this cooling? The specific heat of iron is 0.449 J/(g·°C).

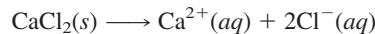
6.65 When steam condenses to liquid water, 2.26 kJ of heat is released per gram. The heat from 168 g of steam is used to heat a room containing 6.44×10^4 g of air (20 ft × 12 ft × 8 ft). The specific heat of air at normal pressure is 1.015 J/(g·°C). What is the change in air temperature, assuming the heat from the steam is all absorbed by air?

6.66 When ice at 0°C melts to liquid water at 0°C, it absorbs 0.334 kJ of heat per gram. Suppose the heat needed to melt 31.5 g of ice is absorbed from the water contained in a glass. If this water has a mass of 0.210 kg and a temperature of 21.0°C, what is the final temperature of the water? (Note that you will also have 31.5 g of water at 0°C from the ice.)

6.67 When 15.3 g of sodium nitrate, NaNO₃, was dissolved in water in a calorimeter, the temperature fell from 25.00°C to 21.56°C. If the heat capacity of the solution and the calorimeter is 1071 J/°C, what is the enthalpy change when 1 mol of sodium nitrate dissolves in water? The solution process is



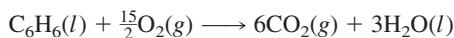
6.68 When 23.6 g of calcium chloride, CaCl₂, was dissolved in water in a calorimeter, the temperature rose from 25.0°C to 38.7°C. If the heat capacity of the solution and the calorimeter is 1258 J/°C, what is the enthalpy change when 1.20 mol of calcium chloride dissolves in water? The solution process is



6.69 A sample of ethanol, C₂H₅OH, weighing 2.84 g was burned in an excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rose from 25.00°C to 33.73°C. If the heat capacity of the calorimeter and contents was 9.63 kJ/°C, what is the value of q for burning 1 mol of ethanol at constant volume and 25.00°C? The reaction is

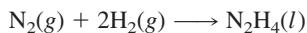


6.70 A sample of benzene, C_6H_6 , weighing 3.51 g was burned in an excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rose from $25.00^\circ C$ to $37.18^\circ C$. If the heat capacity of the calorimeter and contents was $12.05 \text{ kJ}/^\circ C$, what is the value of q for burning 1.25 mol of benzene at constant volume and $25.00^\circ C$? The reaction is

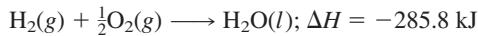
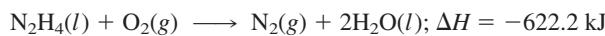


Hess's Law

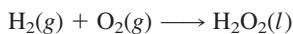
6.71 Hydrazine, N_2H_4 , is a colorless liquid used as a rocket fuel. What is the enthalpy change for the process in which hydrazine is formed from its elements?



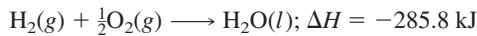
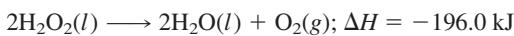
Use the following reactions and enthalpy changes:



6.72 Hydrogen peroxide, H_2O_2 , is a colorless liquid whose solutions are used as a bleach and an antiseptic. H_2O_2 can be prepared in a process whose overall change is



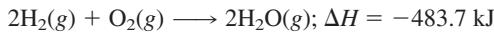
Calculate the enthalpy change using the following data:



6.73 Ammonia will burn in the presence of a platinum catalyst to produce nitric oxide, NO.



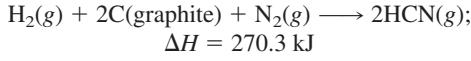
What is the heat of reaction at constant pressure? Use the following thermochemical equations:



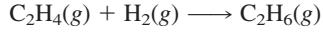
6.74 Hydrogen cyanide is a highly poisonous, volatile liquid. It can be prepared by the reaction



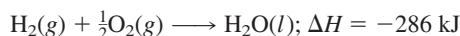
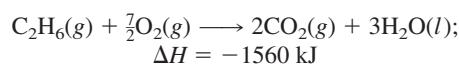
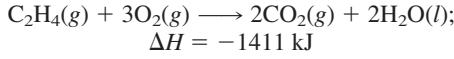
What is the heat of reaction at constant pressure? Use the following thermochemical equations:



6.75 Compounds with carbon–carbon double bonds, such as ethylene, C_2H_4 , add hydrogen in a reaction called hydrogenation.



