5 Gases

Contents

The steaming fumaroles located in Bjarnarflag, Iceland release a variety of gases.

Matter exists in three distinct physical states: gas, liquid, and solid. Although relatively few substances exist in the gaseous state under typical conditions, gases are very important. For example, we live immersed in a gaseous solution. The earth's atmosphere is a mixture of gases that consists mainly of elemental nitrogen (N_2) and oxygen (O_2). The atmosphere both supports life and acts as a waste receptacle for the exhaust gases that accompany many industrial processes. The chemical reactions of these waste gases in the atmosphere lead to various types of pollution, including smog and acid rain. The gases in the atmosphere also shield us from harmful radiation from the sun and keep the earth warm by reflecting heat radiation back toward the earth. In fact, there is now great concern that an increase in atmospheric carbon dioxide, a product of the combustion of fossil fuels, is causing a dangerous warming of the earth.

In this chapter we will look carefully at the properties of gases. First we will see how measurements of gas properties lead to various types of laws—statements that show how the properties are related to each other. Then we will construct a model to explain why gases behave as they do. This model will show how the behavior of the individual particles of a gas leads to the observed properties of the gas itself (a collection of many, many particles).

The study of gases provides an excellent example of the scientific method in action. It illustrates how observations lead to natural laws, which in turn can be accounted for by models.

5.1 Pressure

A gas uniformly fills any container, is easily compressed, and mixes completely with any other gas. One of the most obvious properties of a gas is that it exerts pressure on its surroundings. For example, when you blow up a balloon, the air inside pushes against the elastic sides of the balloon and keeps it firm.

As a gas, water occupies 1200 times as much space as it does as a liquid at 25°C and atmospheric pressure.

As mentioned earlier, the gases most familiar to us form the earth's atmosphere. The pressure exerted by this gaseous mixture that we call air can be dramatically demonstrated by the experiment shown in Fig. 5.1. A small volume of water is placed in a metal can,

Visualization: Collapsing Can

FIGURE 5.1
The pressure exerted by the gases in the atmosphere can be demonstrated by boiling water in a large metal can (a) and then turning off the heat and sealing the can. As the can cools, the water vapor condenses, lowering the gas pressure inside the can. This causes the can to crumple (b).

and the water is boiled, which fills the can with steam. The can is then sealed and allowed to cool. Why does the can collapse as it cools? It is the atmospheric pressure that crumples the can. When the can is cooled after being sealed so that no air can flow in, the water vapor (steam) condenses to a very small volume of liquid water. As a gas, the water filled the can, but when it is condensed to a liquid, the liquid does not come close to filling the can. The H_2O molecules formerly present as a gas are now collected in a very small volume of liquid, and there are very few molecules of gas left to exert pressure outward and counteract the air pressure. As a result, the pressure exerted by the gas molecules in the atmosphere smashes the can.

A device to measure atmospheric pressure, the **barometer,** was invented in 1643 by an Italian scientist named Evangelista Torricelli (1608–1647), who had been a student of Galileo. Torricelli's barometer is constructed by filling a glass tube with liquid mercury and inverting it in a dish of mercury, as shown in Fig. 5.2. Notice that a large quantity of mercury stays in the tube. In fact, at sea level the height of this column of mercury averages 760 mm. Why does this mercury stay in the tube, seemingly in defiance of gravity? Figure 5.2 illustrates how the pressure exerted by the atmospheric gases on the surface of mercury in the dish keeps the mercury in the tube.

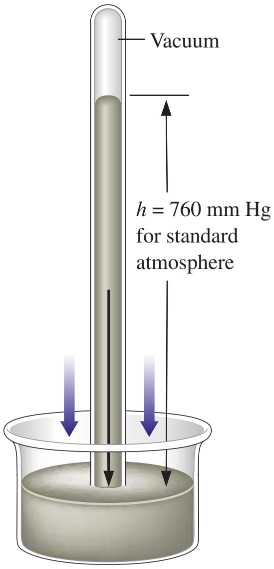


FIGURE 5.2
A torricellian barometer. The tube, completely filled with mercury, is inverted in a dish of mercury. Mercury flows out of the tube until the pressure of the column of mercury (shown by the black arrow) "standing on the surface" of the mercury in the dish is equal to the pressure of the air (shown by the purple arrows) on the rest of the surface of the mercury in the dish.

Atmospheric pressure results from the mass of the air being pulled toward the center of the earth by gravity—in other words, it results from the weight of the air. Changing weather conditions cause the atmospheric pressure to vary, so the height of the column of Hg supported by the atmosphere at sea level varies; it is not always 760 mm. The meteorologist who says a "low" is approaching means that the atmospheric pressure is going to decrease. This condition often occurs in conjunction with a storm.

Atmospheric pressure also varies with altitude. For example, when Torricelli's experiment is done in Breckenridge, Colorado (elevation 9600 feet), the atmosphere supports a column of mercury only about 520 mm high because the air is "thinner." That is, there is less air pushing down on the earth's surface at Breckenridge than at sea level.

Soon after Torricelli died, a German physicist named Otto von Guericke invented an air pump. In a famous demonstration for the King of Prussia in 1663, Guericke placed two hemispheres together, pumped the air out of the resulting sphere through a valve, and showed that teams of horses could not pull the hemispheres apart. Then, after secretly opening the air valve, Guericke easily separated the hemispheres by hand. The King of Prussia was so impressed that he awarded Guericke a lifetime pension!

Units of Pressure

Because instruments used for measuring pressure, such as the **manometer** (Fig. 5.3), often contain mercury, the most commonly used units for pressure are based on the height

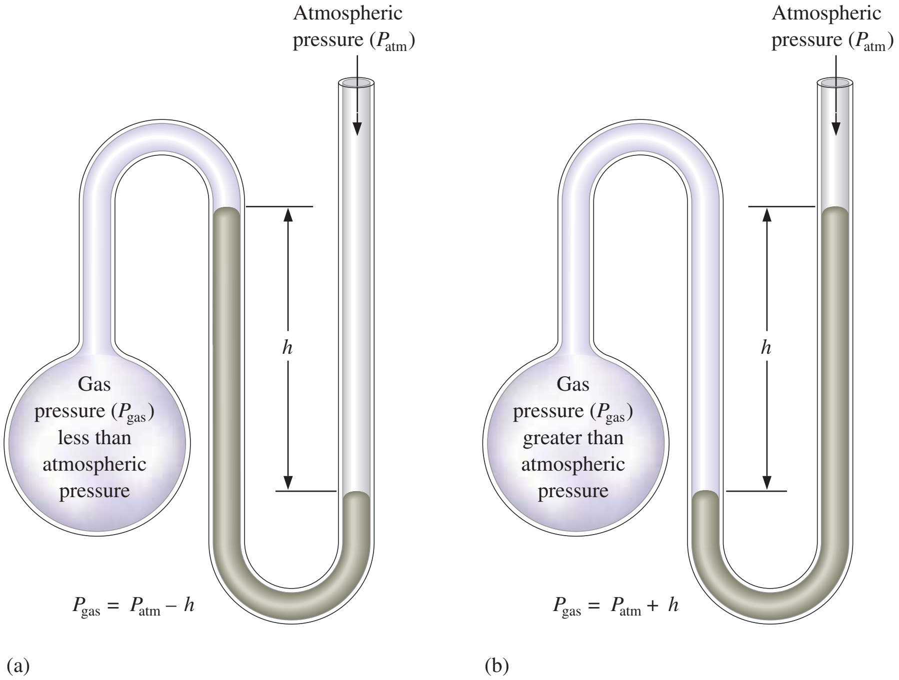


FIGURE 5.3
A simple manometer, a device for measuring the pressure of a gas in a container. The pressure of the gas is given by h (the difference in mercury levels) in units of torr (equivalent to mm Hg). (a) Gas pressure = atmospheric pressure − h. (b) Gas pressure = atmospheric pressure + h.

Checking tire pressure.

of the mercury column (in millimeters) that the gas pressure can support. The unit **mm Hg** (millimeter of mercury) is often called the **torr** in honor of Torricelli. The terms *torr* and *mm Hg* are used interchangeably by chemists. A related unit for pressure is the **standard atmosphere** (abbreviated atm):

$$1 \text{ standard atmosphere} = 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

However, since pressure is defined as force per unit area,

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

the fundamental units of pressure involve units of force divided by units of area. In the SI system, the unit of force is the newton (N) and the unit of area is meters squared (m^2). (For a review of the SI system, see Chapter 1.) Thus the unit of pressure in the SI system is newtons per meter squared (N/m^2) and is called the **pascal** (Pa). In terms of pascals, the standard atmosphere is

$$1 \text{ standard atmosphere} = 101{,}325 \text{ Pa}$$

Thus 1 atmosphere is about 10^5 pascals. Since the pascal is so small, and since it is not commonly used in the United States, we will use it sparingly in this book. However, converting from torrs or atmospheres to pascals is straightforward, as shown in Sample Exercise 5.1.

Sample Exercise 5.1

Pressure Conversions

The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals.

1 atm = 760 mm Hg
= 760 torr
= 101,325 Pa
= 29.92 in Hg
= 14.7 lb/in^2

Solution

$$49 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 6.4 \times 10^{-2} \text{ atm}$$

$$6.4 \times 10^{-2} \cancel{\text{atm}} \times \frac{101{,}325 \text{ Pa}}{1 \cancel{\text{atm}}} = 6.5 \times 10^{3} \text{ Pa}$$

See Exercises 5.27 and 5.28.

5.2 The Gas Laws of Boyle, Charles, and Avogadro

In this section we will consider several mathematical laws that relate the properties of gases. These laws derive from experiments involving careful measurements of the relevant gas properties. From these experimental results, the mathematical relationships among the properties can be discovered. These relationships are often represented pictorially by means of graphs (plots).

We will take a historical approach to these laws to give you some perspective on the scientific method in action.

Visualization: Boyle's Law: A Graphical View

Boyle's Law

The first quantitative experiments on gases were performed by an Irish chemist, Robert Boyle (1627–1691). Using a J-shaped tube closed at one end (Fig. 5.4), which he reportedly set up in the multistory entryway of his house, Boyle studied the relationship between the pressure of the trapped gas and its volume. Representative values from Boyle's experiments are given in Table 5.1. These data show that the product of the pressure and

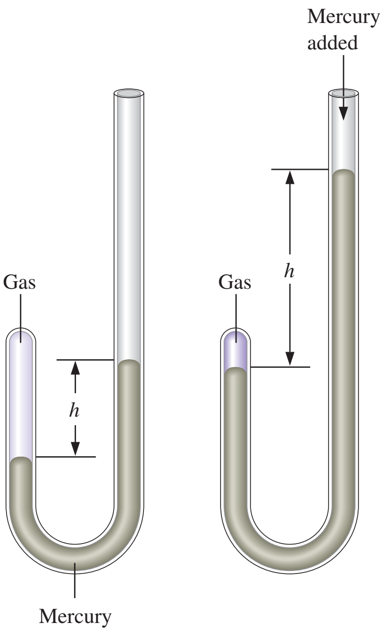


FIGURE 5.4
A J-tube similar to the one used by Boyle.

Boyle's law: $V \propto 1/P$ at constant temperature.

Graphing is reviewed in Appendix 1.3.

TABLE 5.1 Actual Data from Boyle's Experiment

Volume (in^3)	Pressure (in Hg)	Pressure × Volume (in Hg × in^3)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

volume for the trapped air sample is constant within the accuracies of Boyle's measurements (note the third column in Table 5.1). This behavior can be represented by the equation

$$PV = k$$

which is called **Boyle's law** and where k is a constant for a given sample of air at a specific temperature.

It is convenient to represent the data in Table 5.1 by using two different plots. The first type of plot, P versus V, forms a curve called a *hyperbola* shown in Fig. 5.5(a). Looking at this plot, note that as the volume drops by about half (from 58.8 to 29.1), the pressure doubles (from 24.0 to 48.0). In other words, there is an *inverse relationship* between pressure and volume. The second type of plot can be obtained by rearranging Boyle's law to give

$$V = \frac{k}{P} = k\frac{1}{P}$$

which is the equation for a straight line of the type

$$y = mx + b$$

where m represents the slope and b the intercept of the straight line. In this case, $y = V$, $x = 1/P$, $m = k$, and $b = 0$. Thus a plot of V versus $1/P$ using Boyle's data gives a straight line with an intercept of zero, as shown in Fig. 5.5(b).

In the three centuries since Boyle carried out his studies, the sophistication of measuring techniques has increased tremendously. The results of highly accurate measurements show that Boyle's law holds precisely only at very low pressures. Measurements at higher pressures reveal that PV is not constant but varies as the pressure is varied. Results for several gases at pressures below 1 atm are shown in Fig. 5.6. Note the very small changes that occur in the product PV as the pressure is changed at these low pressures. Such changes become

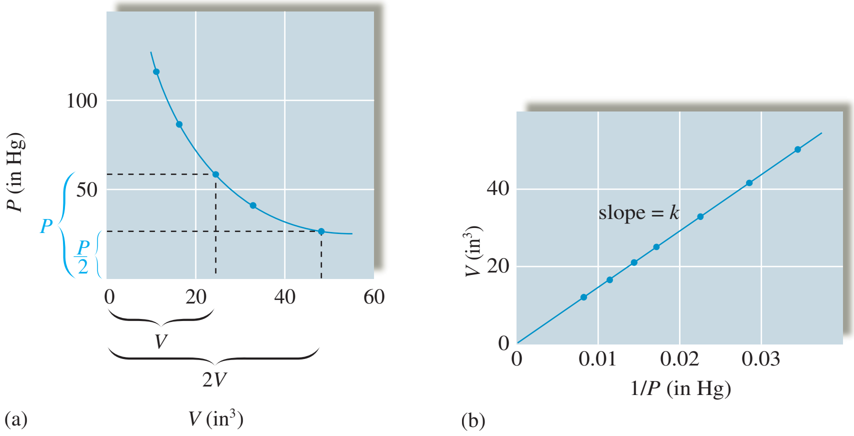


FIGURE 5.5
Plotting Boyle's data from Table 5.1. (a) A plot of P versus V shows that the volume doubles as the pressure is halved. (b) A plot of V versus $1/P$ gives a straight line. The slope of this line equals the value of the constant k.

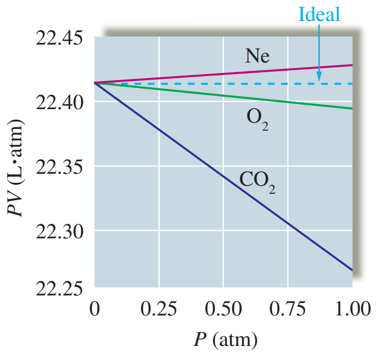
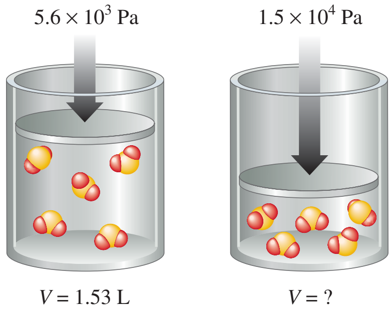


FIGURE 5.6
A plot of *PV* versus *P* for several gases at pressures below 1 atm. An ideal gas is expected to have a constant value of *PV*, as shown by the dotted line. Carbon dioxide shows the largest change in *PV*, and this change is actually quite small: *PV* changes from about 22.39 L · atm at 0.25 atm to 22.26 L · atm at 1.00 atm. Thus Boyle's law is a good approximation at these relatively low pressures.

more significant at much higher pressures, where the complex nature of the dependence of *PV* on pressure becomes more obvious. We will discuss these deviations and the reasons for them in detail in Section 5.8. *A gas that strictly obeys Boyle's law is called an* ***ideal gas.*** We will describe the characteristics of an ideal gas more completely in Section 5.3.

One common use of Boyle's law is to predict the new volume of a gas when the pressure is changed (at constant temperature), or vice versa. Because deviations from Boyle's law are so slight at pressures close to 1 atm, in our calculations we will assume that gases obey Boyle's law (unless stated otherwise).

Sample Exercise 5.2 Boyle's Law I



As pressure increases, the volume of SO_2 decreases.

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53-L sample of gaseous SO_2 at a pressure of 5.6×10^3 Pa. If the pressure is changed to 1.5×10^4 Pa at a constant temperature, what will be the new volume of the gas?

Solution

We can solve this problem using Boyle's law,

$$PV = k$$

which also can be written as

$$P_1V_1 = k = P_2V_2 \quad \text{or} \quad P_1V_1 = P_2V_2$$

where the subscripts 1 and 2 represent two states (conditions) of the gas (both at the same temperature). In this case,

$$P_1 = 5.6 \times 10^3 \text{ Pa} \qquad P_2 = 1.5 \times 10^4 \text{ Pa}$$
$$V_1 = 1.53 \text{ L} \qquad V_2 = ?$$

We can solve the preceding equation for V_2:

$$V_2 = \frac{P_1V_1}{P_2} = \frac{5.6 \times 10^3 \cancel{\text{Pa}} \times 1.53 \text{ L}}{1.5 \times 10^4 \cancel{\text{Pa}}} = 0.57 \text{ L}$$

Boyle's law also can be written as

$$P_1V_1 = P_2V_2$$

The new volume will be 0.57 L.

See Exercise 5.33.

The fact that the volume decreases in Sample Exercise 5.2 makes sense because the pressure was increased. *To help eliminate errors, make it a habit to check whether an answer to a problem makes physical sense.*

Always check that your answer makes physical (common!) sense.

We mentioned before that Boyle's law is only approximately true for real gases. To determine the significance of the deviations, studies of the effect of changing pressure on the volume of a gas are often done, as shown in Sample Exercise 5.3.

Sample Exercise 5.3 Boyle's Law II

In a study to see how closely gaseous ammonia obeys Boyle's law, several volume measurements were made at various pressures, using 1.0 mol NH_3 gas at a temperature of 0°C. Using the results listed on the following page, calculate the Boyle's law constant for NH_3 at the various pressures.

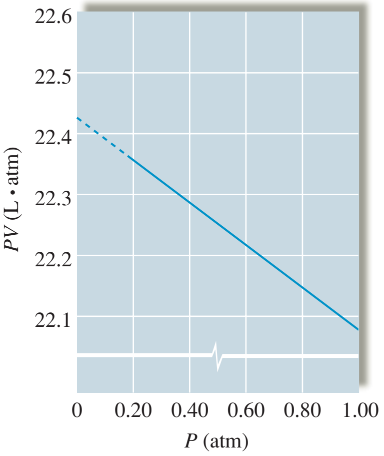


FIGURE 5.7
A plot of PV versus P for 1 mol of ammonia. The dashed line shows the extrapolation of the data to zero pressure to give the "ideal" value of PV of 22.41 L · atm.

Experiment	Pressure (atm)	Volume (L)
1	0.1300	172.1
2	0.2500	89.28
3	0.3000	74.35
4	0.5000	44.49
5	0.7500	29.55
6	1.000	22.08

Solution

To determine how closely NH_3 gas follows Boyle's law under these conditions, we calculate the value of k (in L · atm) for each set of values:

Experiment	1	2	3	4	5	6
$k = PV$	22.37	22.32	22.31	22.25	22.16	22.08

Although the deviations from true Boyle's law behavior are quite small at these low pressures, note that the value of k changes regularly in one direction as the pressure is increased. Thus, to calculate the "ideal" value of k for NH_3, we can plot PV versus P, as shown in Fig. 5.7, and extrapolate (extend the line beyond the experimental points) back to zero pressure, where, for reasons we will discuss later, a gas behaves most ideally. The value of k obtained by this extrapolation is 22.41 L · atm. Notice that this is the same value obtained from similar plots for the gases CO_2, O_2, and Ne at 0°C, as shown in Fig. 5.6.

See Exercise 5.97.

Charles's Law

In the century following Boyle's findings, scientists continued to study the properties of gases. One of these scientists was a French physicist, Jacques Charles (1746–1823), who was the first person to fill a balloon with hydrogen gas and who made the first solo balloon flight. Charles found in 1787 that the volume of a gas at constant pressure increases *linearly* with the temperature of the gas. That is, a plot of the volume of a gas (at constant pressure) versus its temperature (°C) gives a straight line. This behavior is shown for samples of several gases in Fig. 5.8. The slopes of the lines in this graph are different

Visualization: Liquid Nitrogen and Balloons

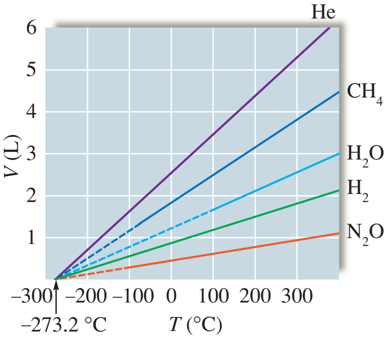


FIGURE 5.8
Plots of V versus T (°C) for several gases. The solid lines represent experimental measurements on gases. The dashed lines represent extrapolation of the data into regions where these gases would become liquids or solids. Note that the samples of the various gases contain different numbers of moles.

A snowmaking machine, in which water is blown through nozzles by compressed air. The mixture is cooled by expansion to form ice crystals of snow.

