Gases

5

Easter Market at the Moscow Kremlin, 1917 (oil on canvas), Kustodiev, Boris Mikhailovich (1878–1927)/State Art Museum, Nizhny Novgorod, Russia/Bridgeman Art Library

The gas in the balloons is most likely helium. Balloons are buoyant because the density of helium is less than that of air.

At 1.4 million atmospheres
xenon, a gas, goes metallic.

—ROALD HOFFMANN
Giving In

By far the most familiar gas to all of us is the air we breathe. The Greeks considered air to be one of the four fundamental elements of nature, along with earth, water, and fire. Late in the eighteenth century, Cavendish, Priestley, and Lavoisier studied the composition of air, which is primarily a mixture of nitrogen and oxygen with smaller amounts of argon, carbon dioxide, and water vapor. Today it appears that the concentrations of some of the minor components of the atmosphere may be changing, with adverse effects on the environment. The depletion of the ozone layer and increases in the amounts of "greenhouse" gases are topics for the evening news, television dramas, and movies.

All gases resemble one another closely in their physical behavior. Their volumes respond in almost exactly the same way to changes in pressure, temperature, or amount of gas. In fact, it is possible to write a simple equation relating these four variables that is valid for all gases. This equation, known as the ideal gas law, is the central theme of this chapter; it is introduced in Section 5-2. The law is applied to

- pure gases in Section 5-3.
- gases in chemical reactions in Section 5-4.
- gas mixtures in Section 5-5.

Section 5-6 considers the kinetic theory of gases, the molecular model on which the ideal gas law is based. Finally, in Section 5-7 we describe the extent to which real gases deviate from the law.

Chapter Outline

5-1 Measurements on Gases

To completely describe the state of a gaseous substance, its volume, amount, temperature, and pressure are specified. The first three of these quantities were discussed in earlier chapters and will be reviewed briefly in this section. Pressure, a somewhat more abstract quantity, will be examined in more detail.

Volume, Amount, and Temperature

A gas expands uniformly to fill any container in which it is placed. This means that the volume of a gas is the volume of its container. Volumes of gases can be expressed in liters, cubic centimeters, or cubic meters:

$$1\ \text{L} = 10^3\ \text{cm}^3 = 10^{-3}\ \text{m}^3$$

Most commonly, the amount of matter in a gaseous sample is expressed in terms of the number of moles (n). In some cases, the mass in grams is given instead. These two quantities are related through the molar mass, MM:

$$n = \frac{\text{mass}}{\text{MM}}$$

The temperature of a gas is ordinarily measured using a thermometer marked in degrees Celsius. However, as we will see in Section 5-2, ***in any calculation involving the physical behavior of gases, temperatures must be expressed on the Kelvin scale.*** To convert between °C and K, use the relation introduced in Chapter 1:

$$T_\text{K} = t_{^\circ\text{C}} + 273.15$$

Typically, in gas law calculations, temperatures are expressed only to the nearest degree. In that case, the Kelvin temperature can be found by simply adding 273 to the Celsius temperature.

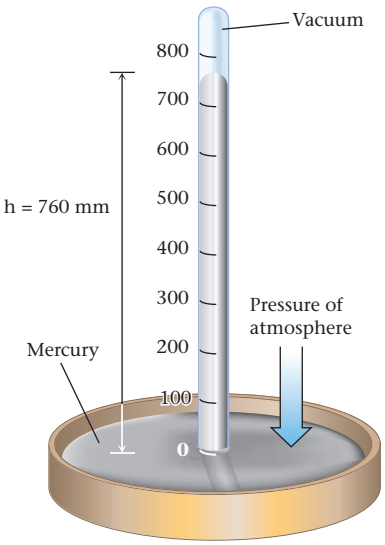


Figure 5.1 A mercury barometer. This is the type of barometer first constructed by Torricelli. The pressure of the atmosphere pushes the mercury in the dish to rise into the glass tube. The height of the column of mercury is a measure of the atmospheric pressure.

Pressure

Pressure is defined as force per unit area. You are probably familiar with the English unit "pounds per square inch," often abbreviated psi. When we say that a gas exerts a pressure of 15 psi, we mean that the pressure on the walls of the gas container is 15 pounds (of force) per square inch of wall area.

A device commonly used to measure atmospheric pressure is the mercury *barometer* (Figure 5.1), first constructed by Evangelista Torricelli in the seventeenth century. This consists of a closed gas tube filled with mercury inverted over a pool of mercury. The pressure exerted by the mercury column exactly equals that of the atmosphere. Hence the height of the column is a measure of the atmospheric pressure. At or near sea level, it typically varies from 740 to 760 mm, depending on weather conditions.

Most barometers contain mercury rather than some other liquid. Its high density allows the barometer to be a convenient size. A water barometer needs to be 10,340 mm (34 ft) high to register atmospheric pressure!

The pressure of a confined gas can be measured by a *manometer* of the type shown in Figure 5.2. Here again the fluid used is mercury. If the level in the inner tube (A) is lower than that in the outer tube (B), the pressure of the gas is greater than that of the atmosphere. If the reverse is true, the gas pressure is less than atmospheric pressure.

Because of the way in which gas pressure is measured, it is often expressed in **millimeters of mercury (mm Hg).** Thus we might say that the atmospheric pressure on a certain day is 772 mm Hg. This means that the pressure of the air is equal to that exerted by a column of mercury 772 mm (30.4 in) high.