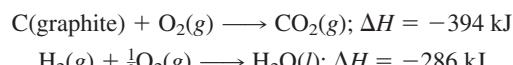
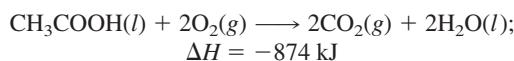
Calculate the enthalpy change for this reaction, using the following combustion data:



6.76 Acetic acid, CH_3COOH , is contained in vinegar. Suppose acetic acid was formed from its elements, according to the following equation:



Find the enthalpy change, ΔH , for this reaction, using the following data:



Standard Enthalpies of Formation

6.77 The cooling effect of alcohol on the skin is due to its evaporation. Calculate the heat of vaporization of ethanol (ethyl alcohol), C_2H_5OH .



The standard enthalpy of formation of $C_2H_5OH(l)$ is -277.7 kJ/mol and that of $C_2H_5OH(g)$ is -235.4 kJ/mol .

6.78 Carbon tetrachloride, CCl_4 , is a liquid used as an industrial solvent and in the preparation of fluorocarbons. What is the heat of vaporization of carbon tetrachloride?



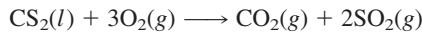
Use standard enthalpies of formation (Table 6.2).

6.79 Hydrogen sulfide gas is a poisonous gas with the odor of rotten eggs. It occurs in natural gas and is produced during the decay of organic matter, which contains sulfur. The gas burns in oxygen as follows:



Calculate the standard enthalpy change for this reaction using standard enthalpies of formation.

6.80 Carbon disulfide is a colorless liquid. When pure, it is nearly odorless, but the commercial product smells vile. Carbon disulfide is used in the manufacture of rayon and cellophane. The liquid burns as follows:



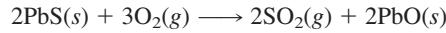
Calculate the standard enthalpy change for this reaction using standard enthalpies of formation.

6.81 Iron is obtained from iron ore by reduction with carbon monoxide. The overall reaction is



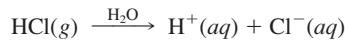
Calculate the standard enthalpy change for this equation. See Appendix C for data.

6.82 The first step in the preparation of lead from its ore (galena, PbS) consists of roasting the ore.



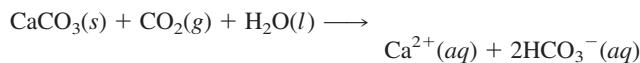
Calculate the standard enthalpy change for this reaction, using enthalpies of formation (see Appendix C).

6.83 Hydrogen chloride gas dissolves in water to form hydrochloric acid (an ionic solution).



Find ΔH° for the above reaction. The data are given in Table 6.2.

6.84 Carbon dioxide from the atmosphere “weathers,” or dissolves, limestone (CaCO_3) by the reaction



Obtain ΔH° for this reaction. See Table 6.2 for the data.

6.85 The Group IIA carbonates decompose when heated. For example,



Use enthalpies of formation (see Appendix C) and calculate the heat required to decompose 10.0 g of magnesium carbonate.

6.86 The Group IIA carbonates decompose when heated. For example,



Use enthalpies of formation (see Appendix C) and calculate the heat required to decompose 10.0 g of barium carbonate.

General Problems

6.87 The energy, E , needed to move an object a distance d by applying a force F is $E = F \times d$. What must be the SI unit of force if this equation is to be consistent with the SI unit of energy for E ?

6.88 The potential energy of an object in the gravitational field of the earth is $E_p = mgh$. What must be the SI unit of g if this equation is to be consistent with the SI unit of energy for E_p ?

6.89 Liquid hydrogen peroxide has been used as a propellant for rockets. Hydrogen peroxide decomposes into oxygen and water, giving off heat energy equal to 686 Btu per pound of propellant. What is this energy in joules per gram of hydrogen peroxide? (1 Btu = 252 cal; see also Table 1.4.)

6.90 Hydrogen is an ideal fuel in many respects; for example, the product of its combustion, water, is nonpolluting. The heat given off in burning hydrogen to gaseous water is 5.16×10^4 Btu per pound. What is this heat energy in joules per gram? (1 Btu = 252 cal; see also Table 1.4.)