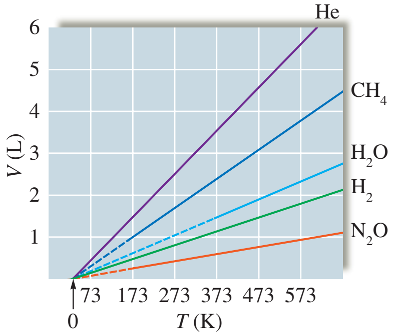


FIGURE 5.9
Plots of V versus T as in Fig. 5.8, except here the Kelvin scale is used for temperature.

because the samples contain different numbers of moles of gas. A very interesting feature of these plots is that the volumes of all the gases extrapolate to zero at the same temperature, −273.2°C. On the Kelvin temperature scale this point is defined as 0 K, which leads to the following relationship between the Kelvin and Celsius scales:

$$\text{K} = {}^\circ\text{C} + 273$$

When the volumes of the gases shown in Fig. 5.8 are plotted versus temperature on the Kelvin scale, the plots in Fig. 5.9 result. In this case, the volume of each gas is *directly proportional to temperature* and extrapolates to zero when the temperature is 0 K. This behavior is represented by the equation known as **Charles's law,**

$$V = bT$$

where T is in kelvins and b is a proportionality constant.

Before we illustrate the uses of Charles's law, let us consider the importance of 0 K. At temperatures below this point, the extrapolated volumes would become negative. The fact that a gas cannot have a negative volume suggests that 0 K has a special significance. In fact, 0 K is called **absolute zero,** and there is much evidence to suggest that this temperature cannot be attained. Temperatures of approximately 0.000001 K have been produced in laboratories, but 0 K has never been reached.

Visualization: Charles's Law: A Graphical View

Charles's law: $V \propto T$ (expressed in K) of constant pressure.

Sample Exercise 5.4 Charles's Law

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

Solution

Charles's law, which describes the dependence of the volume of a gas on temperature at constant pressure, can be used to solve this problem. Charles's law in the form $V = bT$ can be rearranged to

$$\frac{V}{T} = b$$

Charles's law also can be written as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

An equivalent statement is

$$\frac{V_1}{T_1} = b = \frac{V_2}{T_2}$$

where the subscripts 1 and 2 represent two states for a given sample of gas at constant pressure. In this case, we are given the following (note that the temperature values *must* be changed to the Kelvin scale):

T_1 = 15°C + 273 = 288 K T_2 = 38°C + 273 = 311 K
V_1 = 2.58 L V_2 = ?

Solving for V_2 gives

$$V_2 = \left(\frac{T_2}{T_1}\right)V_1 = \left(\frac{311\ \cancel{\text{K}}}{288\ \cancel{\text{K}}}\right)2.58\text{ L} = 2.79\text{ L}$$

Reality Check: The new volume is greater than the initial volume, which makes physical sense because the gas will expand as it is heated.

See Exercise 5.35.

Avogadro's Law

In Chapter 2 we noted that in 1811 the Italian chemist Avogadro postulated that equal volumes of gases at the same temperature and pressure contain the same number of "particles." This observation is called **Avogadro's law,** which is illustrated by Fig. 5.10. Stated mathematically, Avogadro's law is

$$V = an$$

where V is the volume of the gas, n is the number of moles of gas particles, and a is a proportionality constant. This equation states that *for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas.* This relationship is obeyed closely by gases at low pressures.

Sample Exercise 5.5

Avogadro's Law

Suppose we have a 12.2-L sample containing 0.50 mol oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25°C. If all this O_2 were converted to ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

Avogadro's law also can be written as

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Solution

The balanced equation for the reaction is

$$3O_2(g) \longrightarrow 2O_3(g)$$

To calculate the moles of O_3 produced, we must use the appropriate mole ratio:

$$0.50\ \cancel{\text{mol } O_2} \times \frac{2\text{ mol } O_3}{3\ \cancel{\text{mol } O_2}} = 0.33\text{ mol } O_3$$

Avogadro's law states that $V = an$, which can be rearranged to give

$$\frac{V}{n} = a$$

Since a is a constant, an alternative representation is

$$\frac{V_1}{n_1} = a = \frac{V_2}{n_2}$$

where V_1 is the volume of n_1 moles of O_2 gas and V_2 is the volume of n_2 moles of O_3 gas. In this case we have

$n_1 = 0.50$ mol $\qquad n_2 = 0.33$ mol

$V_1 = 12.2$ L $\qquad V_2 = ?$

Solving for V_2 gives

$$V_2 = \left(\frac{n_2}{n_1}\right)V_1 = \left(\frac{0.33\ \cancel{\text{mol}}}{0.50\ \cancel{\text{mol}}}\right)12.2\text{ L} = 8.1\text{ L}$$

Reality Check: Note that the volume decreases, as it should, since fewer moles of gas molecules will be present after O_2 is converted to O_3.

See Exercises 5.35 and 5.36.

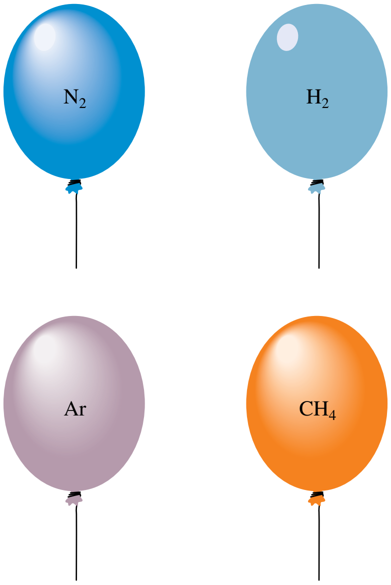


FIGURE 5.10
These balloons each hold 1.0 L of gas at 25°C and 1 atm. Each balloon contains 0.041 mol of gas, or 2.5×10^{22} molecules.

5.3 The Ideal Gas Law

We have considered three laws that describe the behavior of gases as revealed by experimental observations:

Boyle's law: $V = \frac{k}{P}$ (at constant T and n)

Charles's law: $V = bT$ (at constant P and n)

Avogadro's law: $V = an$ (at constant T and P)

These relationships, which show how the volume of a gas depends on pressure, temperature, and number of moles of gas present, can be combined as follows:

$$V = R\left(\frac{Tn}{P}\right)$$

$R = 0.08206\,\frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$

where R is the combined proportionality constant called the **universal gas constant.** When the pressure is expressed in atmospheres and the volume in liters, R has the value 0.08206 L · atm/K · mol. The preceding equation can be rearranged to the more familiar form of the **ideal gas law:**

$$PV = nRT$$

Visualization: The Ideal Gas Law, $PV = nRT$

The ideal gas law is an *equation of state* for a gas, where the state of the gas is its condition at a given time. A particular *state* of a gas is described by its pressure, volume, temperature, and number of moles. Knowledge of any three of these properties is enough to completely define the state of a gas, since the fourth property can then be determined from the equation for the ideal gas law.

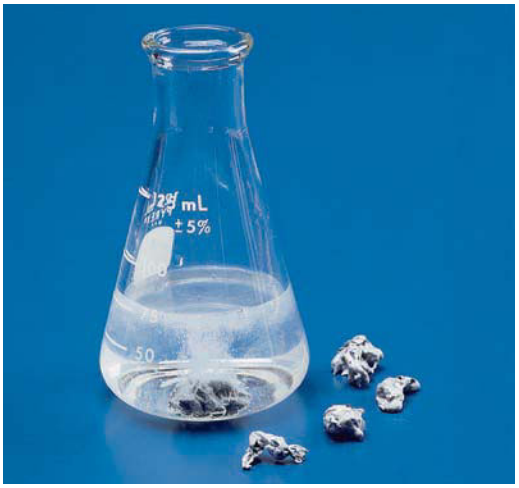
The ideal gas law applies best at pressures smaller than 1 atm.

It is important to recognize that the ideal gas law is an empirical equation—it is based on experimental measurements of the properties of gases. A gas that obeys this equation is said to behave *ideally.* The ideal gas equation is best regarded as a limiting law—it expresses behavior that real gases *approach* at low pressures and high temperatures. Therefore, an ideal gas is a hypothetical substance. However, most gases obey the ideal gas equation closely enough at pressures below 1 atm that only minimal errors result from assuming ideal behavior. Unless you are given information to the contrary, you should assume ideal gas behavior when solving problems involving gases in this text.

The ideal gas law can be used to solve a variety of problems. Sample Exercise 5.6 demonstrates one type, where you are asked to find one property characterizing the state of a gas, given the other three.

Sample Exercise 5.6 Ideal Gas Law I

A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of 0°C and a pressure of 1.5 atm. Calculate the moles of H_2 molecules present in this gas sample.



The reaction of zinc with hydrochloric acid to produce bubbles of hydrogen gas.

Solution

Solving the ideal gas law for n gives

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

In this case $P = 1.5$ atm, $V = 8.56$ L, $T = 0°\text{C} + 273 = 273$ K, and $R = 0.08206$ L · atm/K · mol. Thus

$$n = \frac{(1.5\ \cancel{\text{atm}})(8.56\ \cancel{\text{L}})}{\left(0.08206\,\frac{\cancel{\text{L}} \cdot \cancel{\text{atm}}}{\cancel{\text{K}} \cdot \text{mol}}\right)(273\ \cancel{\text{K}})} = 0.57 \text{ mol}$$

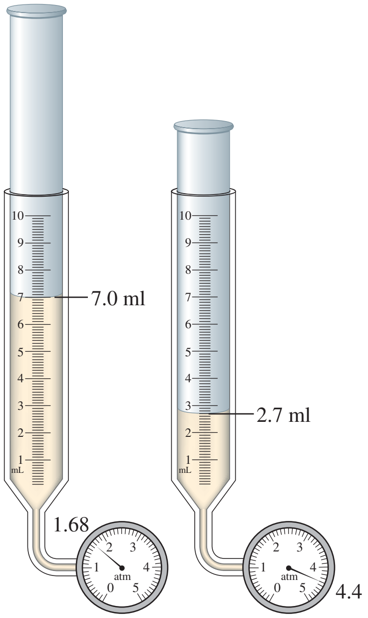
See Exercises 5.37 through 5.42.

The ideal gas law is also used to calculate the changes that will occur when the conditions of the gas are changed.

Sample Exercise 5.7

Ideal Gas Law II

Suppose we have a sample of ammonia gas with a volume of 7.0 mL at a pressure of 1.68 atm. The gas is compressed to a volume of 2.7 mL at a constant temperature. Use the ideal gas law to calculate the final pressure.



As pressure increases, the volume decreases.

Solution

The basic assumption we make when using the ideal gas law to describe a change in state for a gas is that the equation applies equally well to both the initial and the final states. In dealing with a change in state, we always *place the variables that change on one side of the equals sign and the constants on the other.* In this case the pressure and volume change, and the temperature and the number of moles remain constant (as does R, by definition). Thus we write the ideal gas law as

$$\underset{\substack{\nearrow \\ \text{Change}}}{PV} = \underset{\substack{\nwarrow \\ \text{Remain constant}}}{nRT}$$

Since n and T remain the same in this case, we can write $P_1V_1 = nRT$ and $P_2V_2 = nRT$. Combining these gives

$$P_1V_1 = nRT = P_2V_2 \qquad \text{or} \qquad P_1V_1 = P_2V_2$$

We are given $P_1 = 1.68$ atm, $V_1 = 7.0$ mL, and $V_2 = 2.7$ mL. Solving for P_2 thus gives

$$P_2 = \left(\frac{V_1}{V_2}\right)P_1 = \left(\frac{7.0\ \cancel{\text{mL}}}{2.7\ \cancel{\text{mL}}}\right)1.68\ \text{atm} = 4.4\ \text{atm}$$

Reality Check: Does this answer make sense? The volume decreased (at constant temperature), so the pressure should increase, as the result of the calculation indicates. Note that the calculated final pressure is 4.4 atm. Most gases do not behave ideally above 1 atm. Therefore, we might find that if we *measured* the pressure of this gas sample, the observed pressure would differ slightly from 4.4 atm.

See Exercises 5.43 and 5.44.

Sample Exercise 5.8

Ideal Gas Law III

A sample of methane gas that has a volume of 3.8 L at 5°C is heated to 86°C at constant pressure. Calculate its new volume.

Solution

To solve this problem, we take the ideal gas law and segregate the changing variables and the constants by placing them on opposite sides of the equation. In this case, volume and temperature change, and the number of moles and pressure (and, of course, R) remain constant. Thus $PV = nRT$ becomes

$$\frac{V}{T} = \frac{nR}{P}$$

which leads to

$$\frac{V_1}{T_1} = \frac{nR}{P} \quad \text{and} \quad \frac{V_2}{T_2} = \frac{nR}{P}$$

Combining these gives

$$\frac{V_1}{T_1} = \frac{nR}{P} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

We are given

$$T_1 = 5°\text{C} + 273 = 278\ \text{K} \qquad T_2 = 86°\text{C} + 273 = 359\ \text{K}$$
$$V_1 = 3.8\ \text{L} \qquad V_2 = ?$$

Thus

$$V_2 = \frac{T_2V_1}{T_1} = \frac{(359\ \cancel{\text{K}})(3.8\ \text{L})}{278\ \cancel{\text{K}}} = 4.9\ \text{L}$$

Reality Check: Is the answer sensible? In this case the temperature increased (at constant pressure), so the volume should increase. Thus the answer makes sense.

See Exercises 5.45 and 5.46.

The problem in Sample Exercise 5.8 could be described as a "Charles's law problem," whereas the problem in Sample Exercise 5.7 might be called a "Boyle's law problem." In both cases, however, we started with the ideal gas law. The real advantage of using the ideal gas law is that it applies to virtually any problem dealing with gases and is easy to remember.

Sample Exercise 5.9

Ideal Gas Law IV

A sample of diborane gas (B_2H_6), a substance that bursts into flame when exposed to air, has a pressure of 345 torr at a temperature of −15°C and a volume of 3.48 L. If conditions are changed so that the temperature is 36°C and the pressure is 468 torr, what will be the volume of the sample?

Solution

Visualization: Changes in Gas Volume, Pressure, and Concentration

Since, for this sample, pressure, temperature, and volume all change while the number of moles remains constant, we use the ideal gas law in the form

$$\frac{PV}{T} = nR$$

which leads to

$$\frac{P_1V_1}{T_1} = nR = \frac{P_2V_2}{T_2} \quad \text{or} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Then

$$V_2 = \frac{T_2P_1V_1}{T_1P_2}$$

We have

$$P_1 = 345\ \text{torr} \qquad P_2 = 468\ \text{torr}$$
$$T_1 = -15°\text{C} + 273 = 258\ \text{K} \qquad T_2 = 36°\text{C} + 273 = 309\ \text{K}$$
$$V_1 = 3.48\ \text{L} \qquad V_2 = ?$$

Thus

$$V_2 = \frac{(309\ \cancel{\text{K}})(345\ \cancel{\text{torr}})(3.48\ \text{L})}{(258\ \cancel{\text{K}})(468\ \cancel{\text{torr}})} = 3.07\ \text{L}$$

See Exercises 5.47 and 5.48.

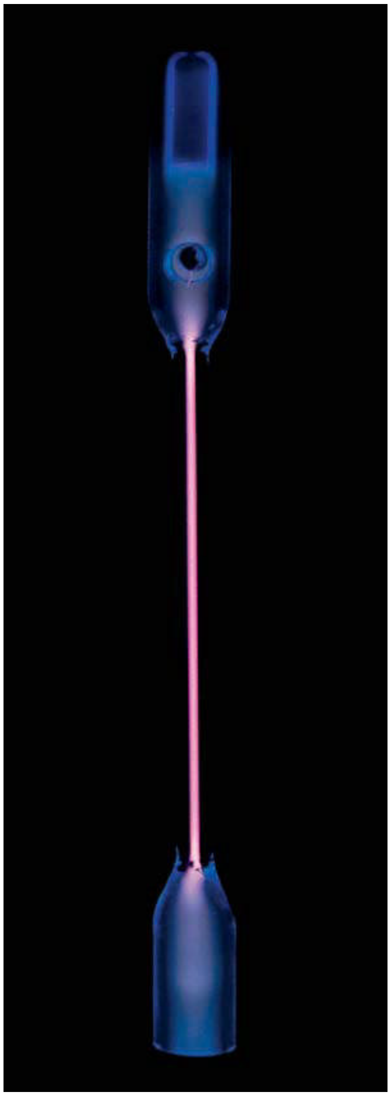
Always convert the temperature to the Kelvin scale when applying the ideal gas law.

Since the equation used in Sample Exercise 5.9 involves a *ratio* of pressures, it was unnecessary to convert pressures to units of atmospheres. The units of torrs cancel. (You will obtain the same answer by inserting $P_1 = \frac{345}{760}$ and $P_2 = \frac{468}{760}$ into the equation.) However, temperature *must always* be converted to the Kelvin scale; since this conversion involves *addition* of 273, the conversion factor does not cancel. Be careful.

One of the many other types of problems dealing with gases that can be solved using the ideal gas law is illustrated in Sample Exercise 5.10.

Sample Exercise 5.10 Ideal Gas Law V

A sample containing 0.35 mol argon gas at a temperature of 13°C and a pressure of 568 torr is heated to 56°C and a pressure of 897 torr. Calculate the change in volume that occurs.



Argon glowing in a discharge tube.

Solution

We use the ideal gas law to find the volume for each set of conditions:

State 1	State 2
$n_1 = 0.35$ mol	$n_2 = 0.35$ mol
$P_1 = 568 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 0.747 \text{ atm}$	$P_2 = 897 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 1.18 \text{ atm}$
$T_1 = 13°\text{C} + 273 = 286 \text{ K}$	$T_2 = 56°\text{C} + 273 = 329 \text{ K}$

Solving the ideal gas law for volume gives

$$V_1 = \frac{n_1RT_1}{P_1} = \frac{(0.35 \cancel{\text{mol}})(0.08206 \text{ L} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \cancel{\text{mol}})(286 \cancel{\text{K}})}{(0.747 \cancel{\text{atm}})} = 11 \text{ L}$$

and

$$V_2 = \frac{n_2RT_2}{P_2} = \frac{(0.35 \cancel{\text{mol}})(0.08206 \text{ L} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \cancel{\text{mol}})(329 \cancel{\text{K}})}{(1.18 \cancel{\text{atm}})} = 8.0 \text{ L}$$

Thus, in going from state 1 to state 2, the volume changes from 11 L to 8.0 L. The change in volume, ΔV (Δ is the Greek capital letter delta), is then

$$\Delta V = V_2 - V_1 = 8.0 \text{ L} - 11 \text{ L} = -3 \text{ L}$$

The *change* in volume is negative because the volume decreases. Note that for this problem (unlike Sample Exercise 5.9) the pressures must be converted from torrs to atmospheres, as required by the atmosphere part of the units for R, since each volume was found separately and the conversion factor does not cancel.

See Exercise 5.49.

5.4 Gas Stoichiometry

When 273.15 K is used in this calculation, the molar volume obtained in Sample Exercise 5.3 is the same value as 22.41 L.

Suppose we have 1 mole of an ideal gas at 0°C (273.2 K) and 1 atm. From the ideal gas law, the volume of the gas is given by

$$V = \frac{nRT}{P} = \frac{(1.000 \cancel{\text{mol}})(0.08206 \text{ L} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \cancel{\text{mol}})(273.2 \cancel{\text{K}})}{1.000 \cancel{\text{atm}}} = 22.42 \text{ L}$$

TABLE 5.2 Molar Volumes for Various Gases at 0°C and 1 atm

Gas	Molar Volume (L)
Oxygen (O_2)	22.397
Nitrogen (N_2)	22.402
Hydrogen (H_2)	22.433
Helium (He)	22.434
Argon (Ar)	22.397
Carbon dioxide (CO_2)	22.260
Ammonia (NH_3)	22.079

FIGURE 5.11
22.4 L of a gas would just fit into this box.

This volume of 22.42 liters is the **molar volume** of an ideal gas (at 0°C and 1 atm). The measured molar volumes of several gases are listed in Table 5.2. Note that the molar volumes of some of the gases are very close to the ideal value, while others deviate significantly. Later in this chapter we will discuss some of the reasons for the deviations.

STP: 0°C and 1 atm

The conditions 0°C and 1 atm, called **standard temperature and pressure** (abbreviated **STP**), are common reference conditions for the properties of gases. For example, the molar volume of an ideal gas is 22.42 liters at STP (see Fig. 5.11).

Sample Exercise 5.11 Gas Stoichiometry I

A sample of nitrogen gas has a volume of 1.75 L at STP. How many moles of N_2 are present?

Solution

We could solve this problem by using the ideal gas equation, but we can take a shortcut by using the molar volume of an ideal gas at STP. Since 1 mole of an ideal gas at STP has a volume of 22.42 L, 1.75 L of N_2 at STP will contain less than 1 mole. We can find how many moles using the ratio of 1.75 L to 22.42 L:

$$1.75\ \cancel{\text{L N}_2} \times \frac{1\ \text{mol N}_2}{22.42\ \cancel{\text{L N}_2}} = 7.81 \times 10^{-2}\ \text{mol N}_2$$

See Exercises 5.51 and 5.52.

Many chemical reactions involve gases. By assuming ideal behavior for these gases, we can carry out stoichiometric calculations if the pressure, volume, and temperature of the gases are known.

Sample Exercise 5.12 Gas Stoichiometry II

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate ($CaCO_3$). Calculate the volume of CO_2 at STP produced from the decomposition of 152 g $CaCO_3$ by the reaction

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

Solution

We employ the same strategy we used in the stoichiometry problems earlier in this book. That is, we compute the number of moles of $CaCO_3$ consumed and the number of moles of CO_2 produced. The moles of CO_2 can then be converted to volume using the molar volume of an ideal gas.

Using the molar mass of $CaCO_3$ (100.09 g/mol), we can calculate the number of moles of $CaCO_3$:

$$152\ \cancel{\text{g CaCO}_3} \times \frac{1\ \text{mol CaCO}_3}{100.09\ \cancel{\text{g CaCO}_3}} = 1.52\ \text{mol CaCO}_3$$

Since each mole of $CaCO_3$ produces a mole of CO_2, 1.52 mol CO_2 will be formed. We can compute the volume of CO_2 at STP by using the molar volume:

$$1.52\ \cancel{\text{mol CO}_2} \times \frac{22.42\ \text{L CO}_2}{1\ \cancel{\text{mol CO}_2}} = 34.1\ \text{L CO}_2$$

Thus the decomposition of 152 g $CaCO_3$ produces 34.1 L CO_2 at STP.

See Exercises 5.53 through 5.56.

Remember that the molar volume of an ideal gas is 22.42 L when measured at STP.

Note that in Sample Exercise 5.12 the final step involved calculation of the volume of gas from the number of moles. Since the conditions were specified as STP, we were able to use the molar volume of a gas at STP. If the conditions of a problem are different from STP, the ideal gas law must be used to compute the volume.

Sample Exercise 5.13

Gas Stoichiometry III

A sample of methane gas having a volume of 2.80 L at 25°C and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31°C and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO_2 formed at a pressure of 2.50 atm and a temperature of 125°C.

Solution

From the description of the reaction, the unbalanced equation is

$$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

which can be balanced to give

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

Next, we must find the limiting reactant, which requires calculating the numbers of moles of each reactant. We convert the given volumes of methane and oxygen to moles using the ideal gas law as follows:

$$n_{CH_4} = \frac{PV}{RT} = \frac{(1.65\ \cancel{\text{atm}})(2.80\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \text{mol})(298\ \cancel{\text{K}})} = 0.189\ \text{mol}$$

$$n_{O_2} = \frac{PV}{RT} = \frac{(1.25\ \cancel{\text{atm}})(35.0\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \text{mol})(304\ \cancel{\text{K}})} = 1.75\ \text{mol}$$

In the balanced equation for the combustion reaction, 1 mol CH_4 requires 2 mol O_2. Thus the moles of O_2 required by 0.189 mol CH_4 can be calculated as follows:

$$0.189\ \cancel{\text{mol CH}_4} \times \frac{2\ \text{mol O}_2}{1\ \cancel{\text{mol CH}_4}} = 0.378\ \text{mol O}_2$$

Since 1.75 mol O_2 is available, O_2 is in excess. The limiting reactant is CH_4. The number of moles of CH_4 available must be used to calculate the number of moles of CO_2 produced:

$$0.189\ \cancel{\text{mol CH}_4} \times \frac{1\ \text{mol CO}_2}{1\ \cancel{\text{mol CH}_4}} = 0.189\ \text{mol CO}_2$$

Since the conditions stated are not STP, we must use the ideal gas law to calculate the volume:

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

In this case $n = 0.189$ mol, $T = 125°\text{C} + 273 = 398$ K, $P = 2.50$ atm, and $R = 0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol}$. Thus

$$V = \frac{(0.189\ \cancel{\text{mol}})(0.08206\ \text{L} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \cancel{\text{mol}})(398\ \cancel{\text{K}})}{2.50\ \cancel{\text{atm}}} = 2.47\ \text{L}$$

This represents the volume of CO_2 produced under these conditions.

See Exercises 5.57 and 5.58.

Molar Mass of a Gas

One very important use of the ideal gas law is in the calculation of the molar mass (molecular weight) of a gas from its measured density. To see the relationship between gas density and molar mass, consider that the number of moles of gas n can be expressed as

$$n = \frac{\text{grams of gas}}{\text{molar mass}} = \frac{\text{mass}}{\text{molar mass}} = \frac{m}{\text{molar mass}}$$

Substitution into the ideal gas equation gives

$$P = \frac{nRT}{V} = \frac{(m/\text{molar mass})RT}{V} = \frac{m(RT)}{V(\text{molar mass})}$$

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

However, m/V is the gas density d in units of grams per liter. Thus

$$P = \frac{dRT}{\text{molar mass}}$$

or

$$\text{Molar mass} = \frac{dRT}{P} \tag{5.1}$$

Thus, if the density of a gas at a given temperature and pressure is known, its molar mass can be calculated.

Sample Exercise 5.14

Gas Density/Molar Mass

The density of a gas was measured at 1.50 atm and 27°C and found to be 1.95 g/L. Calculate the molar mass of the gas.

Solution

Using Equation (5.1), we calculate the molar mass as follows:

$$\text{Molar mass} = \frac{dRT}{P} = \frac{\left(1.95\ \frac{\text{g}}{\cancel{\text{L}}}\right)\left(0.08206\ \frac{\cancel{\text{L}} \cdot \cancel{\text{atm}}}{\cancel{\text{K}} \cdot \text{mol}}\right)(300.\ \cancel{\text{K}})}{1.50\ \cancel{\text{atm}}} = 32.0\ \text{g/mol}$$

Reality Check: These are the units expected for molar mass.

See Exercises 5.61 through 5.64.

You could memorize the equation involving gas density and molar mass, but it is better simply to remember the total gas equation, the definition of density, and the relationship between number of moles and molar mass. You can then derive the appropriate equation when you need it. This approach ensures that you understand the concepts and means one less equation to memorize.

5.5 Dalton's Law of Partial Pressures

Among the experiments that led John Dalton to propose the atomic theory were his studies of mixtures of gases. In 1803 Dalton summarized his observations as follows: *For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.* This statement, known as **Dalton's law of partial pressures,** can be expressed as follows:

$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots$$

where the subscripts refer to the individual gases (gas 1, gas 2, and so on). The symbols P_1, P_2, P_3, and so on represent each **partial pressure,** the pressure that a particular gas would exert if it were alone in the container.

Assuming that each gas behaves ideally, the partial pressure of each gas can be calculated from the ideal gas law:

$$P_1 = \frac{n_1RT}{V}, \qquad P_2 = \frac{n_2RT}{V}, \qquad P_3 = \frac{n_3RT}{V}, \qquad \cdots$$

The total pressure of the mixture P_{TOTAL} can be represented as

$$\begin{aligned} P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots &= \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \cdots \\ &= (n_1 + n_2 + n_3 + \cdots)\left(\frac{RT}{V}\right) \\ &= n_{\text{TOTAL}}\left(\frac{RT}{V}\right) \end{aligned}$$

where n_{TOTAL} is the sum of the numbers of moles of the various gases. Thus, for a mixture of ideal gases, it is the *total number of moles of particles* that is important, not the identity or composition of the involved gas particles. This idea is illustrated in Fig. 5.12.

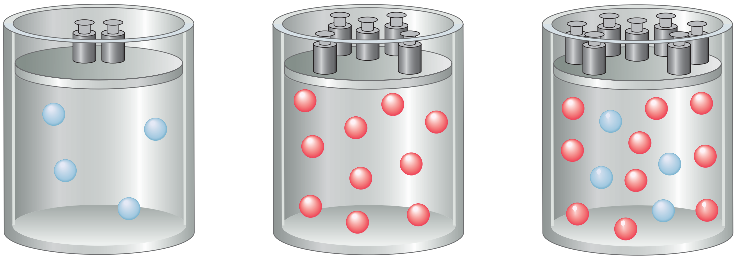


FIGURE 5.12
The partial pressure of each gas in a mixture of gases in a container depends on the number of moles of that gas. The total pressure is the sum of the partial pressures and depends on the total moles of gas particles present, no matter what they are.

This important observation indicates some fundamental characteristics of an ideal gas. The fact that the pressure exerted by an ideal gas is not affected by the identity (composition) of the gas particles reveals two things about ideal gases: (1) the volume of the individual gas particle must not be important, and (2) the forces among the particles must not be important. If these factors were important, the pressure exerted by the gas would depend on the nature of the individual particles. These observations will strongly influence the model that we will eventually construct to explain ideal gas behavior.

Sample Exercise 5.15

Dalton's Law I

Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent "the bends." For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O_2 at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Solution

The first step is to calculate the number of moles of each gas using the ideal gas law in the form:

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

$$n_{\text{He}} = \frac{(1.0\ \cancel{\text{atm}})(46\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \text{mol})(298\ \cancel{\text{K}})} = 1.9\ \text{mol}$$

$$n_{O_2} = \frac{(1.0\ \cancel{\text{atm}})(12\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \text{mol})(298\ \cancel{\text{K}})} = 0.49\ \text{mol}$$

The tank containing the mixture has a volume of 5.0 L, and the temperature is 25°C. We can use these data and the ideal gas law to calculate the partial pressure of each gas:

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

$$P_{\text{He}} = \frac{(1.9\ \cancel{\text{mol}})(0.08206\ \cancel{\text{L}} \cdot \text{atm}/\cancel{\text{K}} \cdot \cancel{\text{mol}})(298\ \cancel{\text{K}})}{5.0\ \cancel{\text{L}}} = 9.3\ \text{atm}$$

$$P_{O_2} = \frac{(0.49\ \cancel{\text{mol}})(0.08206\ \cancel{\text{L}} \cdot \text{atm}/\cancel{\text{K}} \cdot \cancel{\text{mol}})(298\ \cancel{\text{K}})}{5.0\ \cancel{\text{L}}} = 2.4\ \text{atm}$$

The total pressure is the sum of the partial pressures:

$$P_{\text{TOTAL}} = P_{\text{He}} + P_{O_2} = 9.3\ \text{atm} + 2.4\ \text{atm} = 11.7\ \text{atm}$$

See Exercises 5.65 and 5.66.

At this point we need to define the **mole fraction:** *the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.* The Greek lowercase letter chi (χ) is used to symbolize the mole fraction. For example, for a given component in a mixture, the mole fraction χ_1 is

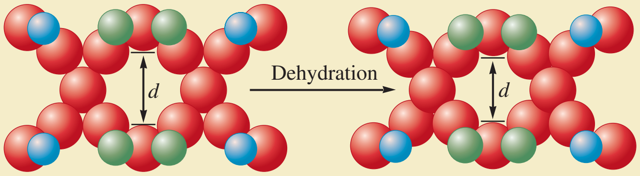
$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{n_1}{n_1 + n_2 + n_3 + \cdots}$$

CHEMICAL IMPACT

Separating Gases

Assume you work for an oil company that owns a huge natural gas reservoir containing a mixture of methane and nitrogen gases. In fact, the gas mixture contains so much nitrogen that it is unusable as a fuel. Your job is to separate the nitrogen (N_2) from the methane (CH_4). How might you accomplish this task? You clearly need some sort of "molecular filter" that will stop the slightly larger methane molecules (size $\approx$ 430 pm) and allow the nitrogen molecules (size $\approx$ 410 pm) to pass through. To accomplish the separation of molecules so similar in size will require a very precise "filter."

The good news is that such a filter exists. Recent work by Steven Kuznick and Valerie Bell at Engelhard Corporation in New Jersey and Michael Tsapatsis at the University of Massachusetts has produced a "molecular sieve" in which the pore (passage) sizes can be adjusted precisely enough to separate N_2 molecules from CH_4 molecules. The material involved is a special hydrated titanosilicate (contains H_2O, Ti, Si, O, and Sr) compound patented by Engelhard known as ETS-4 (Engelhard TitanoSilicate-4). When sodium ions are substituted for the strontium ions in ETS-4 and the new material is carefully dehydrated, a uniform and controllable pore-size reduction occurs (see figure). The researchers have shown that the material can be used to separate N_2 ($\approx$ 410 pm) from O_2 ($\approx$ 390 pm). They have also shown that it is possible to reduce the nitrogen content of natural gas from 18% to less than 5% with a 90% recovery of methane.



Molecular sieve framework of titanium (blue), silicon (green), and oxygen (red) atoms contracts on heating—at room temperature (left), d = 4.27 Å; at 250°C (right), d = 3.94 Å.

From the ideal gas equation we know that the number of moles of a gas is directly proportional to the pressure of the gas, since

$$n = P\left(\frac{V}{RT}\right)$$

That is, for each component in the mixture,

$$n_1 = P_1\left(\frac{V}{RT}\right), \qquad n_2 = P_2\left(\frac{V}{RT}\right), \qquad \cdots$$

Therefore, we can represent the mole fraction in terms of pressures:

$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{\overbrace{P_1(V/RT)}^{n_1}}{\underbrace{P_1(V/RT)}_{n_1} + \underbrace{P_2(V/RT)}_{n_2} + \underbrace{P_3(V/RT)}_{n_3} + \cdots}$$

$$= \frac{(V/RT)P_1}{(V/RT)(P_1 + P_2 + P_3 + \cdots)}$$

$$= \frac{P_1}{P_1 + P_2 + P_3 + \cdots} = \frac{P_1}{P_{\text{TOTAL}}}$$

In fact, the mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure:

$$\chi_2 = \frac{n_2}{n_{\text{TOTAL}}} = \frac{P_2}{P_{\text{TOTAL}}}$$

CHEMICAL IMPACT

The Chemistry of Air Bags

Most experts agree that air bags represent a very important advance in automobile safety. These bags, which are stored in the auto's steering wheel or dash, are designed to inflate rapidly (within about 40 ms) in the event of a crash, cushioning the front-seat occupants against impact. The bags then deflate immediately to allow vision and movement after the crash. Air bags are activated when a severe deceleration (an impact) causes a steel ball to compress a spring and electrically ignite a detonator cap, which, in turn, causes sodium azide (NaN_3) to decompose explosively, forming sodium and nitrogen gas:

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

This system works very well and requires a relatively small amount of sodium azide (100 g yields 56 L $N_2(g)$ at 25°C and 1.0 atm).

When a vehicle containing air bags reaches the end of its useful life, the sodium azide present in the activators must be given proper disposal. Sodium azide, besides being explosive, has a toxicity roughly equal to that of sodium cyanide. It also forms hydrazoic acid (HN_3), a toxic and explosive liquid, when treated with acid.

The air bag represents an application of chemistry that has already saved thousands of lives.

Inflated air bags.

Sample Exercise 5.16 Dalton's Law II

The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.

Solution

The mole fraction of O_2 can be calculated from the equation

$$\chi_{O_2} = \frac{P_{O_2}}{P_{\text{TOTAL}}} = \frac{156\ \cancel{\text{torr}}}{743\ \cancel{\text{torr}}} = 0.210$$

Note that the mole fraction has no units.

See Exercise 5.69.

The expression for the mole fraction,

$$\chi_1 = \frac{P_1}{P_{\text{TOTAL}}}$$

can be rearranged to give

$$P_1 = \chi_1 \times P_{\text{TOTAL}}$$

That is, *the partial pressure of a particular component of a gaseous mixture is the mole fraction of that component times the total pressure.*

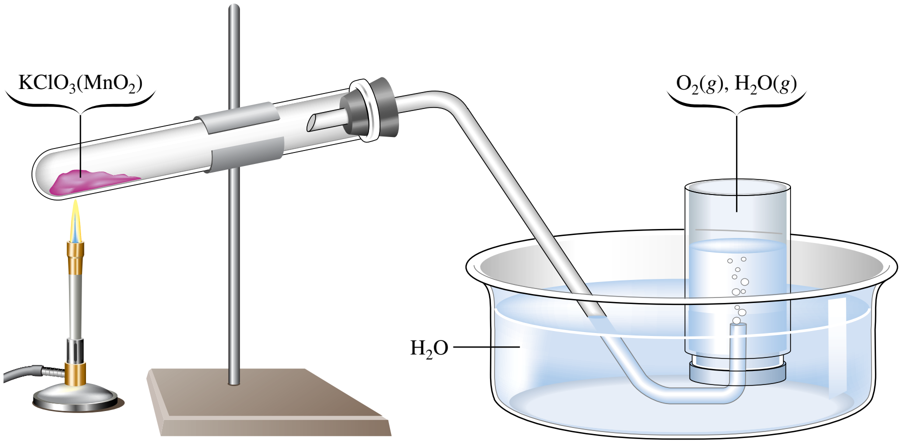


FIGURE 5.13
The production of oxygen by thermal decomposition of $KClO_3$. The MnO_2 is mixed with the $KClO_3$ to make the reaction faster.

Sample Exercise 5.17 Dalton's Law III

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N_2 in air when the atmospheric pressure is 760. torr.

Solution

The partial pressure of N_2 can be calculated as follows:

$$P_{N_2} = \chi_{N_2} \times P_{\text{TOTAL}} = 0.7808 \times 760.\ \text{torr} = 593\ \text{torr}$$

See Exercise 5.70.

Collecting a Gas over Water

Vapor pressure will be discussed in detail in Chapter 10. A table of water vapor pressure values is given in Section 10.8.

A mixture of gases results whenever a gas is collected by displacement of water. For example, Fig. 5.13 shows the collection of oxygen gas produced by the decomposition of solid potassium chlorate. In this situation, the gas in the bottle is a mixture of water vapor and the oxygen being collected. Water vapor is present because molecules of water escape from the surface of the liquid and collect in the space above the liquid. Molecules of water also return to the liquid. When the rate of escape equals the rate of return, the number of water molecules in the vapor state remains constant, and thus the pressure of water vapor remains constant. This pressure, which depends on temperature, is called the *vapor pressure of water.*

Sample Exercise 5.18 Gas Collection over Water

A sample of solid potassium chlorate ($KClO_3$) was heated in a test tube (see Fig. 5.13) and decomposed by the following reaction:

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of $KClO_3$ in the sample that was decomposed.

Solution

First we find the partial pressure of O_2 from Dalton's law of partial pressures:

$$P_{\text{TOTAL}} = P_{O_2} + P_{H_2O} = P_{O_2} + 21\ \text{torr} = 754\ \text{torr}$$

Thus

$$P_{O_2} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr}$$

Now we use the ideal gas law to find the number of moles of O_2:

$$n_{O_2} = \frac{P_{O_2}V}{RT}$$

In this case,

$$P_{O_2} = 733 \text{ torr} = \frac{733 \cancel{\text{torr}}}{760 \cancel{\text{torr}}/\text{atm}} = 0.964 \text{ atm}$$

$$V = 0.650 \text{ L}$$

$$T = 22°\text{C} + 273 = 295 \text{ K}$$

$$R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$$

Thus

$$n_{O_2} = \frac{(0.964 \cancel{\text{atm}})(0.650 \cancel{\text{L}})}{(0.08206 \cancel{\text{L}} \cdot \cancel{\text{atm}}/\cancel{\text{K}} \cdot \text{mol})(295 \cancel{\text{K}})} = 2.59 \times 10^{-2} \text{ mol}$$

Next we will calculate the moles of $KClO_3$ needed to produce this quantity of O_2. From the balanced equation for the decomposition of $KClO_3$, we have a mole ratio of 2 mol $KClO_3$/3 mol O_2. The moles of $KClO_3$ can be calculated as follows:

$$2.59 \times 10^{-2} \cancel{\text{mol } O_2} \times \frac{2 \text{ mol } KClO_3}{3 \cancel{\text{mol } O_2}} = 1.73 \times 10^{-2} \text{ mol } KClO_3$$

Using the molar mass of $KClO_3$ (122.6 g/mol), we calculate the grams of $KClO_3$:

$$1.73 \times 10^{-2} \cancel{\text{mol } KClO_3} \times \frac{122.6 \text{ g } KClO_3}{1 \cancel{\text{mol } KClO_3}} = 2.12 \text{ g } KClO_3$$

Thus the original sample contained 2.12 g $KClO_3$.

See Exercises 5.71 through 5.73.

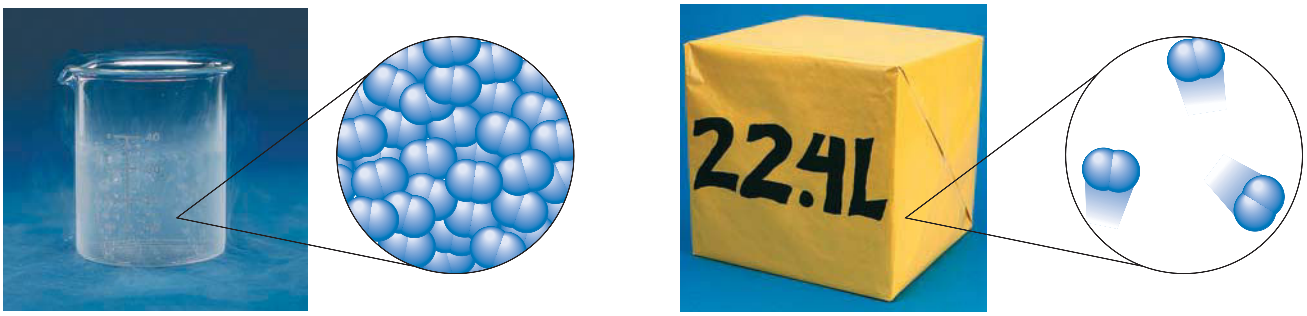
5.6 The Kinetic Molecular Theory of Gases

We have so far considered the behavior of gases from an experimental point of view. Based on observations from different types of experiments, we know that at pressures of less than 1 atm most gases closely approach the behavior described by the ideal gas law. Now we want to construct a model to explain this behavior.

Before we do this, let's briefly review the scientific method. Recall that a law is a way of generalizing behavior that has been observed in many experiments. Laws are very useful, since they allow us to predict the behavior of similar systems. For example, if a chemist prepares a new gaseous compound, a measurement of the gas density at known pressure and temperature can provide a reliable value for the compound's molar mass.