6.91 Niagara Falls has a height of 167 ft (American Falls). What is the potential energy in joules of 1.00 lb of water at the top of the falls if we take water at the bottom to have a potential energy of zero? What would be the speed of this water at the bottom of the falls if we neglect friction during the descent of the water?



6.92 Any object, be it a space satellite or a molecule, must attain an initial upward velocity of at least 11.2 km/s in order to escape the gravitational attraction of the earth. What would be

the kinetic energy in joules of a satellite weighing 2354 lb that has the speed equal to this escape velocity of 11.2 km/s?

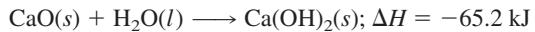


6.93 When calcium carbonate, CaCO_3 (the major constituent of limestone and seashells), is heated, it decomposes to calcium oxide (quicklime).



How much heat is required to decompose 21.3 g of calcium carbonate?

6.94 Calcium oxide (quicklime) reacts with water to produce calcium hydroxide (slaked lime).



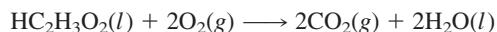
The heat released by this reaction is sufficient to ignite paper. How much heat is released when 24.5 g of calcium oxide reacts?

6.95 Formic acid, HCHO_2 , was first discovered in ants (*formica* is Latin for “ant”). In an experiment, 5.48 g of formic acid was burned at constant pressure.



If 30.3 kJ of heat evolved, what is ΔH per mole of formic acid?

6.96 Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is the sour constituent of vinegar (*acetum* is Latin for “vinegar”). In an experiment, 3.58 g of acetic acid was burned.



If 52.0 kJ of heat evolved, what is ΔH per mole of acetic acid?

6.97 Suppose you mix 21.0 g of water at 52.7°C with 54.9 g of water at 31.5°C in an insulated cup. What is the maximum temperature of the solution after mixing?

6.98 Suppose you mix 20.5 g of water at 66.2°C with 45.4 g of water at 35.7°C in an insulated cup. What is the maximum temperature of the solution after mixing?

6.99 A piece of lead of mass 121.6 g was heated by an electrical coil. From the resistance of the coil, the current, and the time the current flowed, it was calculated that 235 J of heat was added to the lead. The temperature of the lead rose from 20.4°C to 35.5°C. What is the specific heat of the lead?

6.100 The specific heat of copper metal was determined by putting a piece of the metal weighing 35.4 g in hot water. The quantity of heat absorbed by the metal was calculated to be 47.0 J from the temperature drop of the water. What was the specific heat of the metal if the temperature of the metal rose 3.45°C?

6.101 A 50.0-g sample of water at 100.00°C was placed in an insulated cup. Then 25.3 g of zinc metal at 25.00°C was added to the water. The temperature of the water dropped to 96.68°C. What is the specific heat of zinc?

6.102 A 19.6-g sample of a metal was heated to 61.67°C. When the metal was placed into 26.7 g of water in a calorimeter, the temperature of the water increased from 25.00°C to 30.00°C. What is the specific heat of the metal?

6.103 A 14.1-mL sample of 0.996 M NaOH is mixed with 32.3 mL of 0.905 M HCl in a coffee-cup calorimeter (see Section 6.6 of your text for a description of a coffee-cup calorimeter). The enthalpy of the reaction, written with the lowest whole-number coefficients, is −55.8 kJ. Both solutions are at 21.6°C prior to mixing and reacting. What is the final temperature of the reaction mixture? When solving this problem, assume that no heat is lost from the calorimeter to the surroundings, the density of all solutions is 1.00 g/mL, the specific heat of all solutions is the same as that of water, and volumes are additive.

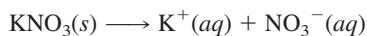
6.104 A 29.1-mL sample of 1.05 M KOH is mixed with 20.9 mL of 1.07 M HBr in a coffee-cup calorimeter (see Section 6.6 of your text for a description of a coffee-cup calorimeter). The enthalpy of the reaction, written with the lowest whole-number coefficients, is −55.8 kJ. Both solutions are at 21.8°C prior to mixing and reacting. What is the final temperature of the reaction mixture? When solving this problem, assume that no heat is lost from the calorimeter to the surroundings, the density of all solutions is 1.00 g/mL, and volumes are additive.