However, although laws summarize observed behavior, they do not tell us *why* nature behaves in the observed fashion. This is the central question for scientists. To try to answer this question, we construct theories (build models). The models in chemistry consist of speculations about what the individual atoms or molecules (microscopic particles) might be doing to cause the observed behavior of the macroscopic systems (collections of very large numbers of atoms and molecules).

A model is considered successful if it explains the observed behavior in question and predicts correctly the results of future experiments. It is important to understand that a model can never be proved absolutely true. In fact, *any model is an approximation* by its



(a)

(b)

FIGURE 5.14
(a) One mole of $N_2(l)$ has a volume of approximately 35 mL and a density of 0.81 g/mL. (b) One mole of $N_2(g)$ has a volume of 22.4 L (STP) and a density of 1.2×10^{-3} g/mL. Thus the ratio of the volumes of gaseous N_2 and liquid N_2 is $22.4/0.035 = 640$ and the spacing of the molecules is 9 times farther apart in $N_2(g)$.

very nature and is bound to fail at some point. Models range from the simple to the extraordinarily complex. We use simple models to predict approximate behavior and more complicated models to account very precisely for observed quantitative behavior. In this text we will stress simple models that provide an approximate picture of what might be happening and that fit the most important experimental results.

An example of this type of model is the **kinetic molecular theory (KMT),** a simple model that attempts to explain the properties of an ideal gas. This model is based on speculations about the behavior of the individual gas particles (atoms or molecules). The postulates of the kinetic molecular theory as they relate to the particles of an ideal gas can be stated as follows:

1. The particles are so small compared with the distances between them that *the volume of the individual particles can be assumed to be negligible* (zero). See Fig. 5.14.

Visualization: Visualizing Molecular Motion: Single Molecule

2. *The particles are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.*
3. *The particles are assumed to exert no forces on each other;* they are assumed neither to attract nor to repel each other.

Visualization: Visualizing Molecular Motion: Many Molecules

4. *The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.*

Of course, the molecules in a real gas have finite volumes and do exert forces on each other. Thus *real gases* do not conform to these assumptions. However, we will see that these postulates do indeed explain *ideal gas* behavior.

The true test of a model is how well its predictions fit the experimental observations. The postulates of the kinetic molecular model picture an ideal gas as consisting of particles having no volume and no attractions for each other, and the model assumes that the gas produces pressure on its container by collisions with the walls.

Let's consider how this model accounts for the properties of gases as summarized by the ideal gas law: $PV = nRT$.

Visualization: Boyle's Law: A Molecular-Level View

Pressure and Volume (Boyle's Law)

We have seen that for a given sample of gas at a given temperature (n and T are constant) that if the volume of a gas is decreased, the pressure increases:

$$P = \underset{\substack{\uparrow \\ \text{Constant}}}{(nRT)}\frac{1}{V}$$

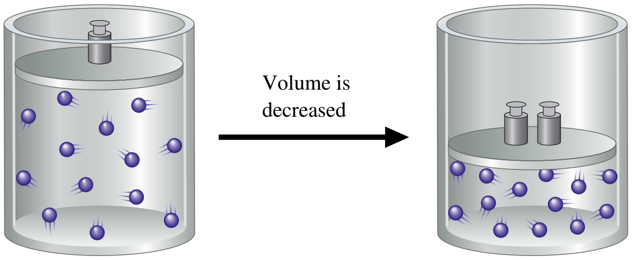


FIGURE 5.15
The effects of decreasing the volume of a sample of gas at constant temperature.

This makes sense based on the kinetic molecular theory, since a decrease in volume means that the gas particles will hit the wall more often, thus increasing pressure, as illustrated in Fig. 5.15.

Pressure and Temperature

From the ideal gas law we can predict that for a given sample of an ideal gas at a constant volume, the pressure will be directly proportional to the temperature:

$$P = \underbrace{\left(\frac{nR}{V}\right)}_{\text{Constant}} T$$

The KMT accounts for this behavior because when the temperature of a gas increases, the speeds of its particles increase, the particles hitting the wall with greater force and greater frequency. Since the volume remains the same, this would result in increased gas pressure, as illustrated in Fig. 5.16.

Volume and Temperature (Charles's Law)

The ideal gas law indicates that for a given sample of gas at a constant pressure, the volume of the gas is directly proportional to the temperature in kelvins:

$$V = \underbrace{\left(\frac{nR}{P}\right)}_{\text{Constant}} T$$

Visualization: Charles's Law: A Molecular-Level View

This can be visualized from the KMT, as shown in Fig. 5.17. When the gas is heated to a higher temperature, the speeds of its molecules increase and thus they hit the walls more often and with more force. The only way to keep the pressure constant in this situation is to increase the volume of the container. This compensates for the increased particle speeds.

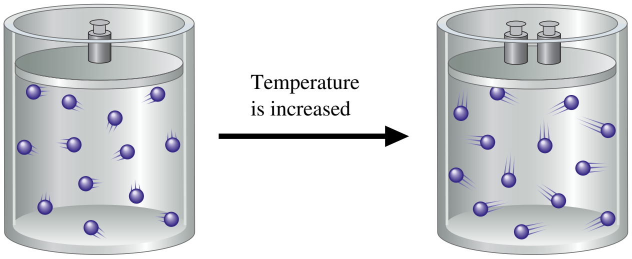


FIGURE 5.16
The effects of increasing the temperature of a sample of gas at constant volume.

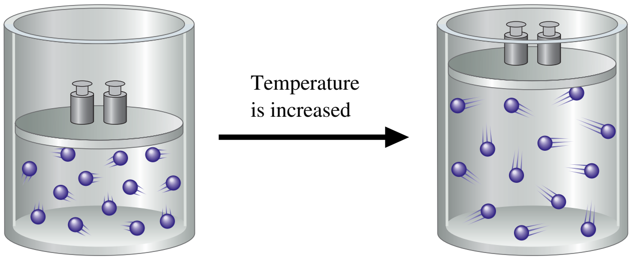


FIGURE 5.17
The effects of increasing the temperature of a sample of gas at constant pressure.

Volume and Number of Moles (Avogadro's Law)

The ideal gas law predicts that the volume of a gas at a constant temperature and pressure depends directly on the number of gas particles present:

$$V = \underbrace{\left(\frac{RT}{P}\right)}_{\text{Constant}} n$$

This makes sense in terms of the KMT, because an increase in the number of gas particles at the same temperature would cause the pressure to increase if the volume were held constant (see Fig. 5.18). The only way to return the pressure to its original value is to increase the volume.

It is important to recognize that the volume of a gas (at constant P and T) depends only on the *number* of gas particles present. The individual volumes of the particles are not a factor because the particle volumes are so small compared with the distances between the particles (for a gas behaving ideally).

Mixture of Gases (Dalton's Law)

The observation that the total pressure exerted by a mixture of gases is the sum of the pressures of the individual gases is expected because the KMT assumes that all gas particles are independent of each other and that the volumes of the individual particles are unimportant. Thus the identities of the gas particles do not matter.

Deriving the Ideal Gas Law

We have shown qualitatively that the assumptions of the KMT successfully account for the observed behavior of an ideal gas. We can go further. By applying the principles of physics to the assumptions of the KMT, we can in effect derive the ideal gas law.

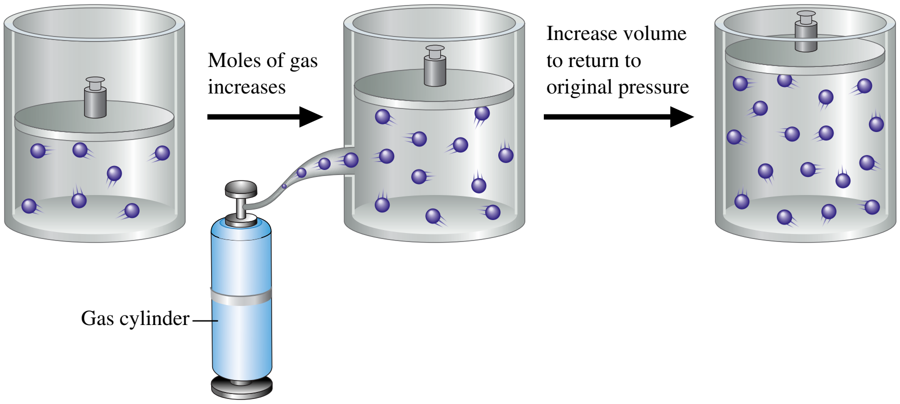


FIGURE 5.18
The effects of increasing the number of moles of gas particles at constant temperature and pressure.

As shown in detail in Appendix 2, we can apply the definitions of velocity, momentum, force, and pressure to the collection of particles in an ideal gas and *derive* the following expression for pressure:

$$P = \frac{2}{3}\left[\frac{nN_A(\frac{1}{2}m\overline{u^2})}{V}\right]$$

where P is the pressure of the gas, n is the number of moles of gas, N_A is Avogadro's number, m is the mass of each particle, $\overline{u^2}$ is the average of the square of the velocities of the particles, and V is the volume of the container.

The quantity $\frac{1}{2}m\overline{u^2}$ represents the average kinetic energy of a gas particle. If the average kinetic energy of an individual particle is multiplied by N_A, the number of particles in a mole, we get the average kinetic energy for a mole of gas particles:

$$(\text{KE})_{\text{avg}} = N_A(\tfrac{1}{2}m\overline{u^2})$$

Kinetic energy (KE) given by the equation KE $= \frac{1}{2}m\overline{u^2}$ is the energy due to the motion of a particle. We will discuss this further in Section 6.1.

Using this definition, we can rewrite the expression for pressure as

$$P = \frac{2}{3}\left[\frac{n(\text{KE})_{\text{avg}}}{V}\right] \quad \text{or} \quad \frac{PV}{n} = \frac{2}{3}(\text{KE})_{\text{avg}}$$

The fourth postulate of the kinetic molecular theory is that the average kinetic energy of the particles in the gas sample is directly proportional to the temperature in Kelvins. Thus, since $(\text{KE})_{\text{avg}} \propto T$, we can write

$$\frac{PV}{n} = \frac{2}{3}(\text{KE})_{\text{avg}} \propto T \quad \text{or} \quad \frac{PV}{n} \propto \text{T}$$

Visualization: Liquid Nitrogen and Balloons

Note that this expression has been *derived* from the assumptions of the kinetic molecular theory. How does it compare to the ideal gas law—the equation obtained from experiment? Compare the ideal gas law,

$$\frac{PV}{n} = RT \quad \text{From experiment}$$

with the result from the kinetic molecular theory,

$$\frac{PV}{n} \propto T \quad \text{From theory}$$

(a) A balloon filled with air at room temperature. (b) The balloon is dipped into liquid nitrogen at 77 K. (c) The balloon collapses as the molecules inside slow down due to the decreased temperature. Slower molecules produce a lower pressure.

These expressions have exactly the same form if R, the universal gas constant, is considered the proportionality constant in the second case.

The agreement between the ideal gas law and the predictions of the kinetic molecular theory gives us confidence in the validity of the model. The characteristics we have assumed for ideal gas particles must agree, at least under certain conditions, with their actual behavior.

The Meaning of Temperature

We have seen from the kinetic molecular theory that the Kelvin temperature indicates the average kinetic energy of the gas particles. The exact relationship between temperature and average kinetic energy can be obtained by combining the equations:

$$\frac{PV}{n} = RT = \frac{2}{3}(\mathrm{KE})_{\mathrm{avg}}$$

which yields the expression

$$(\mathrm{KE})_{\mathrm{avg}} = \frac{3}{2}RT$$

This is a very important relationship. It summarizes the meaning of the Kelvin temperature of a gas: The Kelvin temperature is an index of the random motions of the particles of a gas, with higher temperature meaning greater motion. (As we will see in Chapter 10, temperature is an index of the random motions in solids and liquids as well as in gases.)

Root Mean Square Velocity

In the equation from the kinetic molecular theory, the average velocity of the gas particles is a special kind of average. The symbol $\overline{u^2}$ means the average of the *squares* of the particle velocities. The square root of $\overline{u^2}$ is called the **root mean square velocity** and is symbolized by u_{rms}:

$$u_{\mathrm{rms}} = \sqrt{\overline{u^2}}$$

We can obtain an expression for u_{rms} from the equations

$$(\mathrm{KE})_{\mathrm{avg}} = N_{\mathrm{A}}(\tfrac{1}{2}m\overline{u^2}) \quad \text{and} \quad (\mathrm{KE})_{\mathrm{avg}} = \frac{3}{2}RT$$

Combination of these equations gives

$$N_{\mathrm{A}}(\tfrac{1}{2}m\overline{u^2}) = \frac{3}{2}RT \quad \text{or} \quad \overline{u^2} = \frac{3RT}{N_{\mathrm{A}}m}$$

Taking the square root of both sides of the last equation produces

$$\sqrt{\overline{u^2}} = u_{\mathrm{rms}} = \sqrt{\frac{3RT}{N_{\mathrm{A}}m}}$$

In this expression m represents the mass in kilograms of a single gas particle. When N_{A}, the number of particles in a mole, is multiplied by m, the product is the mass of a *mole* of gas particles in *kilograms*. We will call this quantity M. Substituting M for $N_{\mathrm{A}}m$ in the equation for u_{rms}, we obtain

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}}$$

Before we can use this equation, we need to consider the units for R. So far we have used 0.08206 L · atm/K · mol as the value of R. But to obtain the desired units (meters

$R = 0.08206\frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$

$R = 8.3145\frac{\text{J}}{\text{K} \cdot \text{mol}}$

per second) for u_{rms}, R must be expressed in different units. As we will see in more detail in Chapter 6, the energy unit most often used in the SI system is the joule (J). A **joule** is defined as a kilogram meter squared per second squared ($\text{kg} \cdot \text{m}^2/\text{s}^2$). When R is converted to include the unit of joules, it has the value 8.3145 J/K · mol. When R in these units is used in the expression $\sqrt{3RT/M}$, u_{rms} is obtained in the units of meters per second as desired.

Sample Exercise 5.19 Root Mean Square Velocity

Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C.

Solution

The formula for root mean square velocity is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Visualization: Kinetic-Molecular Theory/Heat Transfer

In this case $T = 25°\text{C} + 273 = 298\text{ K}$, $R = 8.3145\text{ J/K} \cdot \text{mol}$, and M is the mass of a mole of helium in kilograms:

$$M = 4.00\frac{\cancel{\text{g}}}{\text{mol}} \times \frac{1\text{ kg}}{1000\ \cancel{\text{g}}} = 4.00 \times 10^{-3}\text{ kg/mol}$$

Thus

$$u_{\text{rms}} = \sqrt{\frac{3\left(8.3145\frac{\text{J}}{\cancel{\text{K}} \cdot \cancel{\text{mol}}}\right)(298\ \cancel{\text{K}})}{4.00 \times 10^{-3}\frac{\text{kg}}{\cancel{\text{mol}}}}} = \sqrt{1.86 \times 10^6\frac{\text{J}}{\text{kg}}}$$

Since the units of J are $\text{kg} \cdot \text{m}^2/\text{s}^2$, this expression becomes

$$\sqrt{1.86 \times 10^6\frac{\cancel{\text{kg}} \cdot \text{m}^2}{\cancel{\text{kg}} \cdot \text{s}^2}} = 1.36 \times 10^3\text{ m/s}$$

Note that the resulting units (m/s) are appropriate for velocity.

See Exercises 5.79 and 5.80.

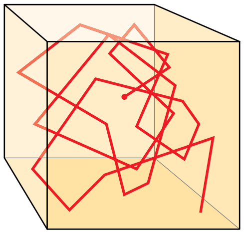


FIGURE 5.19
Path of one particle in a gas. Any given particle will continuously change its course as a result of collisions with other particles, as well as with the walls of the container.

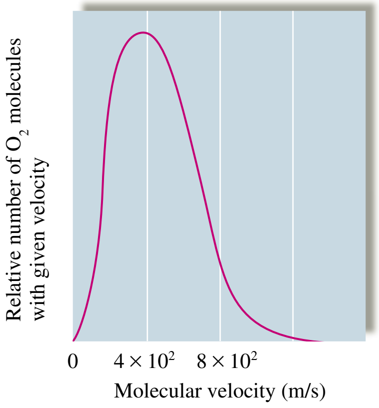


FIGURE 5.20
A plot of the relative number of O_2 molecules that have a given velocity at STP.

So far we have said nothing about the range of velocities actually found in a gas sample. In a real gas there are large numbers of collisions between particles. For example, as we will see in the next section, when an odorous gas such as ammonia is released in a room, it takes some time for the odor to permeate the air. This delay results from collisions between the NH_3 molecules and the O_2 and N_2 molecules in the air, which greatly slow the mixing process.

If the path of a particular gas particle could be monitored, it would look very erratic, something like that shown in Fig. 5.19. The average distance a particle travels between collisions in a particular gas sample is called the *mean free path.* It is typically a very small distance (1×10^{-7} m for O_2 at STP). One effect of the many collisions among gas particles is to produce a large range of velocities as the particles collide and exchange kinetic energy. Although u_{rms} for oxygen gas at STP is approximately 500 meters per second, the majority of O_2 molecules do not have this velocity. The actual distribution of molecular velocities for oxygen gas at STP is shown in Fig. 5.20. This figure shows the relative number of gas molecules having each particular velocity.

We are also interested in the effect of *temperature* on the velocity distribution in a gas. Figure 5.21 shows the velocity distribution for nitrogen gas at three temperatures. Note that as the temperature is increased, the curve peak moves toward higher values and the range

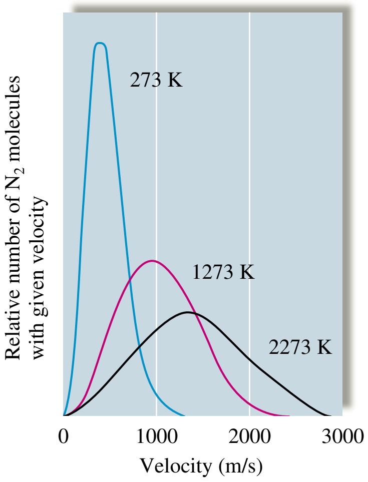


FIGURE 5.21
A plot of the relative number of N_2 molecules that have a given velocity at three temperatures. Note that as the temperature increases, both the average velocity and the spread of velocities increase.

of velocities becomes much larger. The peak of the curve reflects the most probable velocity (the velocity found most often as we sample the movement of the various particles in the gas). Because the kinetic energy increases with temperature, it makes sense that the peak of the curve should move to higher values as the temperature of the gas is increased.

5.7 Effusion and Diffusion

We have seen that the postulates of the kinetic molecular theory, when combined with the appropriate physical principles, produce an equation that successfully fits the experimentally observed behavior of gases as they approach ideal behavior. Two phenomena involving gases provide further tests of this model.

Diffusion is the term used to describe the mixing of gases. When a small amount of pungent-smelling ammonia is released at the front of a classroom, it takes some time before everyone in the room can smell it, because time is required for the ammonia to mix with the air. The rate of diffusion is the rate of the mixing of gases. **Effusion** is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber, as shown in Fig. 5.22. The rate of effusion measures the speed at which the gas is transferred into the chamber.

Effusion

Visualization: Effusion of a Gas

Thomas Graham (1805–1869), a Scottish chemist, found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. Stated in another way, the relative rates of effusion of two gases at the same temperature and pressure are given by the inverse ratio of the square roots of the masses of the gas particles:

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

where M_1 and M_2 represent the molar masses of the gases. This equation is called **Graham's law of effusion.**

In Graham's law the units for molar mass can be g/mol or kg/mol, since the units cancel in the ratio $\sqrt{M_2}/\sqrt{M_1}$.

Sample Exercise 5.20 Effusion Rates

Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6), a gas used in the enrichment process to produce fuel for nuclear reactors (see Fig. 5.23).

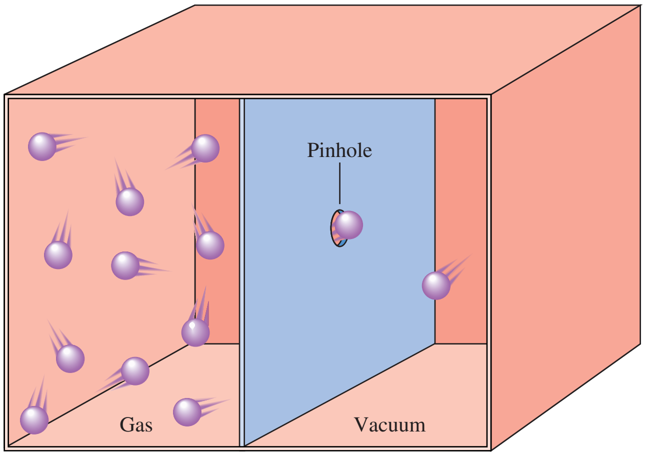


FIGURE 5.22
The effusion of a gas into an evacuated chamber. The rate of effusion (the rate at which the gas is transferred across the barrier through the pin hole) is inversely proportional to the square root of the mass of the gas molecules.

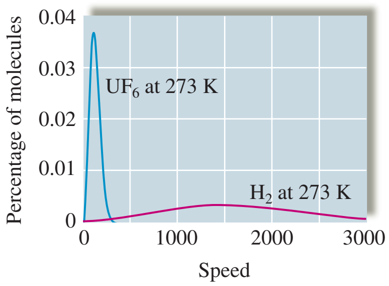


FIGURE 5.23
Relative molecular speed distribution of H_2 and UF_6.

Solution

First we need to compute the molar masses: Molar mass of H_2 = 2.016 g/mol, and molar mass of UF_6 = 352.02 g/mol. Using Graham's law,

$$\frac{\text{Rate of effusion for H}_2}{\text{Rate of effusion for UF}_6} = \frac{\sqrt{M_{\text{UF}_6}}}{\sqrt{M_{\text{H}_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.2$$

The effusion rate of the very light H_2 molecules is about 13 times that of the massive UF_6 molecules.

See Exercises 5.85 through 5.88.

Does the kinetic molecular model for gases correctly predict the relative effusion rates of gases summarized by Graham's law? To answer this question, we must recognize that the effusion rate for a gas depends directly on the average velocity of its particles. The faster the gas particles are moving, the more likely they are to pass through the effusion orifice. This reasoning leads to the following *prediction* for two gases at the same pressure and temperature (T):

$$\frac{\text{Effusion rate for gas 1}}{\text{Effusion rate for gas 2}} = \frac{u_{\text{rms}} \text{ for gas 1}}{u_{\text{rms}} \text{ for gas 2}} = \frac{\sqrt{\dfrac{3RT}{M_1}}}{\sqrt{\dfrac{3RT}{M_2}}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

This equation is identical to Graham's law. Thus the kinetic molecular model does fit the experimental results for the effusion of gases.

Diffusion

Visualization: Diffusion of Gases

Visualization: Gaseous Ammonia and Hydrochloric Acid

Diffusion is frequently illustrated by the lecture demonstration represented in Fig. 5.24, in which two cotton plugs soaked in ammonia and hydrochloric acid are simultaneously placed at the ends of a long tube. A white ring of ammonium chloride (NH_4Cl) forms where the NH_3 and HCl molecules meet several minutes later:

$$\underset{}{NH_3(g)} + HCl(g) \longrightarrow \underset{\text{White solid}}{NH_4Cl(s)}$$

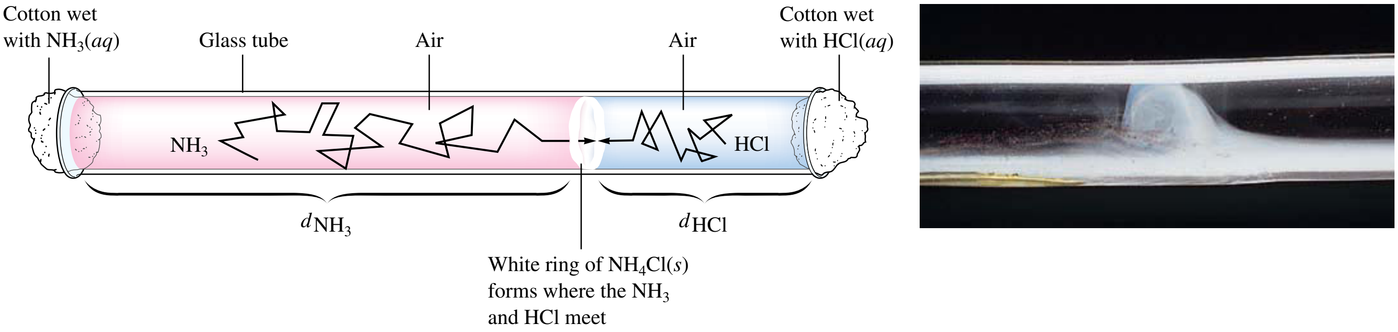


FIGURE 5.24
(above right) When HCl(g) and NH_3(g) meet in the tube, a white ring of NH_4Cl(s) forms. (above left) A demonstration of the relative diffusion rates of NH_3 and HCl molecules through air. Two cotton plugs, one dipped in HCl(aq) and one dipped in NH_3(aq), are simultaneously inserted into the ends of the tube. Gaseous NH_3 and HCl vaporizing from the cotton plugs diffuse toward each other and, where they meet, react to form NH_4Cl(s).

As a first approximation we might expect that the distances traveled by the two gases are related to the relative velocities of the gas molecules:

$$\frac{\text{Distance traveled by NH}_3}{\text{Distance traveled by HCl}} = \frac{u_{\text{rms}} \text{ for NH}_3}{u_{\text{rms}} \text{ for HCl}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} = 1.5$$

However, careful experiments produce an observed ratio of less than 1.5, indicating that a quantitative analysis of diffusion requires a more complex analysis.

The diffusion of the gases through the tube is surprisingly slow in light of the fact that the velocities of HCl and NH_3 molecules at 25°C are about 450 and 660 meters per second, respectively. Why does it take several minutes for the NH_3 and HCl molecules to meet? The answer is that the tube contains air and thus the NH_3 and HCl molecules undergo many collisions with O_2 and N_2 molecules as they travel through the tube. Because so many collisions occur when gases mix, diffusion is quite complicated to describe theoretically.

5.8 Real Gases

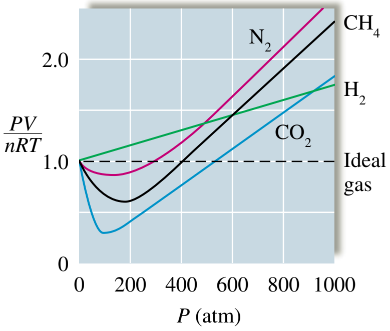


FIGURE 5.25
Plots of PV/nRT versus P for several gases (200 K). Note the significant deviations from ideal behavior ($PV/nRT = 1$). The behavior is close to ideal only at low pressures (less than 1 atm).

An ideal gas is a hypothetical concept. No gas *exactly* follows the ideal gas law, although many gases come very close at low pressures and/or high temperatures. Thus ideal gas behavior can best be thought of as the behavior *approached by real gases* under certain conditions.

We have seen that a very simple model, the kinetic molecular theory, by making some rather drastic assumptions (no interparticle interactions and zero volume for the gas particles), successfully explains ideal behavior. However, it is important that we examine real gas behavior to see how it differs from that predicted by the ideal gas law and to determine what modifications are needed in the kinetic molecular theory to explain the observed behavior. Since a model is an approximation and will inevitably fail, we must be ready to learn from such failures. In fact, we often learn more about nature from the failures of our models than from their successes.

We will examine the experimentally observed behavior of real gases by measuring the pressure, volume, temperature, and number of moles for a gas and noting how the quantity PV/nRT depends on pressure. Plots of PV/nRT versus P are shown for several gases in Fig. 5.25. For an ideal gas, PV/nRT equals 1 under all conditions, but notice that for real gases, PV/nRT approaches 1 only at very low pressures (typically below 1 atm). To illustrate the effect of temperature, PV/nRT is plotted versus P for nitrogen gas at several temperatures in Fig. 5.26. Note that the behavior of the gas appears to become more nearly ideal as the temperature is increased. The most important conclusion to be drawn from these figures is that a real gas typically exhibits behavior that is closest to ideal behavior at *low pressures* and *high temperatures.*

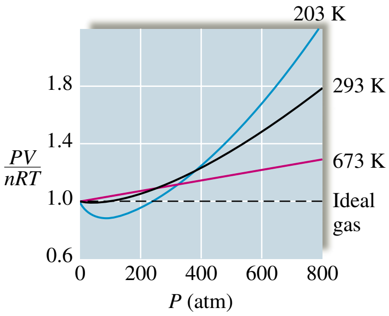


FIGURE 5.26
Plots of PV/nRT versus P for nitrogen gas at three temperatures. Note that although nonideal behavior is evident in each case, the deviations are smaller at the higher temperatures.

One of the most important procedures in science is correcting our models as we collect more data. We will understand more clearly how gases actually behave if we can figure out how to correct the simple model that explains the ideal gas law so that the new model fits the behavior we actually observe for gases. So the question is: How can we modify the assumptions of the kinetic molecular theory to fit the behavior of real gases? The first person to do important work in this area was Johannes van der Waals (1837–1923), a physics professor at the University of Amsterdam who in 1910 received a Nobel Prize for his work. To follow his analysis, we start with the ideal gas law,

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

Remember that this equation describes the behavior of a hypothetical gas consisting of volumeless entities that do not interact with each other. In contrast, a real gas consists of atoms or molecules that have finite volumes. Therefore, the volume available to a given particle in a real gas is less than the volume of the container because the gas particles themselves take up some of the space. To account for this discrepancy, van der Waals represented the actual volume as the volume of the container V minus a correction factor for the volume of the molecules nb, where n is the number of moles of gas and b is an empirical constant (one determined by fitting the equation to the experimental results). Thus the volume *actually available* to a given gas molecule is given by the difference $V - nb$.

This modification of the ideal gas equation leads to the equation

P' is corrected for the finite volume of the particles. The attractive forces have not yet been taken into account.

$$P' = \frac{nRT}{V - nb}$$

The volume of the gas particles has now been taken into account.

The next step is to allow for the attractions that occur among the particles in a real gas. The effect of these attractions is to make the observed pressure P_{obs} smaller than it would be if the gas particles did not interact:

$$P_{\text{obs}} = (P' - \text{correction factor}) = \left(\frac{nRT}{V - nb} - \text{correction factor}\right)$$

The attractive forces among molecules will be discussed in Chapter 10.

This effect can be understood using the following model. When gas particles come close together, attractive forces occur, which cause the particles to hit the wall very slightly less often than they would in the absence of these interactions (see Fig. 5.27).

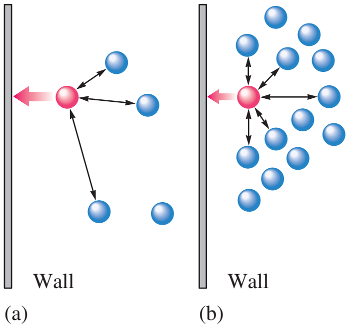


FIGURE 5.27
(a) Gas at low concentration—relatively few interactions between particles. The indicated gas particle exerts a pressure on the wall close to that predicted for an ideal gas. (b) Gas at high concentration—many more interactions between particles. The indicated gas particle exerts a much lower pressure on the wall than would be expected in the absence of interactions.

The size of the correction factor depends on the concentration of gas molecules defined in terms of moles of gas particles per liter (n/V). The higher the concentration, the more likely a pair of gas particles will be close enough to attract each other. For large numbers of particles, the number of interacting *pairs* of particles depends on the square of the number of particles and thus on the square of the concentration, or $(n/V)^2$. This can be justified as follows: In a gas sample containing N particles, there are $N - 1$ partners available for each particle, as shown in Fig. 5.28. Since the $1 \cdots 2$ pair is the same as the $2 \cdots 1$ pair, this analysis counts each pair twice. Thus, for N particles, there are $N(N - 1)/2$ pairs. If N is a very large number, $N - 1$ approximately equals N, giving $N^2/2$ possible pairs. Thus the pressure, corrected for the attractions of the particles, has the form

$$P_{\text{obs}} = P' - a\left(\frac{n}{V}\right)^2$$

where a is a proportionality constant (which includes the factor of $\frac{1}{2}$ from $N^2/2$). The value of a for a given real gas can be determined from observing the actual behavior of that gas. Inserting the corrections for both the volume of the particles and the attractions of the particles gives the equation

$$\underset{\text{Observed pressure}}{P_{\text{obs}}} = \frac{nRT}{\underset{\substack{\text{Volume}\\\text{of the}\\\text{container}}}{V} - \underbrace{nb}_{\substack{\text{Volume}\\\text{correction}}}} - a\underbrace{\left(\frac{n}{V}\right)^2}_{\substack{\text{Pressure}\\\text{correction}}}$$

We have now corrected for both the finite volume and the attractive forces of the particles.

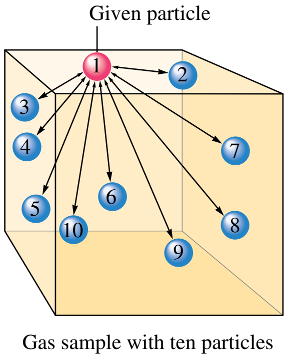


FIGURE 5.28
Illustration of pairwise interactions among gas particles. In a sample with 10 particles, each particle has 9 possible partners, to give $10(9)/2 = 45$ distinct pairs. The factor of $\frac{1}{2}$ arises because when particle 1 is the particle of interest we count the ① ⋯ ② pair, and when particle ② is the particle of interest we count the ② ⋯ ① pair. However, ① ⋯ ② and ② ⋯ ① are the same pair that we have counted twice. Therefore, we must divide by 2 to get the actual number of pairs.

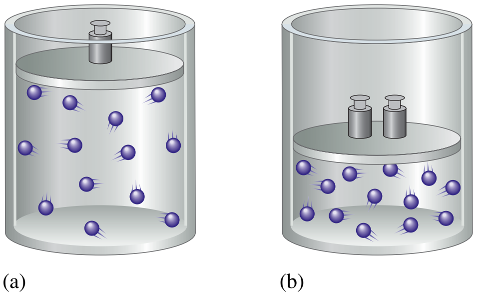


FIGURE 5.29
The volume taken up by the gas particles themselves is less important at (a) large container volume (low pressure) than at (b) small container volume (high pressure).

This equation can be rearranged to give the **van der Waals equation:**

P_{obs} is usually called just P.

$$\underbrace{\underbrace{\left[P_{\text{obs}} + a\left(\frac{n}{V}\right)^2\right]}_{\text{Corrected pressure}}}_{P_{\text{ideal}}} \times \underbrace{\underbrace{(V - nb)}_{\text{Corrected volume}}}_{V_{\text{ideal}}} = nRT$$

TABLE 5.3 Values of the van der Waals Constants for Some Common Gases

Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
NH_3	4.17	0.0371
H_2O	5.46	0.0305

The values of the weighting factors a and b are determined for a given gas by fitting experimental behavior. That is, a and b are varied until the best fit of the observed pressure is obtained under all conditions. The values of a and b for various gases are given in Table 5.3.

Experimental studies indicate that the changes van der Waals made in the basic assumptions of the kinetic molecular theory correct the major flaws in the model. First, consider the effects of volume. For a gas at low pressure (large volume), the volume of the container is very large compared with the volumes of the gas particles. That is, in this case the volume available to the gas is essentially equal to the volume of the container, and the gas behaves ideally. On the other hand, for a gas at high pressure (small container volume), the volume of the particles becomes significant so that the volume available to the gas is significantly less than the container volume. These cases are illustrated in Fig. 5.29. Note from Table 5.3 that the volume correction constant b generally increases with the size of the gas molecule, which gives further support to these arguments.

The fact that a real gas tends to behave more ideally at high temperatures also can be explained in terms of the van der Waals model. At high temperatures the particles are moving so rapidly that the effects of interparticle interactions are not very important.

The corrections to the kinetic molecular theory that van der Waals found necessary to explain real gas behavior make physical sense, which makes us confident that we understand the fundamentals of gas behavior at the particle level. This is significant because so much important chemistry takes place in the gas phase. In fact, the mixture of gases called the atmosphere is vital to our existence. In Section 5.10 we consider some of the important reactions that occur in the atmosphere.

5.9 Characteristics of Several Real Gases

We can understand gas behavior more completely if we examine the characteristics of several common gases. Note from Figure 5.25 that the gases H_2, N_2, CH_4, and CO_2 show different behavior when the compressibility $(\frac{PV}{nRT})$ is plotted versus P. For example, notice that the plot for $H_2(g)$ never drops below the ideal value (1.0) in contrast to all the other gases. What is special about H_2 compared to these other gases? Recall from Section 5.8 that the reason that the compressibility of a real gas falls below 1.0 is that the actual (observed) pressure is lower than the pressure expected for an ideal gas due to the intermolecular attractions that occur in real gases. This must mean that H_2 molecules have very low attractive forces for each other. This idea is borne out by looking at the van der Waals *a* value for H_2 in Table 5.3. Note that H_2 has the lowest value among the gases H_2, N_2, CH_4, and CO_2. Remember that the value of *a* reflects how much of a correction must be made to adjust the observed pressure up to the expected ideal pressure:

$$P_{\text{ideal}} = P_{\text{observed}} + a\left(\frac{n}{V}\right)^2$$

A low value for *a* reflects weak intermolecular forces among the gas molecules.

Also notice that although the compressibility for N_2 dips below 1.0, it does not show as much deviation as that for CH_4, which in turn does not show as much deviation as the compressibility for CO_2. Based on this behavior we can surmise that the importance of intermolecular interactions increases in this order:

$$H_2 < N_2 < CH_4 < CO_2$$

This order is reflected by the relative *a* values for these gases in Table 5.3. In Section 10.1, we will see how these variations in intermolecular interactions can be explained. The main point to be made here is that real gas behavior can tell us about the relative importance of intermolecular attractions among gas molecules.

TABLE 5.4 Atmospheric Composition Near Sea Level (Dry Air)*

Component	Mole Fraction
N_2	0.78084
O_2	0.20948
Ar	0.00934
CO_2	0.000345
Ne	0.00001818
He	0.00000524
CH_4	0.00000168
Kr	0.00000114
H_2	0.0000005
NO	0.0000005
Xe	0.000000087

*The atmosphere contains various amounts of water vapor depending on conditions.

5.10 Chemistry in the Atmosphere

The most important gases to us are those in the **atmosphere** that surrounds the earth's surface. The principal components are N_2 and O_2, but many other important gases, such as H_2O and CO_2, are also present. The average composition of the earth's atmosphere near sea level, with the water vapor removed, is shown in Table 5.4. Because of gravitational effects, the composition of the earth's atmosphere is not constant; heavier molecules tend to be near the earth's surface, and light molecules tend to migrate to higher altitudes, with some eventually escaping into space. The atmosphere is a highly complex and dynamic system, but for convenience we divide it into several layers based on the way the temperature changes with altitude. (The lowest layer, called the *troposphere,* is shown in Fig. 5.30.) Note that in contrast to the complex temperature profile of the atmosphere, the pressure decreases in a regular way with increasing altitude.

The chemistry occurring in the higher levels of the atmosphere is mostly determined by the effects of high-energy radiation and particles from the sun and other sources in space. In fact, the upper atmosphere serves as an important shield to prevent this high-energy radiation from reaching the earth, where it would damage the relatively fragile molecules sustaining life. In particular, the ozone in the upper atmosphere helps prevent high-energy ultraviolet radiation from penetrating to the earth. Intensive research is in progress to determine the natural factors that control the ozone concentration and how it is affected by chemicals released into the atmosphere.

The chemistry occurring in the troposphere, the layer of atmosphere closest to the earth's surface, is strongly influenced by human activities. Millions of tons of gases and particulates are released into the troposphere by our highly industrial civilization. Actually, it is amazing that the atmosphere can absorb so much material with relatively small permanent changes (so far).

Significant changes, however, are occurring. Severe **air pollution** is found around many large cities, and it is probable that long-range changes in our planet's weather are taking place. We will discuss some of the long-range effects of pollution in Chapter 6. In this section we will deal with short-term, localized effects of pollution.

The two main sources of pollution are transportation and the production of electricity. The combustion of petroleum in vehicles produces CO, CO_2, NO, and NO_2, along with unburned molecules from petroleum. When this mixture is trapped close to the ground in stagnant air, reactions occur producing chemicals that are potentially irritating and harmful to living systems.

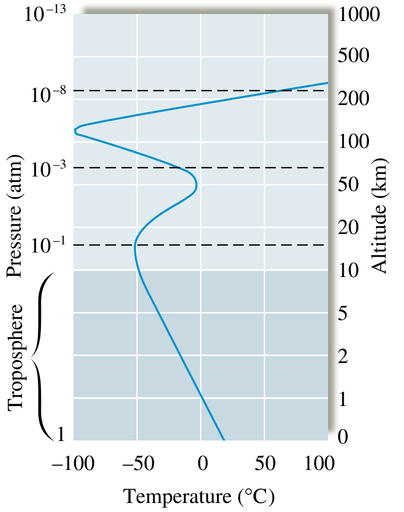


FIGURE 5.30
The variation of temperature (blue) and pressure (dashed lines) with altitude. Note that the pressure steadily decreases with altitude, but the temperature increases and decreases.

CHEMICAL IMPACT

Acid Rain: A Growing Problem

Rainwater, even in pristine wilderness areas, is slightly acidic because some of the carbon dioxide present in the atmosphere dissolves in the raindrops to produce H^+ ions by the following reaction:

$$H_2O(l) + CO_2(g) \longrightarrow H^+(aq) + HCO_3^-(aq)$$

This process produces only very small concentrations of H^+ ions in the rainwater. However, gases such as NO_2 and SO_2, which are by-products of energy use, can produce significantly higher H^+ concentrations. Nitrogen dioxide reacts with water to give a mixture of nitrous acid and nitric acid:

$$2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$$

Sulfur dioxide is oxidized to sulfur trioxide, which then reacts with water to form sulfuric acid:

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

The damage caused by the acid formed in polluted air is a growing worldwide problem. Lakes are dying in Norway, the forests are under stress in Germany, and buildings and statues are deteriorating all over the world.

The Field Museum in Chicago contains more white Georgia marble than any other structure in the world. But nearly 70 years of exposure to the elements has taken such a toll on it that the building has recently undergone a multimillion-dollar renovation to replace the damaged marble with freshly quarried material.

What is the chemistry of the deterioration of marble by sulfuric acid? Marble is produced by geologic processes at high temperatures and pressures from limestone, a sedimentary rock formed by slow deposition of calcium carbonate from the shells of marine organisms. Limestone and marble are chemically identical ($CaCO_3$) but differ in physical properties; limestone is composed of smaller particles of calcium carbonate and is thus more porous and more workable. Although both limestone and marble are used for buildings, marble can be polished to a higher sheen and is often preferred for decorative purposes.