6.105 In a calorimetric experiment, 6.48 g of lithium hydroxide, LiOH, was dissolved in water. The temperature of the calorimeter rose from 25.00°C to 36.66°C. What is ΔH for the solution process?



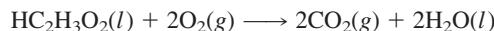
The heat capacity of the calorimeter and its contents is 547 J/°C.

6.106 When 21.45 g of potassium nitrate, KNO₃, was dissolved in water in a calorimeter, the temperature fell from 25.00°C to 14.14°C. What is the ΔH for the solution process?



The heat capacity of the calorimeter and its contents is 682 J/°C.

6.107 A 10.00-g sample of acetic acid, HC₂H₃O₂, was burned in a bomb calorimeter in an excess of oxygen.



The temperature of the calorimeter rose from 25.00°C to 35.84°C. If the heat capacity of the calorimeter and its contents is 13.43 kJ/°C, what is the enthalpy change for the reaction?

6.108 The sugar arabinose, C₅H₁₀O₅, is burned completely in oxygen in a calorimeter.



Burning a 0.548-g sample caused the temperature to rise from 20.00°C to 20.54°C. The heat capacity of the calorimeter and its contents is 15.8 kJ/°C. Calculate ΔH for the combustion reaction per mole of arabinose.

6.109 Hydrogen sulfide, H₂S, is a poisonous gas with the odor of rotten eggs. The reaction for the formation of H₂S from the elements is



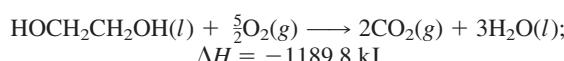
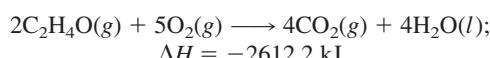
Use Hess's law to obtain the enthalpy change for this reaction from the following enthalpy changes:



6.110 Ethylene glycol, HOCH₂CH₂OH, is used as antifreeze. It is produced from ethylene oxide, C₂H₄O, by the reaction



Use Hess's law to obtain the enthalpy change for this reaction from the following enthalpy changes:



6.111 Hydrogen, H₂, is prepared by *steam reforming*, in which hydrocarbons are reacted with steam. For CH₄,



Calculate the enthalpy change ΔH° for this reaction, using standard enthalpies of formation.

6.112 Hydrogen is prepared from natural gas (mainly methane, CH₄) by partial oxidation.



Calculate the enthalpy change ΔH° for this reaction, using standard enthalpies of formation.

6.113 Calcium oxide, CaO, is prepared by heating calcium carbonate (from limestone and seashells).



Calculate the standard enthalpy of reaction, using enthalpies of formation. The ΔH_f° of CaO(s) is −635 kJ/mol. Other values are given in Table 6.2.

6.114 Sodium carbonate, Na_2CO_3 , is used to manufacture glass. It is obtained from sodium hydrogen carbonate, NaHCO_3 , by heating.



Calculate the standard enthalpy of reaction, using enthalpies of formation (Table 6.2).

6.115 Calculate the heat released when 2.000 L O_2 with a density of 1.11 g/L at 25°C reacts with an excess of hydrogen to form liquid water at 25°C.

6.116 Calculate the heat released when 4.000 L Cl_2 with a density of 2.46 g/L at 25°C reacts with an excess of sodium metal to form solid sodium chloride at 25°C.

6.117 Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is common table sugar. The enthalpy change at 25°C and 1 atm for the complete burning of 1 mol of sucrose in oxygen to give $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ is −5641 kJ. From this and from data given in Table 6.2, calculate the standard enthalpy of formation of sucrose.

6.118 Acetone, CH_3COCH_3 , is a liquid solvent. The enthalpy change at 25°C and 1 atm for the complete burning of 1 mol of acetone in oxygen to give $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ is −1791 kJ. From

this and from data given in Table 6.2, calculate the standard enthalpy of formation of acetone.

6.119 Ammonium nitrate is an oxidizing agent and can give rise to explosive mixtures. A mixture of 2.00 mol of powdered aluminum and 3.00 mol of ammonium nitrate crystals reacts exothermically, yielding nitrogen gas, water vapor, and aluminum oxide. How many grams of the mixture are required to provide 245 kJ of heat? See Appendix C for data.

6.120 The thermite reaction is a very exothermic reaction; it has been used to produce liquid iron for welding. A mixture of 2 mol of powdered aluminum metal and 1 mol of iron(III) oxide yields liquid iron and solid aluminum oxide. How many grams of the mixture are needed to produce 348 kJ of heat? See Appendix C for data.

6.121 Describe the physical characteristics of white phosphorus. Is it found in any modern matches? Why or why not?

6.122 What is the phosphorus compound used in “strike anywhere” matches. What is the chemical equation for the burning of this compound in air?

Strategy Problems

6.123 How fast (in meters per second) must an iron ball with a mass of 56.6 g be traveling in order to have a kinetic energy of 15.75 J? The density of iron is 7.87 g/cm³.

6.124 Sulfur dioxide gas reacts with oxygen, $\text{O}_2(g)$, to produce $\text{SO}_3(g)$. This reaction releases 99.0 kJ of heat (at constant pressure) for each mole of sulfur dioxide that reacts. Write the thermochemical equation for the reaction of 2 mol of sulfur dioxide, and then also for the decomposition of 3 mol of sulfur trioxide gas into oxygen gas and sulfur dioxide gas. Do you need any other information to answer either question?

6.125 When solid iron burns in oxygen gas (at constant pressure) to produce $\text{Fe}_2\text{O}_3(s)$, 1651 kJ of heat is released for every 4 mol of iron burned. How much heat is released when 10.3 g $\text{Fe}_2\text{O}_3(s)$ is produced (at constant pressure)? What additional information would you need to calculate the heat released to produce this much $\text{Fe}_2\text{O}_3(s)$ if you burned iron in ozone gas, $\text{O}_3(g)$, instead of $\text{O}_2(g)$?

6.126 How many grams of oxygen gas are required to produce 7.60 kJ of heat when hydrogen gas burns at constant pressure to produce gaseous water?



Liquid water has a heat of vaporization of 44.0 kJ per mole at 25°C.

6.127 Hydrogen is burned in oxygen to release heat. How many grams of hydrogen gas must be burned to release enough heat to warm a 50.0-g block of iron, giving 2 mol of water?



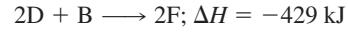
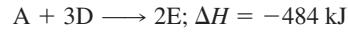
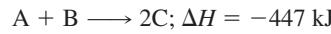
Iron has a specific heat of 0.449 J/(g·°C).

6.128 A piece of iron was heated to 95.4°C and dropped into a constant-pressure calorimeter containing 284 g of water at 32.2°C. The final temperature of the water and iron was 51.9°C. Assuming that the calorimeter itself absorbs a negligible amount

of heat, what was the mass (in grams) of the piece of iron? The specific heat of iron is 0.449 J/(g·°C), and the specific heat of water is 4.18 J/(g·°C).

6.129 The enthalpy of combustion, ΔH , for benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is −3226 kJ/mol. When a sample of benzoic acid was burned in a calorimeter (at constant pressure), the temperature of the calorimeter and contents rose from 23.44°C to 27.65°C. The heat capacity of the calorimeter and contents was 12.41 kJ/°C. What mass of benzoic acid was burned?

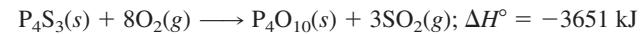
6.130 Given the following (hypothetical) thermochemical equations:



Calculate ΔH , in kJ, for the equation



6.131 The head of a “strike anywhere” match contains tetraphosphorus trisulfide, P_4S_3 . In an experiment, a student burned this compound in an excess of oxygen and found that it evolved 3651 kJ of heat per mole of P_4S_3 at a constant pressure of 1 atm. She wrote the following thermochemical equation:



Calculate the standard enthalpy of formation of P_4S_3 , using this student’s result and the following standard enthalpies of formation: $\text{P}_4\text{O}_{10}(s)$, −3009.9 kJ/mol; $\text{SO}_2(g)$, −296.8 kJ/mol. How does this value compare with the value given in Appendix C?

6.132 Toluene, $\text{C}_6\text{H}_5\text{CH}_3$, has an enthalpy of combustion of −3908 kJ/mol. Using data from Appendix C, calculate the enthalpy of formation of toluene.