Both marble and limestone react with sulfuric acid to form calcium sulfate. The process can be represented most

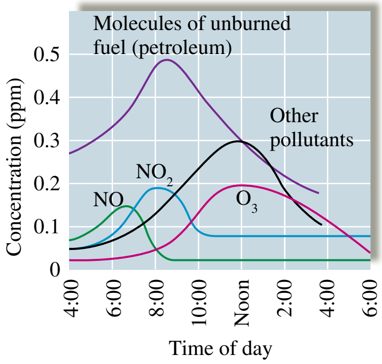


FIGURE 5.31
Concentration (in molecules per million molecules of "air") for some smog components versus time of day.
(From "Photochemistry of Air Pollution," by P. A. Leighton, in *Physical Chemistry: A Series of Monographs*, edited by Eric Hutchinson and P. Van Rysselberghe, copyright 1961 and renewed 1989, Elsevier Science (USA), reproduced by permission of the publisher.)

The complex chemistry of polluted air appears to center around the nitrogen oxides (NO_x). At the high temperatures found in the gasoline and diesel engines of cars and trucks, N_2 and O_2 react to form a small quantity of NO that is emitted into the air with the exhaust gases (see Fig. 5.31). This NO is immediately oxidized in air to NO_2, which, in turn, absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atoms:

$$NO_2(g) \xrightarrow{\text{Radiant energy}} NO(g) + O(g)$$

Oxygen atoms are very reactive and can combine with O_2 to form *ozone:*

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

Ozone is also very reactive and can react directly with other pollutants, or the ozone can absorb light and break up to form an energetically excited O_2 molecule (O_2*) and an energetically excited oxygen atom (O*). The latter species readily reacts with a water molecule to form two hydroxyl radicals (OH):

$$O^* + H_2O \longrightarrow 2OH$$

The hydroxyl radical is a very reactive oxidizing agent. For example, OH can react with NO_2 to form nitric acid:

$$OH + NO_2 \longrightarrow HNO_3$$

The OH radical has no charge [it has one fewer electron than the hydroxide ion (OH^-)].

The OH radical also can react with the unburned hydrocarbons in the polluted air to produce chemicals that cause the eyes to water and burn and are harmful to the respiratory system.

simply as

$$\mathrm{CaCO_3}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{SO_4{}^{2-}}(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}(g)$$

In this equation the calcium sulfate is represented by separate hydrated ions because calcium sulfate is quite water soluble and dissolves in rainwater. Thus, in areas bathed by rainwater, the marble slowly dissolves away.

In areas of the building protected from the rain, the calcium sulfate can form the mineral gypsum ($\mathrm{CaSO_4 \cdot 2H_2O}$). The $\cdot\, \mathrm{2H_2O}$ in the formula of gypsum indicates the presence of two water molecules (called *waters of hydration*) for each $\mathrm{CaSO_4}$ formula unit in the solid. The smooth surface of the marble is thus replaced by a thin layer of gypsum, a more porous material that binds soot and dust.

What can be done to protect limestone and marble structures from this kind of damage? Of course, one approach is to lower sulfur dioxide emissions from power plants (see Fig. 5.33). In addition, scientists are experimenting with coatings to protect marble from the acidic atmosphere. However, a coating can do more harm than good unless it "breathes." If moisture trapped beneath the coating freezes, the expanding ice can fracture the marble. Needless to say, it is difficult to find a coating that will allow water, but not acid, to pass—but the search continues.

The damaging effects of acid rain can be seen by comparing these photos of a decorative statue on the Field Museum in Chicago. The first photo was taken about 1920, the second in 1990.

The end product of this whole process is often referred to as **photochemical smog,** so called because light is required to initiate some of the reactions. The production of photochemical smog can be understood more clearly by examining as a group the reactions discussed above:

$$\begin{aligned} \mathrm{NO_2}(g) &\longrightarrow \mathrm{NO}(g) + \mathrm{O}(g) \\ \mathrm{O}(g) + \mathrm{O_2}(g) &\longrightarrow \mathrm{O_3}(g) \\ \mathrm{NO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) &\longrightarrow \mathrm{NO_2}(g) \\ \hline \text{Net reaction:}\quad \tfrac{3}{2}\mathrm{O_2}(g) &\longrightarrow \mathrm{O_3}(g) \end{aligned}$$

Although represented here as $\mathrm{O_2}$, the actual oxidant for NO is OH or an organic peroxide such as $\mathrm{CH_3COO}$, formed by oxidation of organic pollutants.

Note that the $\mathrm{NO_2}$ molecules assist in the formation of ozone without being themselves used up. The ozone formed then leads to the formation of OH and other pollutants.

We can observe this process by analyzing polluted air at various times during a day (see Fig. 5.31). As people drive to work between 6 and 8 a.m., the amounts of NO, $\mathrm{NO_2}$, and unburned molecules from petroleum increase. Later, as the decomposition of $\mathrm{NO_2}$ occurs, the concentration of ozone and other pollutants builds up. Current efforts to combat the formation of photochemical smog are focused on cutting down the amounts of molecules from unburned fuel in automobile exhaust and designing engines that produce less nitric oxide.

The other major source of pollution results from burning coal to produce electricity. Much of the coal found in the Midwest contains significant quantities of sulfur, which, when burned, produces sulfur dioxide:

$$\mathrm{S\ (in\ coal)} + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$$

A further oxidation reaction occurs when sulfur dioxide is changed to sulfur trioxide in the air:*

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

The production of sulfur trioxide is significant because it can combine with droplets of water in the air to form sulfuric acid:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Sulfuric acid is very corrosive to both living things and building materials. Another result of this type of pollution is **acid rain.** In many parts of the northeastern United States and southeastern Canada, acid rain has caused some freshwater lakes to become too acidic to support any life (Fig. 5.32).

FIGURE 5.32
An environmental officer in Wales tests the pH of water.

The problem of sulfur dioxide pollution is made more complicated by the energy crisis. As petroleum supplies dwindle and the price increases, our dependence on coal will probably grow. As supplies of low-sulfur coal are used up, high-sulfur coal will be utilized. One way to use high-sulfur coal without further harming the air quality is to remove the sulfur dioxide from the exhaust gas by means of a system called a *scrubber* before it is emitted from the power plant stack. A common method of scrubbing is to blow powdered limestone ($CaCO_3$) into the combustion chamber, where it is decomposed to lime and carbon dioxide:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The lime then combines with the sulfur dioxide to form calcium sulfite:

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

To remove the calcium sulfite and any remaining unreacted sulfur dioxide, an aqueous suspension of lime is injected into the exhaust gases to produce a *slurry* (a thick suspension), as shown in Fig. 5.33.

Unfortunately, there are many problems associated with scrubbing. The systems are complicated and expensive and consume a great deal of energy. The large quantities of calcium sulfite produced in the process present a disposal problem. With a typical scrubber, approximately 1 ton of calcium sulfite per year is produced per person served by the power plant. Since no use has yet been found for this calcium sulfite, it is usually buried in a landfill. As a result of these difficulties, air pollution by sulfur dioxide continues to be a major problem, one that is expensive in terms of damage to the environment and human health as well as in monetary terms.

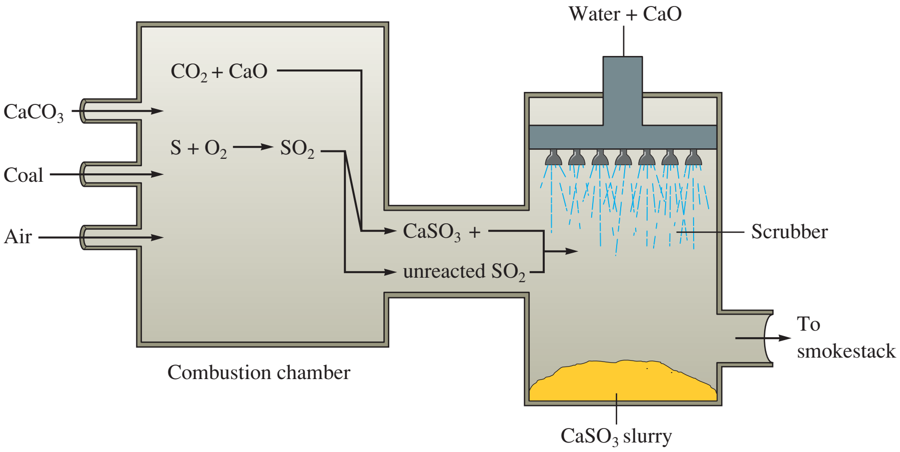


FIGURE 5.33
A schematic diagram of the process for scrubbing sulfur dioxide from stack gases in power plants.

---

*This reaction is very slow unless solid particles are present. See Chapter 12 for a discussion.

Key Terms

Section 5.1
barometer
manometer
mm Hg
torr
standard atmosphere
pascal

Section 5.2
Boyle's law
ideal gas
Charles's law
absolute zero
Avogadro's law

Section 5.3
universal gas constant
ideal gas law

Section 5.4
molar volume
standard temperature and pressure (STP)

Section 5.5
Dalton's law of partial pressures
partial pressure
mole fraction

Section 5.6
kinetic molecular theory (KMT)
root mean square velocity
joule

Section 5.7
diffusion
effusion
Graham's law of effusion

Section 5.8
real gas
van der Waals equation

Section 5.10
atmosphere
air pollution
photochemical smog
acid rain

For Review

State of a gas

- The state of a gas can be described completely by specifying its pressure (P), volume (V), temperature (T) and the amount (moles) of gas present (n)
- Pressure
  - Common units

$$1 \text{ torr} = 1 \text{ mm Hg}$$
$$1 \text{ atm} = 760 \text{ torr}$$

  - SI unit: pascal

$$1 \text{ atm} = 101{,}325 \text{ Pa}$$

Gas laws

- Discovered by observing the properties of gases
- Boyle's law: $PV = k$
- Charles's law: $V = bT$
- Avogadro's law: $V = an$
- Ideal gas law: $PV = nRT$
- Dalton's law of partial pressures: $P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$, where P_n represents the partial pressure of component n in a mixture of gases

Kinetic molecular theory (KMT)

- Model that accounts for ideal gas behavior
- Postulates of the KMT:
  - Volume of gas particles is zero
  - No particle interactions
  - Particles are in constant motion, colliding with the container walls to produce pressure
  - The average kinetic energy of the gas particles is directly proportional to the temperature of the gas in kelvins

Gas properties

- The particles in any gas sample have a range of velocities
- The root mean square (rms) velocity for a gas represents the average of the squares of the particle velocities

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- Diffusion: the mixing of two or more gases
- Effusion: the process in which a gas passes through a small hole into an empty chamber

Real gas behavior

- Real gases behave ideally only at high temperatures and low pressures
- Understanding how the ideal gas equation must be modified to account for real gas behavior helps us understand how gases behave on a molecular level
- Van der Waals found that to describe real gas behavior we must consider particle interactions and particle volumes

REVIEW QUESTIONS

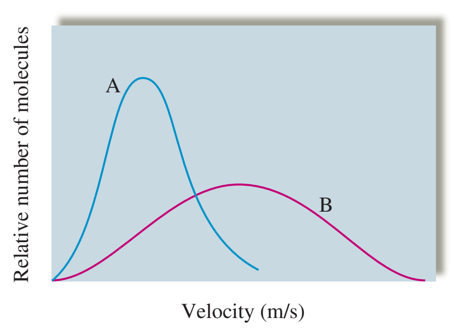
1. Explain how a barometer and a manometer work to measure the pressure of the atmosphere or the pressure of a gas in a container.

2. What are Boyle's law, Charles's law, and Avogadro's law? What plots do you make to show a linear relationship for each law?
3. Show how Boyle's law, Charles's law, and Avogadro's law are special cases of the ideal gas law. Using the ideal gas law, determine the relationship between P and n (at constant V and T) and between P and T (at constant V and n).
4. Rationalize the following observations.
   a. Aerosol cans will explode if heated.
   b. You can drink through a soda straw.
   c. A thin-walled can will collapse when the air inside is removed by a vacuum pump.
   d. Manufacturers produce different types of tennis balls for high and low elevations.
5. Consider the following balanced equation in which gas X forms gas X_2:

$$2X(g) \rightarrow X_2(g)$$

Equal moles of X are placed in two separate containers. One container is rigid so the volume cannot change; the other container is flexible so the volume changes to keep the internal pressure equal to the external pressure. The above reaction is run in each container. What happens to the pressure and density of the gas inside each container as reactants are converted to products?

6. Use the postulates of the kinetic molecular theory (KMT) to explain why Boyle's law, Charles's law, Avogadro's law, and Dalton's law of partial pressures hold true for ideal gases. Use the KMT to explain the P versus n (at constant V and T) relationship and the P versus T (at constant V and n) relationship.
7. Consider the following velocity distribution curves A and B.

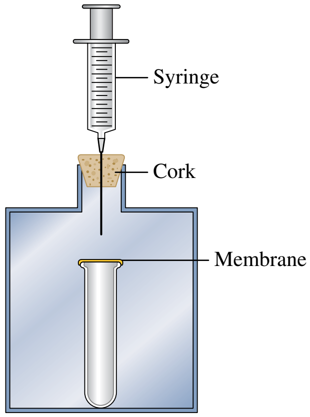


   a. If the plots represent the velocity distribution of 1.0 L of He(g) at STP versus 1.0 L of $Cl_2(g)$ at STP, which plot corresponds to each gas? Explain your reasoning.
   b. If the plots represent the velocity distribution of 1.0 L of $O_2(g)$ at temperatures of 273 K versus 1273 K, which plot corresponds to each temperature? Explain your reasoning. Under which temperature condition would the $O_2(g)$ sample behave most ideally? Explain.
8. Briefly describe two methods one might use to find the molar mass of a newly synthesized gas for which a molecular formula was not known.
9. In the van der Waals equation, why is a term added to the observed pressure and why is a term subtracted from the container volume to correct for nonideal gas behavior?
10. Why do real gases not always behave ideally? Under what conditions does a real gas behave most ideally? Why?

Active Learning Questions

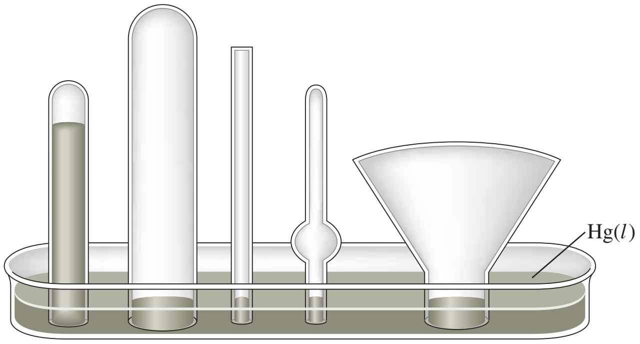
These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Consider the following apparatus: a test tube covered with a nonpermeable elastic membrane inside a container that is closed with a cork. A syringe goes through the cork.

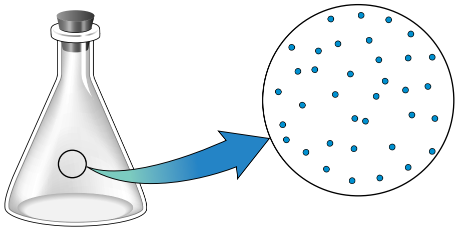


   a. As you push down on the syringe, how does the membrane covering the test tube change?
   b. You stop pushing the syringe but continue to hold it down. In a few seconds, what happens to the membrane?
2. Figure 5.2 shows a picture of a barometer. Which of the following statements is the best explanation of how this barometer works?
   a. Air pressure outside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.
   b. Air pressure inside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.
   c. Air pressure outside the tube counterbalances the weight of the mercury in the tube.
   d. Capillary action of the mercury causes the mercury to go up the tube.
   e. The vacuum that is formed at the top of the tube holds up the mercury.

   Justify your choice, and for the choices you did not pick, explain what is wrong with them. Pictures help!
3. The barometer below shows the level of mercury at a given atmospheric pressure. Fill all the other barometers with mercury for that same atmospheric pressure. Explain your answer.



4. As you increase the temperature of a gas in a sealed, rigid container, what happens to the density of the gas? Would the results be the same if you did the same experiment in a container with a piston at constant pressure? (See Figure 5.17.)
5. A diagram in a chemistry book shows a magnified view of a flask of air as follows:



   What do you suppose is between the dots (the dots represent air molecules)?
   a. air
   b. dust
   c. pollutants
   d. oxygen
   e. nothing
6. If you put a drinking straw in water, place your finger over the opening, and lift the straw out of the water, some water stays in the straw. Explain.
7. A chemistry student relates the following story: I noticed my tires were a bit low and went to the gas station. As I was filling the tires, I thought about the kinetic molecular theory (KMT). I noticed the tires because the volume was low, and I realized that I was increasing both the pressure and volume of the tires. “Hmmm,” I thought, “that goes against what I learned in chemistry, where I was told pressure and volume are inversely proportional.” What is the fault in the logic of the chemistry student in this situation? Explain *why* we think pressure and volume to be inversely related (draw pictures and use the KMT).
8. Chemicals *X* and *Y* (both gases) react to form the gas *XY*, but it takes a bit of time for the reaction to occur. Both *X* and *Y* are placed in a container with a piston (free to move), and you note the volume. As the reaction occurs, what happens to the volume of the container? (See Fig. 5.18.)
9. Which statement best explains why a hot-air balloon rises when the air in the balloon is heated?
   a. According to Charles’s law, the temperature of a gas is directly related to its volume. Thus the volume of the balloon increases, making the density smaller. This lifts the balloon.
   b. Hot air rises inside the balloon, and this lifts the balloon.
   c. The temperature of a gas is directly related to its pressure. The pressure therefore increases, and this lifts the balloon.
   d. Some of the gas escapes from the bottom of the balloon, thus decreasing the mass of gas in the balloon. This decreases the density of the gas in the balloon, which lifts the balloon.
   e. Temperature is related to the root mean square velocity of the gas molecules. Thus the molecules are moving faster, hitting the balloon more, and thus lifting the balloon.

   Justify your choice, and for the choices you did not pick, explain what is wrong with them.

10. Draw a highly magnified view of a sealed, rigid container filled with a gas. Then draw what it would look like if you cooled the gas significantly but kept the temperature above the boiling point of the substance in the container. Also draw what it would look like if you heated the gas significantly. Finally, draw what each situation would look like if you evacuated enough of the gas to decrease the pressure by a factor of 2.

11. If you release a helium balloon, it soars upward and eventually pops. Explain this behavior.

12. If you have any two gases in different containers that are the same size at the same pressure and same temperature, what is true about the moles of each gas? Why is this true?

13. Explain the following seeming contradiction: You have two gases, *A* and *B*, in two separate containers of equal volume and at equal pressure and temperature. Therefore, you must have the same number of moles of each gas. Because the two temperatures are equal, the average kinetic energies of the two samples are equal. Therefore, since the energy given such a system will be converted to translational motion (that is, move the molecules), the root mean square velocities of the two are equal, and thus the particles in each sample move, on average, with the same relative speed. Since *A* and *B* are different gases, they each must have a different molar mass. If *A* has higher molar mass than *B*, the particles of *A* must be hitting the sides of the container with more force. Thus the pressure in the container of gas *A* must be higher than that in the container with gas *B*. However, one of our initial assumptions was that the pressures were equal.

14. You have a balloon covering the mouth of a flask filled with air at 1 atm. You apply heat to the bottom of the flask until the volume of the balloon is equal to that of the flask.

a. Which has more air in it, the balloon or the flask? Or do both have the same amount? Explain.

b. In which is the pressure greater, the balloon or the flask? Or is the pressure the same? Explain.

15. How does Dalton's law of partial pressures help us with our model of ideal gases? That is, what postulates of the kinetic molecular theory does it support?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide.*

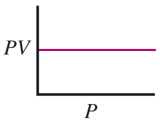
Questions

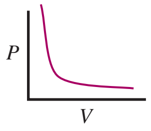
16. At room temperature, water is a liquid with a molar volume of 18 mL. At 105°C and 1 atm pressure, water is a gas and has a molar volume of over 30 L. Explain the large difference in molar volumes.

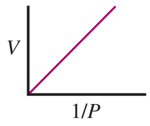
17. If a barometer were built using water ($d = 1.0$ g/cm^3) instead of mercury ($d = 13.6$ g/cm^3), would the column of water be higher than, lower than, or the same as the column of mercury at 1.00 atm? If the level is different, by what factor? Explain.

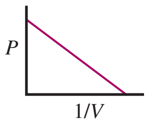
18. A bag of potato chips is packed and sealed in Los Angeles, California, and then shipped to Lake Tahoe, Nevada, during ski season. It is noticed that the volume of the bag of potato chips has increased upon its arrival in Lake Tahoe. What external conditions would most likely cause the volume increase?

19. Boyle's law can be represented graphically in several ways. Which of the following plots does *not* correctly represent Boyle's law (assuming constant *T* and *n*)? Explain.









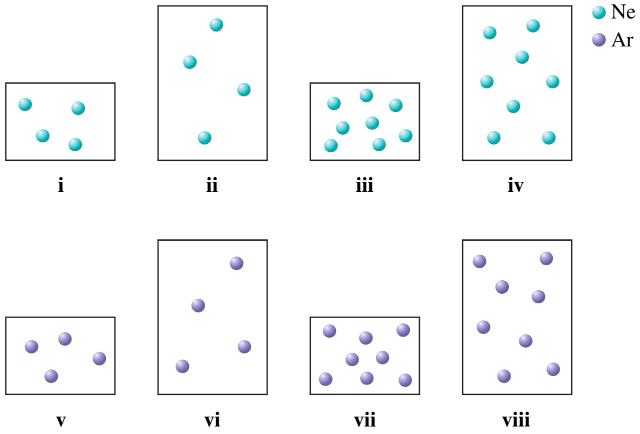
20. As weather balloons rise from the earth's surface, the pressure of the atmosphere becomes less, tending to cause the volume of the balloons to expand. However, the temperature is much lower in the upper atmosphere than at sea level. Would this temperature effect tend to make such a balloon expand or contract? Weather balloons do, in fact, expand as they rise. What does this tell you?

21. Which noble gas has the smallest density at STP? Explain.

22. Consider two different containers, each filled with 2 moles of Ne(g). One of the containers is rigid and has constant volume. The other container is flexible (like a balloon) and is capable of changing its volume to keep the external pressure and internal pressure equal to each other. If you raise the temperature in both containers, what happens to the pressure and density of the gas inside each container? Assume a constant external pressure.

23. Do all the molecules in a 1-mol sample of $CH_4(g)$ have the same kinetic energy at 273 K? Do all molecules in a 1-mol sample of $N_2(g)$ have the same velocity at 546 K? Explain.

24. Consider the following samples of gases at the same temperature.



Arrange each of these samples in order from lowest to highest:

a. pressure

b. average kinetic energy

c. density

d. root mean square velocity

Note: Some samples of gases may have equal values for these attributes. Assume the larger containers have a volume twice the volume of the smaller containers and assume the mass of an argon atom is twice the mass of a neon atom.

25. As $NH_3(g)$ is decomposed into nitrogen gas and hydrogen gas at constant pressure and temperature, the volume of the product gases collected is twice the volume of NH_3 reacted. Explain. As $NH_3(g)$

is decomposed into nitrogen gas and hydrogen gas at constant volume and temperature, the total pressure increases by some factor. Why the increase in pressure and by what factor does the total pressure increase when reactants are completely converted into products? How do the partial pressures of the product gases compare to each other and to the initial pressure of NH_3?

26. Which of the following statements is (are) true? For the false statements, correct them.

a. At constant temperature, the lighter the gas molecules, the faster the average velocity of the gas molecules.

b. At constant temperature, the heavier the gas molecules, the larger the average kinetic energy of the gas molecules.

c. A real gas behaves most ideally when the container volume is relatively large and the gas molecules are moving relatively quickly.

d. As temperature increases, the effect of interparticle interactions on gas behavior is increased.

e. At constant *V* and *T*, as gas molecules are added into a container, the number of collisions per unit area increases resulting in a higher pressure.

f. The kinetic molecular theory predicts that pressure is inversely proportional to temperature at constant volume and mol of gas.

Exercises

In this section similar exercises are paired.

Pressure

27. Freon-12 (CF_2Cl_2) is commonly used as the refrigerant in central home air conditioners. The system is initially charged to a pressure of 4.8 atm. Express this pressure in each of the following units (1 atm = 14.7 psi).

a. mm Hg **b.** torr **c.** Pa **d.** psi

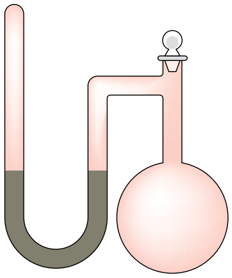
28. A gauge on a compressed gas cylinder reads 2200 psi (pounds per square inch; 1 atm = 14.7 psi). Express this pressure in each of the following units.

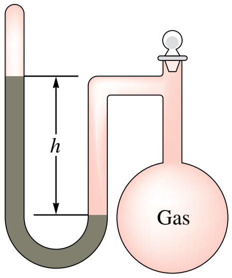
a. standard atmospheres

b. megapascals (MPa)

c. torr

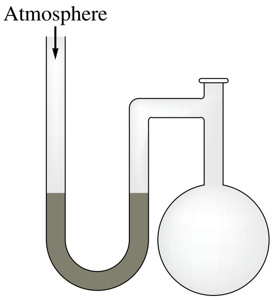
29. A sealed-tube manometer (as shown below) can be used to measure pressures below atmospheric pressure. The tube above the mercury is evacuated. When there is a vacuum in the flask, the mercury levels in both arms of the U-tube are equal. If a gaseous sample is introduced into the flask, the mercury levels are different. The difference *h* is a measure of the pressure of the gas inside the flask. If *h* is equal to 6.5 cm, calculate the pressure in the flask in torr, pascals, and atmospheres.



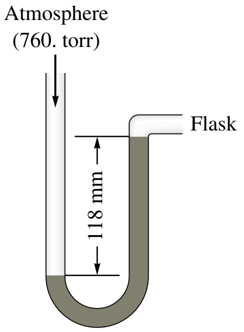


30. If the sealed-tube manometer in Exercise 29 had a height difference of 20.0 inches between the mercury levels, what is the pressure in the flask in torr and atmospheres?

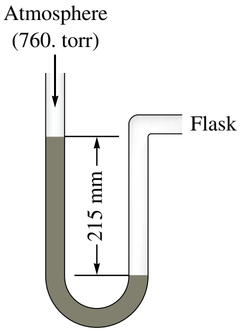
31. A diagram for an open-tube manometer is shown below.



If the flask is open to the atmosphere, the mercury levels are equal. For each of the following situations where a gas is contained in the flask, calculate the pressure in the flask in torr, atmospheres, and pascals.



a.



b.

c. Calculate the pressures in the flask in parts a and b (in torr) if the atmospheric pressure is 635 torr.

32. a. If the open-tube manometer in Exercise 31 contains a nonvolatile silicone oil (density = 1.30 g/cm^3) instead of mercury (density = 13.6 g/cm^3), what are the pressures in the flask as shown in parts a and b in torr, atmospheres, and pascals?

b. What advantage would there be in using a less dense fluid than mercury in a manometer used to measure relatively small differences in pressure?

Gas Laws

33. A particular balloon is designed by its manufacturer to be inflated to a volume of no more than 2.5 L. If the balloon is filled with 2.0 L of helium at sea level, is released, and rises to an altitude at which the atmospheric pressure is only 500. mm Hg, will the balloon burst? (Assume temperature is constant.)

34. A balloon is filled to a volume of 7.00×10^2 mL at a temperature of 20.0°C. The balloon is then cooled at constant pressure to a temperature of 1.00×10^2 K. What is the final volume of the balloon?

35. An 11.2-L sample of gas is determined to contain 0.50 mol of N_2. At the same temperature and pressure, how many moles of gas would there be in a 20.-L sample?

36. Consider the following chemical equation.

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

If 25.0 mL of NO_2 gas is completely converted to N_2O_4 gas under the same conditions, what volume will the N_2O_4 occupy?

37. Complete the following table for an ideal gas.

	P(atm)	*V*(L)	*n*(mol)	*T*
a.	5.00		2.00	155°C
b.	0.300	2.00		155 K
c.	4.47	25.0	2.01	
d.		2.25	10.5	75°C

38. Complete the following table for an ideal gas.

	P	*V*	*n*	*T*
a.	7.74×10^3 Pa	12.2 mL		25°C
b.		43.0 mL	0.421 mol	223 K
c.	455 torr		4.4×10^{-2} mol	331°C
d.	745 mm Hg	11.2 L	0.401 mol	

39. Suppose two 200.0-L tanks are to be filled separately with the gases helium and hydrogen. What mass of each gas is needed to produce a pressure of 135 atm in its respective tank at 24°C?

40. A flask that can withstand an internal pressure of 2500 torr, but no more, is filled with a gas at 21.0°C and 758 torr and heated. At what temperature will it burst?

41. A 2.50-L container is filled with 175 g argon.

a. If the pressure is 10.0 atm, what is the temperature?
b. If the temperature is 225 K, what is the pressure?

42. A person accidentally swallows a drop of liquid oxygen, $O_2(l)$, which has a density of 1.149 g/mL. Assuming the drop has a volume of 0.050 mL, what volume of gas will be produced in the person's stomach at body temperature (37°C) and a pressure of 1.0 atm?

43. A gas sample containing 1.50 mol at 25°C exerts a pressure of 400. torr. Some gas is *added* to the same container and the temperature is increased to 50.°C. If the pressure increases to 800. torr, how many moles of gas were added to the container? Assume a constant-volume container.

44. A bicycle tire is filled with air to a pressure of 100. psi at a temperature of 19°C. Riding the bike on asphalt on a hot day increases the temperature of the tire to 58°C. The volume of the tire increases by 4.0%. What is the new pressure in the bicycle tire?

45. Consider two separate gas containers at the following conditions:

Container A	**Container B**
Contents: $SO_2(g)$	Contents: unknown gas
Pressure = P_A	Pressure = P_B
Moles of gas = 1.0 mol	Moles of gas = 2.0 mol
Volume = 1.0 L	Volume = 2.0 L
Temperature = 7°C	Temperature = 287°C

How is the pressure in container B related to the pressure in container A?

46. A container is filled with an ideal gas to a pressure of 40.0 atm at 0°C.

a. What will be the pressure in the container if it is heated to 45°C?
b. At what temperature would the pressure be 1.50×10^2 atm?
c. At what temperature would the pressure be 25.0 atm?

47. An ideal gas is contained in a cylinder with a volume of 5.0×10^2 mL at a temperature of 30.°C and a pressure of 710. torr. The gas is then compressed to a volume of 25 mL, and the temperature is raised to 820.°C. What is the new pressure of the gas?

48. A compressed gas cylinder contains 1.00×10^3 g of argon gas. The pressure inside the cylinder is 2050. psi (pounds per square inch) at a temperature of 18°C. How much gas remains in the cylinder if the pressure is decreased to 650. psi at a temperature of 26°C?

49. A sealed balloon is filled with 1.00 L of helium at 23°C and 1.00 atm. The balloon rises to a point in the atmosphere where the pressure is 220. torr and the temperature is −31°C. What is the change in volume of the balloon as it ascends from 1.00 atm to a pressure of 220. torr?

50. A hot-air balloon is filled with air to a volume of 4.00×10^3 m^3 at 745 torr and 21°C. The air in the balloon is then heated to 62°C, causing the balloon to expand to a volume of 4.20×10^3 m^3. What is the ratio of the number of moles of air in the heated balloon to the original number of moles of air in the balloon? (*Hint:* Openings in the balloon allow air to flow in and out. Thus the pressure in the balloon is always the same as that of the atmosphere.)

Gas Density, Molar Mass, and Reaction Stoichiometry

51. Consider the following reaction:

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

It takes 2.00 L of pure oxygen gas at STP to react completely with a certain sample of aluminum. What is the mass of aluminum reacted?

52. A student adds 4.00 g of dry ice (solid CO_2) to an empty balloon. What will be the volume of the balloon at STP after all the dry ice sublimes (converts to gaseous CO_2)?

53. Air bags are activated when a severe impact causes a steel ball to compress a spring and electrically ignite a detonator cap. This causes sodium azide (NaN_3) to decompose explosively according to the following reaction:

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

What mass of $NaN_3(s)$ must be reacted to inflate an air bag to 70.0 L at STP?

54. Concentrated hydrogen peroxide solutions are explosively decomposed by traces of transition metal ions (such as Mn or Fe):

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

What volume of pure $O_2(g)$, collected at 27°C and 746 torr, would be generated by decomposition of 125 g of a 50.0% by mass hydrogen peroxide solution? Ignore any water vapor that may be present.

55. In 1897 the Swedish explorer Andreé tried to reach the North Pole in a balloon. The balloon was filled with hydrogen gas. The hydrogen gas was prepared from iron splints and diluted sulfuric acid. The reaction is

$$Fe(s) + H_2SO_4(aq) \longrightarrow FeSO_4(aq) + H_2(g)$$

The volume of the balloon was 4800 m^3 and the loss of hydrogen gas during filling was estimated at 20.%. What mass of iron splints and 98% (by mass) H_2SO_4 were needed to ensure the complete filling of the balloon? Assume a temperature of 0°C, a pressure of 1.0 atm during filling, and 100% yield.

56. Sulfur trioxide, SO_3, is produced in enormous quantities each year for use in the synthesis of sulfuric acid.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

What volume of $O_2(g)$ at 350.°C and a pressure of 5.25 atm is needed to completely convert 5.00 g of sulfur to sulfur trioxide?

57. Consider the reaction between 50.0 mL of liquid methyl alcohol, CH_3OH (density = 0.850 g/mL), and 22.8 L of O_2 at 27°C and a pressure of 2.00 atm. The products of the reaction are $CO_2(g)$ and $H_2O(g)$. Calculate the number of moles of H_2O formed if the reaction goes to completion.

58. Urea (H_2NCONH_2) is used extensively as a nitrogen source in fertilizers. It is produced commercially from the reaction of ammonia and carbon dioxide:

$$2NH_3(g) + CO_2(g) \xrightarrow[\text{Pressure}]{\text{Heat}} H_2NCONH_2(s) + H_2O(g)$$

Ammonia gas at 223°C and 90. atm flows into a reactor at a rate of 500. L/min. Carbon dioxide at 223°C and 45 atm flows into the reactor at a rate of 600. L/min. What mass of urea is produced per minute by this reaction assuming 100% yield?

59. Hydrogen cyanide is prepared commercially by the reaction of methane, $CH_4(g)$, ammonia, $NH_3(g)$, and oxygen, $O_2(g)$, at high temperature. The other product is gaseous water.

a. Write a chemical equation for the reaction.

b. What volume of $HCN(g)$ can be obtained from 20.0 L $CH_4(g)$, 20.0 L $NH_3(g)$, and 20.0 L $O_2(g)$? The volumes of all gases are measured at the same temperature and pressure.

60. Methanol, CH_3OH, can be produced by the following reaction:

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(g)$$

Hydrogen at STP flows into a reactor at a rate of 16.0 L/min. Carbon monoxide at STP flows into the reactor at a rate of 25.0 L/min. If 5.30 g of methanol is produced per minute, what is the percent yield of the reaction?

61. An unknown diatomic gas has a density of 3.164 g/L at STP. What is the identity of the gas?

62. A compound has the empirical formula CHCl. A 256-mL flask, at 373 K and 750. torr, contains 0.800 g of the gaseous compound. Give the molecular formula.

63. Uranium hexafluoride is a solid at room temperature, but it boils at 56°C. Determine the density of uranium hexafluoride at 60.°C and 745 torr.

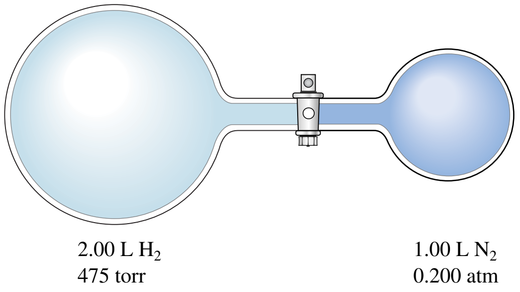
64. Given that a sample of air is made up of nitrogen, oxygen, and argon in the mole fractions 78% N_2, 21% O_2, and 1.0% Ar, what is the density of air at standard temperature and pressure?

Partial Pressure

65. A piece of solid carbon dioxide, with a mass of 7.8 g, is placed in a 4.0-L otherwise empty container at 27°C. What is the pressure in the container after all the carbon dioxide vaporizes? If 7.8 g solid carbon dioxide were placed in the same container but it already contained air at 740 torr, what would be the partial pressure of carbon dioxide and the total pressure in the container after the carbon dioxide vaporizes?

66. A mixture of 1.00 g H_2 and 1.00 g He is placed in a 1.00-L container at 27°C. Calculate the partial pressure of each gas and the total pressure.

67. Consider the flasks in the following diagram. What are the final partial pressures of H_2 and N_2 after the stopcock between the two flasks is opened? (Assume the final volume is 3.00 L.) What is the total pressure (in torr)?



68. Consider the flask apparatus in Exercise 67, which now contains 2.00 L of H_2 at a pressure of 360. torr and 1.00 L of N_2 at an unknown pressure. If the total pressure in the flasks is 320. torr after the stopcock is opened, determine the initial pressure of N_2 in the 1.00-L flask.

69. The partial pressure of $CH_4(g)$ is 0.175 atm and that of $O_2(g)$ is 0.250 atm in a mixture of the two gases.

a. What is the mole fraction of each gas in the mixture?
b. If the mixture occupies a volume of 10.5 L at 65°C, calculate the total number of moles of gas in the mixture.
c. Calculate the number of grams of each gas in the mixture.

70. A 1.00-L gas sample at 100.°C and 600. torr contains 50.0% helium and 50.0% xenon by mass. What are the partial pressures of the individual gases?

71. Small quantities of hydrogen gas can be prepared in the laboratory by the addition of aqueous hydrochloric acid to metallic zinc.

$$\mathrm{Zn}(s) + 2\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g)$$

Typically, the hydrogen gas is bubbled through water for collection and becomes saturated with water vapor. Suppose 240. mL of hydrogen gas is collected at 30.°C and has a total pressure of 1.032 atm by this process. What is the partial pressure of hydrogen gas in the sample? How many grams of zinc must have reacted to produce this quantity of hydrogen? (The vapor pressure of water is 32 torr at 30°C.)

72. Helium is collected over water at 25°C and 1.00 atm total pressure. What total volume of gas must be collected to obtain 0.586 g of helium? (At 25°C the vapor pressure of water is 23.8 torr.)

73. At elevated temperatures, sodium chlorate decomposes to produce sodium chloride and oxygen gas. A 0.8765-g sample of impure sodium chlorate was heated until the production of oxygen gas ceased. The oxygen gas collected over water occupied 57.2 mL at a temperature of 22°C and a pressure of 734 torr. Calculate the mass percent of $NaClO_3$ in the original sample. (At 22°C the vapor pressure of water is 19.8 torr.)

74. Xenon and fluorine will react to form binary compounds when a mixture of these two gases is heated to 400°C in a nickel reaction vessel. A 100.0-mL nickel container is filled with xenon and fluorine, giving partial pressures of 1.24 atm and 10.10 atm, respectively, at a temperature of 25°C. The reaction vessel is heated to 400°C to cause a reaction to occur and then cooled to a temperature at which F_2 is a gas and the xenon fluoride compound produced is a nonvolatile solid. The remaining F_2 gas is transferred to another 100.0-mL nickel container, where the pressure of F_2 at 25°C is 7.62 atm. Assuming all of the xenon has reacted, what is the formula of the product?

75. Hydrogen azide, HN_3, decomposes on heating by the following *unbalanced* reaction:

$$\mathrm{HN_3}(g) \longrightarrow \mathrm{N_2}(g) + \mathrm{H_2}(g)$$

If 3.0 atm of pure $HN_3(g)$ is decomposed initially, what is the final total pressure in the reaction container? What are the partial pressures of nitrogen and hydrogen gas? Assume the volume and temperature of the reaction container are constant.

76. Some very effective rocket fuels are composed of lightweight liquids. The fuel composed of dimethylhydrazine $[(CH_3)_2N_2H_2]$ mixed with dinitrogen tetroxide was used to power the Lunar Lander in its missions to the moon. The two components react according to the following equation:

$$\mathrm{(CH_3)_2N_2H_2}(l) + 2\mathrm{N_2O_4}(l) \longrightarrow 3\mathrm{N_2}(g) + 4\mathrm{H_2O}(g) + 2\mathrm{CO_2}(g)$$

If 150 g of dimethylhydrazine reacts with excess dinitrogen tetroxide and the product gases are collected at 27°C in an evacuated 250-L tank, what is the partial pressure of nitrogen gas produced and what is the total pressure in the tank assuming the reaction has 100% yield?

Kinetic Molecular Theory and Real Gases

77. Calculate the average kinetic energies of CH_4 and N_2 molecules at 273 K and 546 K.

78. A 100.-L flask contains a mixture of methane, CH_4, and argon at 25°C. The mass of argon present is 228 g and the mole fraction of methane in the mixture is 0.650. Calculate the total kinetic energy of the gaseous mixture.

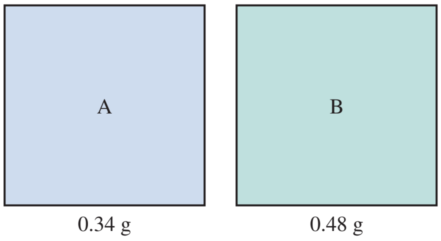
79. Calculate the root mean square velocities of CH_4 and N_2 molecules at 273 K and 546 K.

80. Consider separate 1.0-L samples of He(g) and $UF_6(g)$, both at 1.00 atm and containing the same number of moles. What ratio of temperatures for the two samples would produce the same root mean square velocity?

81. Consider a 1.0-L container of neon gas at STP. Will the average kinetic energy, average velocity, and frequency of collisions of gas molecules with the walls of the container increase, decrease, or remain the same under each of the following conditions?

a. The temperature is increased to 100°C.
b. The temperature is decreased to −50°C.
c. The volume is decreased to 0.5 L.
d. The number of moles of neon is doubled.

82. Consider two gases, A and B, each in a 1.0-L container with both gases at the same temperature and pressure. The mass of gas A in the container is 0.34 g and the mass of gas B in the container is 0.48 g.



a. Which gas sample has the most molecules present? Explain.
b. Which gas sample has the largest average kinetic energy? Explain.

c. Which gas sample has the fastest average velocity? Explain.
d. How can the pressure in the two containers be equal to each other since the larger gas B molecules collide with the container walls more forcefully?