Cumulative-Skills Problems

6.133 What will be the final temperature of a mixture made from 25.0 g of water at 15.0°C, from 45.0 g of water at 50.0°C, and from 15.0 g of water at 37.0°C?

6.134 What will be the final temperature of a mixture made from equal masses of the following: water at 25.0°C, ethanol at 35.5°C, and iron at 95°C?

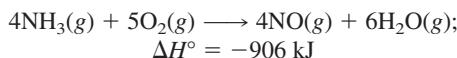
6.135 Graphite is burned in oxygen to give carbon monoxide and carbon dioxide. If the product mixture is 33% CO and 67% CO₂ by mass, what is the heat from the combustion of 1.00 g of graphite?

6.136 A sample of natural gas is 80.0% CH₄ and 20.0% C₂H₆ by mass. What is the heat from the combustion of 1.00 g of this mixture? Assume the products are CO₂(g) and H₂O(l).

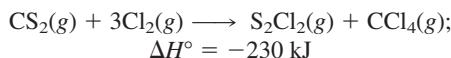
6.137 A sample containing 2.00 mol of graphite reacts completely with a limited quantity of oxygen at 25°C and 1.0 atm pressure, producing 481 kJ of heat and a mixture of CO and CO₂. Calculate the masses of CO and CO₂ produced.

6.138 A 10.0-g sample of a mixture of CH₄ and C₂H₄ reacts with oxygen at 25°C and 1 atm to produce CO₂(g) and H₂O(l). If the reaction produces 520 kJ of heat, what is the mass percentage of CH₄ in the mixture?

6.139 How much heat is released when a mixture containing 10.0 g NH₃ and 20.0 g O₂ reacts by the following equation?



6.140 How much heat is released when a mixture containing 10.0 g CS₂ and 10.0 g Cl₂ reacts by the following equation?



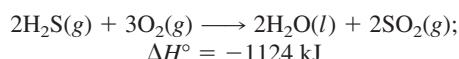
6.141 Consider the Haber process:



The density of ammonia at 25°C and 1.00 atm is 0.696 g/L. The density of nitrogen, N₂, is 1.145 g/L, and the molar heat capacity is 29.12 J/(mol·°C). (a) How much heat is evolved in the production of 1.00 L of ammonia at 25°C and 1.00 atm? (b) What percentage of this heat is required to heat the nitrogen required

for this reaction (0.500 L) from 25°C to 400°C, the temperature at which the Haber process is run?

6.142 An industrial process for manufacturing sulfuric acid, H₂SO₄, uses hydrogen sulfide, H₂S, from the purification of natural gas. In the first step of this process, the hydrogen sulfide is burned to obtain sulfur dioxide, SO₂.



The density of sulfur dioxide at 25°C and 1.00 atm is 2.62 g/L, and the molar heat capacity is 30.2 J/(mol·°C). (a) How much heat would be evolved in producing 1.00 L of SO₂ at 25°C and 1.00 atm? (b) Suppose heat from this reaction is used to heat 1.00 L of SO₂ from 25°C and 1.00 atm to 500°C for its use in the next step of the process. What percentage of the heat evolved is required for this?

6.143 The carbon dioxide exhaled in the breath of astronauts is often removed from the spacecraft by reaction with lithium hydroxide.



Estimate the grams of lithium hydroxide required per astronaut per day. Assume that each astronaut requires 2.50×10^3 kcal of energy per day. Further assume that this energy can be equated to the heat of combustion of a quantity of glucose, C₆H₁₂O₆, to CO₂(g) and H₂O(l). From the amount of glucose required to give 2.50×10^3 kcal of heat, calculate the amount of CO₂ produced and hence the amount of LiOH required. The ΔH_f° for glucose(s) is -1273 kJ/mol .

6.144 A rebreathing gas mask contains potassium superoxide, KO₂, which reacts with moisture in the breath to give oxygen.



Estimate the grams of potassium superoxide required to supply a person's oxygen needs for one hour. Assume a person requires 1.00×10^2 kcal of energy for this time period. Further assume that this energy can be equated to the heat of combustion of a quantity of glucose, C₆H₁₂O₆, to CO₂(g) and H₂O(l). From the amount of glucose required to give 1.00×10^2 kcal of heat, calculate the amount of oxygen consumed and hence the amount of KO₂ required. The ΔH_f° for glucose(s) is -1273 kJ/mol .