83. Consider three identical flasks filled with different gases.
Flask A: CO at 760 torr and 0°C
Flask B: N_2 at 250 torr and 0°C
Flask C: H_2 at 100 torr and 0°C
a. In which flask will the molecules have the greatest average kinetic energy?
b. In which flask will the molecules have the greatest average velocity?

84. Consider separate 1.0-L gaseous samples of H_2, Xe, Cl_2, and O_2 all at STP.
a. Rank the gases in order of increasing average kinetic energy.
b. Rank the gases in order of increasing average velocity.
c. How can separate 1.0-L samples of O_2 and H_2 each have the same average velocity?

85. Freon-12 is used as a refrigerant in central home air conditioners. The rate of effusion of Freon-12 to Freon-11 (molar mass = 137.4 g/mol) is 1.07:1. The formula of Freon-12 is one of the following: CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, or CCl_4. Which formula is correct for Freon-12?

86. The rate of effusion of a particular gas was measured and found to be 24.0 mL/min. Under the same conditions, the rate of effusion of pure methane (CH_4) gas is 47.8 mL/min. What is the molar mass of the unknown gas?

87. One way of separating oxygen isotopes is by gaseous diffusion of carbon monoxide. The gaseous diffusion process behaves like an effusion process. Calculate the relative rates of effusion of $^{12}C^{16}O$, $^{12}C^{17}O$, and $^{12}C^{18}O$. Name some advantages and disadvantages of separating oxygen isotopes by gaseous diffusion of carbon dioxide instead of carbon monoxide.

88. It took 4.5 minutes for 1.0 L helium to effuse through a porous barrier. How long will it take for 1.0 L Cl_2 gas to effuse under identical conditions?

89. Calculate the pressure exerted by 0.5000 mol N_2 in a 1.0000-L container at 25.0°C
a. using the ideal gas law.
b. using the van der Waals equation.
c. Compare the results.

90. Calculate the pressure exerted by 0.5000 mol N_2 in a 10.000-L container at 25.0°C
a. using the ideal gas law.
b. using the van der Waals equation.
c. Compare the results.
d. Compare the results with those in Exercise 89.

Atmosphere Chemistry

91. Use the data in Table 5.4 to calculate the partial pressure of He in dry air assuming that the total pressure is 1.0 atm. Assuming a temperature of 25°C, calculate the number of He atoms per cubic centimeter.

92. A 1.0-L sample of air is collected at 25°C at sea level (1.00 atm). Estimate the volume this sample of air would have at an altitude of 15 km (see Fig. 5.30).

93. Write reactions to show how nitric and sulfuric acids are produced in the atmosphere.

94. Write reactions to show how the nitric and sulfuric acids in acid rain react with marble and limestone. (Both marble and limestone are primarily calcium carbonate.)

Additional Exercises

95. Draw a qualitative graph to show how the first property varies with the second in each of the following (assume 1 mol of an ideal gas and *T* in kelvins).
a. *PV* versus *V* with constant *T*
b. *P* versus *T* with constant *V*
c. *T* versus *V* with constant *P*
d. *P* versus *V* with constant *T*
e. *P* versus $1/V$ with constant *T*
f. PV/T versus *P*

96. At STP, 1.0 L Br_2 reacts completely with 3.0 L F_2, producing 2.0 L of a product. What is the formula of the product? (All substances are gases.)

97. A form of Boyle's law is $PV = k$ (at constant *T* and *n*). Table 5.1 contains actual data from pressure–volume experiments conducted by Robert Boyle. The value of *k* in most experiments is 14.1×10^2 in Hg · in^3. Express *k* in units of atm · L. In Sample Exercise 5.3, *k* was determined for NH_3 at various pressures and volumes. Give some reasons why the *k* values differ so dramatically between Sample Exercise 5.3 and Table 5.1.

98. An ideal gas at 7°C is in a spherical flexible container having a radius of 1.00 cm. The gas is heated at constant pressure to 88°C. Determine the radius of the spherical container after the gas is heated. (Volume of a sphere $= 4/3\pi r^3$.)

99. A 2.747-g sample of manganese metal is reacted with excess HCl gas to produce 3.22 L of $H_2(g)$ at 373 K and 0.951 atm and a manganese chloride compound ($MnCl_x$). What is the formula of the manganese chloride compound produced in the reaction?

100. Equal moles of hydrogen gas and oxygen gas are mixed in a flexible reaction vessel and then sparked to initiate the formation of gaseous water. Assuming that the reaction goes to completion, what is the ratio of the final volume of the gas mixture to the initial volume of the gas mixture if both volumes are measured at the same temperature and pressure?

101. A 15.0-L tank is filled with H_2 to a pressure of 2.00×10^2 atm. How many balloons (each 2.00 L) can be inflated to a pressure of 1.00 atm from the tank? Assume that there is no temperature change and that the tank cannot be emptied below 1.00 atm pressure.

102. A spherical glass container of unknown volume contains helium gas at 25°C and 1.960 atm. When a portion of the helium is withdrawn and adjusted to 1.00 atm at 25°C, it is found to have a volume of 1.75 cm^3. The gas remaining in the first container shows a pressure of 1.710 atm. Calculate the volume of the spherical container.

103. A 2.00-L sample of $O_2(g)$ was collected over water at a total pressure of 785 torr and 25°C. When the $O_2(g)$ was dried (water vapor removed), the gas had a volume of 1.94 L at 25°C and 785 torr. Calculate the vapor pressure of water at 25°C.

104. A 20.0-L stainless steel container was charged with 2.00 atm of hydrogen gas and 3.00 atm of oxygen gas. A spark ignited the mixture, producing water. What is the pressure in the tank at 25°C? at 125°C?

105. Metallic molybdenum can be produced from the mineral molybdenite, MoS_2. The mineral is first oxidized in air to molybdenum trioxide and sulfur dioxide. Molybdenum trioxide is then reduced to metallic molybdenum using hydrogen gas. The balanced equations are

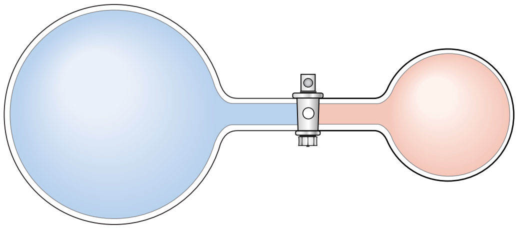
$$MoS_2(s) + \tfrac{7}{2}O_2(g) \rightarrow MoO_3(s) + 2SO_2(g)$$
$$MoO_3(s) + 3H_2(g) \rightarrow Mo(s) + 3H_2O(l)$$

Calculate the volumes of air and hydrogen gas at 17°C and 1.00 atm that are necessary to produce 1.00×10^3 kg of pure molybdenum from MoS_2. Assume air contains 21% oxygen by volume and assume 100% yield for each reaction.

106. Nitric acid is produced commercially by the Ostwald process. In the first step ammonia is oxidized to nitric oxide:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Assume this reaction is carried out in the apparatus diagramed below.



The stopcock between the two reaction containers is opened, and the reaction proceeds using proper catalysts. Calculate the partial pressure of NO after the reaction is complete. Assume 100% yield for the reaction, assume the final container volume is 3.00 L, and assume the temperature is constant.

107. In the "Méthode Champenoise," grape juice is fermented in a wine bottle to produce sparkling wine. The reaction is

$$C_6H_{12}O_6(aq) \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

Fermentation of 750. mL grape juice (density = 1.0 g/cm^3) is allowed to take place in a bottle with a total volume of 825 mL until 12% by volume is ethanol (C_2H_5OH). Assuming that the CO_2 is insoluble in H_2O (actually, a wrong assumption), what would be the pressure of CO_2 inside the wine bottle at 25°C? (The density of ethanol is 0.79 g/cm^3.)

108. One of the chemical controversies of the nineteenth century concerned the element beryllium (Be). Berzelius originally claimed that beryllium was a trivalent element (forming Be^{3+} ions) and that it gave an oxide with the formula Be_2O_3. This resulted in a calculated atomic mass of 13.5 for beryllium. In formulating his periodic table, Mendeleev proposed that beryllium was divalent (forming Be^{2+} ions) and that it gave an oxide with the formula BeO. This assumption gives an atomic mass of 9.0. In 1894, A. Combes (*Comptes Rendus* 1894, p. 1221) reacted beryllium with the anion $C_5H_7O_2^-$ and measured the density of the gaseous product. Combes's data for two different experiments are as follows:

	I	II
Mass	0.2022 g	0.2224 g
Volume	22.6 cm^3	26.0 cm^3
Temperature	13°C	17°C
Pressure	765.2 mm Hg	764.6 mm

If beryllium is a divalent metal, the molecular formula of the product will be $Be(C_5H_7O_2)_2$; if it is trivalent, the formula will be $Be(C_5H_7O_2)_3$. Show how Combes's data help to confirm that beryllium is a divalent metal.

109. The nitrogen content of organic compounds can be determined by the Dumas method. The compound in question is first reacted by passage over hot CuO(*s*):

$$\text{Compound} \xrightarrow[\text{CuO}(s)]{\text{Hot}} N_2(g) + CO_2(g) + H_2O(g)$$

The product gas is then passed through a concentrated solution of KOH to remove the CO_2. After passage through the KOH solution, the gas contains N_2 and is saturated with water vapor. In a given experiment a 0.253-g sample of a compound produced 31.8 mL N_2 saturated with water vapor at 25°C and 726 torr. What is the mass percent of nitrogen in the compound? (The vapor pressure of water at 25°C is 23.8 torr.)

110. A compound containing only C, H, and N yields the following data.

i. Complete combustion of 35.0 mg of the compound produced 33.5 mg of CO_2 and 41.1 mg of H_2O.

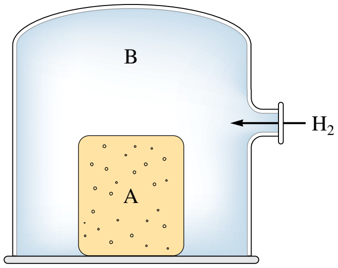
ii. A 65.2-mg sample of the compound was analyzed for nitrogen by the Dumas method (see Exercise 109), giving 35.6 mL of N_2 at 740. torr and 25°C.

iii. The effusion rate of the compound as a gas was measured and found to be 24.6 mL/min. The effusion rate of argon gas, under identical conditions, is 26.4 mL/min.

What is the molecular formula of the compound?

111. An organic compound contains C, H, N, and O. Combustion of 0.1023 g of the compound in excess oxygen yielded 0.2766 g of CO_2 and 0.0991 g of H_2O. A sample of 0.4831 g of the compound was analyzed for nitrogen by the Dumas method (see Exercise 109). At STP, 27.6 mL of dry N_2 was obtained. In a third experiment, the density of the compound as a gas was found to be 4.02 g/L at 127°C and 256 torr. What are the empirical and molecular formulas of the compound?

112. Consider the following diagram:



Container A (with porous walls) is filled with air at STP. It is then inserted into a large enclosed container (B), which is then flushed with $H_2(g)$. What will happen to the pressure inside container A? Explain your answer.

113. Without looking at tables of values, which of the following gases would you expect to have the largest value of the van der Waals constant *b*: H_2, N_2, CH_4, C_2H_6, or C_3H_8? From the values in Table 5.3 for the van der Waals constant *a* for the gases H_2, CO_2, N_2, and CH_4, predict which of these gas molecules show the strongest intermolecular attractions.

Challenge Problems

114. An important process for the production of acrylonitrile (C_3H_3N) is given by the following reaction:

$$2C_3H_6(g) + 2NH_3(g) + 3O_2(g) \longrightarrow 2C_3H_3N(g) + 6H_2O(g)$$

A 150.-L reactor is charged to the following partial pressures at 25°C:

$$P_{C_3H_6} = 0.500 \text{ MPa}$$
$$P_{NH_3} = 0.800 \text{ MPa}$$
$$P_{O_2} = 1.500 \text{ MPa}$$

What mass of acrylonitrile can be produced from this mixture (Mpa $= 10^6$ Pa)?

115. A chemist weighed out 5.14 g of a mixture containing unknown amounts of BaO(*s*) and CaO(*s*) and placed the sample in a 1.50-L flask containing $CO_2(g)$ at 30.0°C and 750. torr. After the reaction to form $BaCO_3(s)$ and $CaCO_3(s)$ was completed, the pressure of $CO_2(g)$ remaining was 230. torr. Calculate the mass percentages of CaO(*s*) and BaO(*s*) in the mixture.

116. A mixture of chromium and zinc weighing 0.362 g was reacted with an excess of hydrochloric acid. After all the metals in the mixture reacted, 225 mL of dry hydrogen gas was collected at 27°C and 750. torr. Determine the mass percent Zn in the metal sample. [Zinc reacts with hydrochloric acid to produce zinc chloride and hydrogen gas; chromium reacts with hydrochloric acid to produce chromium(III) chloride and hydrogen gas.]

117. Consider a sample of a hydrocarbon (a compound consisting of only carbon and hydrogen) at 0.959 atm and 298 K. Upon combusting the entire sample in oxygen, you collect a mixture of gaseous carbon dioxide and water vapor at 1.51 atm and 375 K. This mixture has a density of 1.391 g/L and occupies a volume four times as large as that of the pure hydrocarbon. Determine the molecular formula of the hydrocarbon.

118. You have an equimolar mixture of the gases SO_2 and O_2, along with some He, in a container fitted with a piston. The density of this mixture at STP is 1.924 g/L. Assume ideal behavior and constant temperature and pressure.

a. What is the mole fraction of He in the original mixture?

b. The SO_2 and O_2 react to completion to form SO_3. What is the density of the gas mixture after the reaction is complete?

119. Methane (CH_4) gas flows into a combustion chamber at a rate of 200. L/min at 1.50 atm and ambient temperature. Air is added to the chamber at 1.00 atm and the same temperature, and the gases are ignited.

a. To ensure complete combustion of CH_4 to $CO_2(g)$ and $H_2O(g)$, three times as much oxygen as is necessary is reacted. Assuming air is 21 mole percent O_2 and 79 mole percent N_2, calculate the flow rate of air necessary to deliver the required amount of oxygen.

b. Under the conditions in part a, combustion of methane was not complete as a mixture of $CO_2(g)$ and $CO(g)$ was produced. It was determined that 95.0% of the carbon in the exhaust gas was present in CO_2. The remainder was present as carbon in CO. Calculate the composition of the exhaust gas in terms of mole fraction of CO, CO_2, O_2, N_2, and H_2O. Assume CH_4 is completely reacted and N_2 is unreacted.

120. A steel cylinder contains 5.00 mol of graphite (pure carbon) and 5.00 mol of O_2. The mixture is ignited and all the graphite reacts. Combustion produces a mixture of CO gas and CO_2 gas. After the cylinder has cooled to its original temperature, it is found that the pressure of the cylinder has increased by 17.0%. Calculate the mole fractions of CO, CO_2, and O_2 in the final gaseous mixture.

121. The total mass that can be lifted by a balloon is given by the difference between the mass of air displaced by the balloon and the mass of the gas inside the balloon. Consider a hot-air balloon that approximates a sphere 5.00 m in diameter and contains air heated to 65°C. The surrounding air temperature is 21°C. The pressure in the balloon is equal to the atmospheric pressure, which is 745 torr.

a. What total mass can the balloon lift? Assume that the average molar mass of air is 29.0 g/mol. (*Hint:* Heated air is less dense than cool air.)

b. If the balloon is filled with enough helium at 21°C and 745 torr to achieve the same volume as in part a, what total mass can the balloon lift?

c. What mass could the hot-air balloon in part a lift if it were on the ground in Denver, Colorado, where a typical atmospheric pressure is 630. torr?

122. You have a sealed, flexible balloon filled with argon gas. The atmospheric pressure is 1.00 atm and the temperature is

25°C. The air has a mole fraction of nitrogen of 0.790, the rest being oxygen.

a. Explain why the balloon would float when heated. Make sure to discuss which factors change and which remain constant, and why this matters. Be complete.

b. Above what temperature would you heat the balloon so that it would float?

123. You have a helium balloon at 1.00 atm and 25°C. You want to make a hot-air balloon with the same volume and same lift as the helium balloon. Assume air is 79.0% nitrogen, 21.0% oxygen by volume. The "lift" of a balloon is given by the difference between the mass of air displaced by the balloon and the mass of gas inside the balloon.

a. Will the temperature in the hot-air balloon have to be higher or lower than 25°C? Explain.

b. Calculate the temperature of the air required for the hot-air balloon to provide the same lift as the helium balloon at 1.00 atm and 25°C. Assume atmospheric conditions are 1.00 atm and 25°C.

124. We state that the ideal gas law tends to hold best at low pressures and high temperatures. Show how the van der Waals equation simplifies to the ideal gas law under these conditions.

125. Atmospheric scientists often use mixing ratios to express the concentrations of trace compounds in air. Mixing ratios are often expressed as ppmv (parts per million volume):

$$\text{ppmv of } X = \frac{\text{vol. of } X \text{ at STP}}{\text{total vol. of air at STP}} \times 10^6$$

On a recent autumn day, the concentration of carbon monoxide in the air in downtown Denver, Colorado, reached 3.0×10^2 ppmv. The atmospheric pressure at that time was 628 torr, and the temperature was 0°C.

a. What was the partial pressure of CO?

b. What was the concentration of CO in molecules per cubic centimeter?

126. Nitrogen gas (N_2) reacts with hydrogen gas (H_2) to form ammonia gas (NH_3). You have nitrogen and hydrogen gases in a 15.0-L container fitted with a movable piston (the piston allows the container volume to change so as to keep the pressure constant inside the container). Initially the partial pressure of each reactant gas is 1.00 atm. Assume the temperature is constant and that the reaction goes to completion.

a. Calculate the partial pressure of ammonia in the container after the reaction has reached completion.

b. Calculate the volume of the container after the reaction has reached completion.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

127. In the presence of nitric acid, UO^{2+} undergoes a redox process. It is converted to UO_2^{2+} and nitric oxide (NO) gas is produced according to the following unbalanced equation:

$$NO_3^-(aq) + UO^{2+}(aq) \longrightarrow NO(g) + UO_2^{2+}(aq)$$

If 2.55×10^2 mL of NO(*g*) is isolated at 29°C and 1.5 atm, what amount (moles) of UO^{2+} was used in the reaction?

128. Silane, SiH_4, is the silicon analogue of methane, CH_4. It is prepared industrially according to the following equations:

$$Si(s) + 3HCl(g) \longrightarrow HSiCl_3(l) + H_2(g)$$
$$4HSiCl_3(l) \longrightarrow SiH_4(g) + 3SiCl_4(l)$$

a. If 156 mL of $HSiCl_3$ ($d = 1.34$ g/mL) is isolated when 15.0 L of HCl at 10.0 atm and 35°C is used, what is the percent yield of $HSiCl_3$?

b. When 156 mL of $HSiCl_3$ is heated, what volume of SiH_4 at 10.0 atm and 35°C will be obtained if the percent yield of the reaction is 93.1%?

129. Solid thorium(IV) fluoride has a boiling point of 1680°C. What is the density of a sample of gaseous thorium(IV) fluoride at its boiling point under a pressure of 2.5 atm in a 1.7-L container? Which gas will effuse faster at 1680°C, thorium(IV) fluoride or uranium(III) fluoride? How much faster?

130. Natural gas is a mixture of hydrocarbons, primarily methane (CH_4) and ethane (C_2H_6). A typical mixture might have $\chi_{\text{methane}} = 0.915$ and $\chi_{\text{ethane}} = 0.085$. What are the partial pressures of the two gases in a 15.00-L container of natural gas at 20.°C and 1.44 atm? Assuming complete combustion of both gases in the natural gas sample, what is the total mass of water formed?

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

131. Use the following information to identify element A and compound B, then answer questions a and b.

An empty glass container has a mass of 658.572 g. It has a mass of 659.452 g after it has been filled with nitrogen gas at a pressure of 790. torr and a temperature of 15°C. When the container is evacuated and refilled with a certain element (A) at a pressure of 745 torr and a temperature of 26°C, it has a mass of 660.59 g.

Compound B, a gaseous organic compound that consists of 85.6% carbon and 14.4% hydrogen by mass, is placed in a stainless steel vessel (10.68 L) with excess oxygen gas. The vessel is placed in a constant-temperature bath at 22°C. The pressure in the vessel is 11.98 atm. In the bottom of the vessel is a container that is packed with Ascarite and a desiccant. Ascarite is asbestos impregnated with sodium hydroxide; it quantitatively absorbs carbon dioxide:

$$2NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l)$$

---

*Used with permission from the *Journal of Chemical Education,* Vol. 68, No. 11, 1991, pp. 919–922; copyright © 1991, Division of Chemical Education, Inc.

The desiccant is anhydrous magnesium perchlorate, which quantitatively absorbs the water produced by the combustion reaction as well as the water produced by the above reaction. Neither the Ascarite nor the desiccant reacts with compound B or oxygen. The total mass of the container with the Ascarite and desiccant is 765.3 g.

The combustion reaction of compound B is initiated by a spark. The pressure immediately rises, then begins to decrease, and finally reaches a steady value of 6.02 atm. The stainless steel vessel is carefully opened, and the mass of the container inside the vessel is found to be 846.7 g.

A and B react quantitatively in a 1:1 mole ratio to form one mole of the single product, gas C.

a. How many grams of C will be produced if 10.0 L of A and 8.60 L of B (each at STP) are reacted by opening a stopcock connecting the two samples?

b. What will be the total pressure in the system?

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**