The pressure exerted by a column of mercury depends on its density, which varies slightly with temperature. To get around this ambiguity, the *torr* was defined to be the pressure exerted by 1 mm of mercury at certain specified conditions, notably 0°C. Over time, the unit torr has become a synonym for millimeter of mercury. Throughout this text, we will use millimeter of mercury rather than torr because the former has a clearer physical meaning.

Another unit commonly used to express gas pressure is the standard atmosphere, or simply **atmosphere (atm).** This is the pressure exerted by a column of mercury 760 mm high with the mercury at 0°C. If we say that a gas has a pressure of 0.98 atm, we mean that the pressure is 98% of that exerted by a mercury column 760 mm high.

In the International System (Appendix 1), the standard unit of pressure is the **pascal** (Pa). A pascal is a very small unit; it is approximately the pressure exerted by a film of water 0.1 mm high on the surface beneath it. A related unit is the **bar** (10^5 Pa). A bar is nearly, but not quite, equal to an atmosphere:

$$1.013 \text{ bar} = 1 \text{ atm} = 760 \text{ mm Hg} = 14.7 \text{ psi} = 101.3 \text{ k Pa}$$
$$1 \text{ bar} = 10^5 \text{ Pa}$$

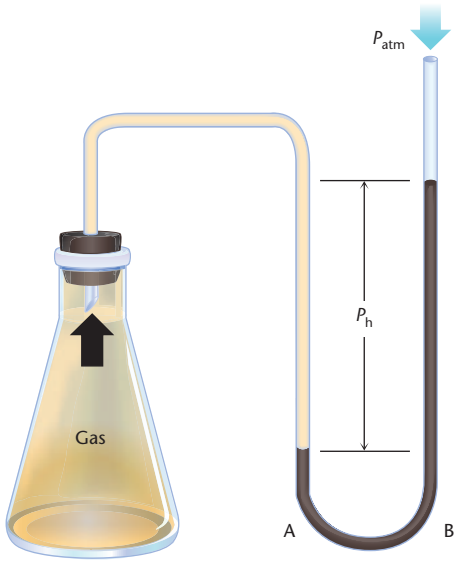


Figure 5.2 A manometer open to the atmosphere, used to measure gas pressure in a closed system. The pressure of the gas is given by $P_{gas} = P_{atm} + P_h$. In the figure, the gas pressure is greater than the atmospheric pressure.

EXAMPLE 5.1

At room temperature, dry ice (solid CO_2) becomes a gas. At 77°F, 13.6 oz of dry ice are put into a steel tank with a volume of 10.00 ft^3. The tank's pressure gauge registers 11.2 psi. Express the volume (V) of the tank in liters, the amount of CO_2 in grams and moles (n), the temperature (T) in °C and K and the pressure (P) in bars, mm Hg, and atmospheres.

ANALYSIS

Information given:	volume (10.00 ft^3); pressure (11.2 psi); temperature (77°F); mass of CO_2 (13.6 oz)
Information implied:	molar mass of CO_2 Table 1.3: conversion factors for volume and mass formulas for temperature conversion from °F to °C and from °C to K
Asked for:	volume in L pressure in atm, mm Hg, and bar temperature in °C and K moles of CO_2

STRATEGY

1. Find the necessary conversion factors.
2. Use the temperature conversion formula.
3. Convert oz to grams and use the molar mass of CO_2 as a conversion factor.

   oz → g → mol

continued

SOLUTION

volume in L	$10.00\ \text{ft}^3 \times \frac{28.32\ \text{L}}{1\ \text{ft}^3} = 283.2\ \text{L}$
pressure in atm	$11.2\ \text{psi} \times \frac{1\ \text{atm}}{14.7\ \text{psi}} = 0.762\ \text{atm}$
pressure in mm Hg	$11.2\ \text{psi} \times \frac{1\ \text{atm}}{14.7\ \text{psi}} \times \frac{760\ \text{mm Hg}}{1\ \text{atm}} = 579\ \text{mm Hg}$
pressure in bar	$11.2\ \text{psi} \times \frac{1.013\ \text{bar}}{14.7\ \text{psi}} = 0.772\ \text{bar}$
temperature in °C	°F = 1.8(°C) + 32; 77° = 1.8(°C) + 32°C; °C = 25°C
temperature in K	K = (°C) + 273.15; K = 25°C + 273.15 = 298 K
mol CO_2	$13.6\ \text{oz} \times \frac{1\ \text{g}}{0.03527\ \text{oz}} \times \frac{1\ \text{mol}}{44.01\ \text{g}} = 8.77\ \text{mol}$

5-2 The Ideal Gas Law

All gases closely resemble each other in the dependence of volume on amount, temperature, and pressure.

1. ***Volume is directly proportional to amount.*** Figure 5.3a shows a typical plot of volume (V) versus number of moles (n) for a gas. Notice that the graph is a straight line passing through the origin. The general equation for such a plot is

$$V = k_1 n \qquad \text{(constant } T, P\text{)}$$

where k_1 is a constant (the slope of the line in Figure 5.3a). That means k_1 is independent of individual values of V, n, and the nature of the gas. This is the equation of a direct proportionality.

2. ***Volume is directly proportional to absolute temperature.*** The dependence of volume (V) on the Kelvin temperature (T) is shown in Figure 5.3b. The graph is a straight line through the origin. The equation of the line is

$$V = k_2 T \qquad \text{(constant } n, P\text{)}$$

where k_2 is again the slope of the line in Figure 5.3b. This relationship was first suggested in a different form, by two French scientists, Jacques Charles (1746–1823) and Joseph Gay-Lussac (1778–1850),ℹ both of whom were balloonists.

ℹ Gay-Lussac isolated boron and was the first to prepare HF.

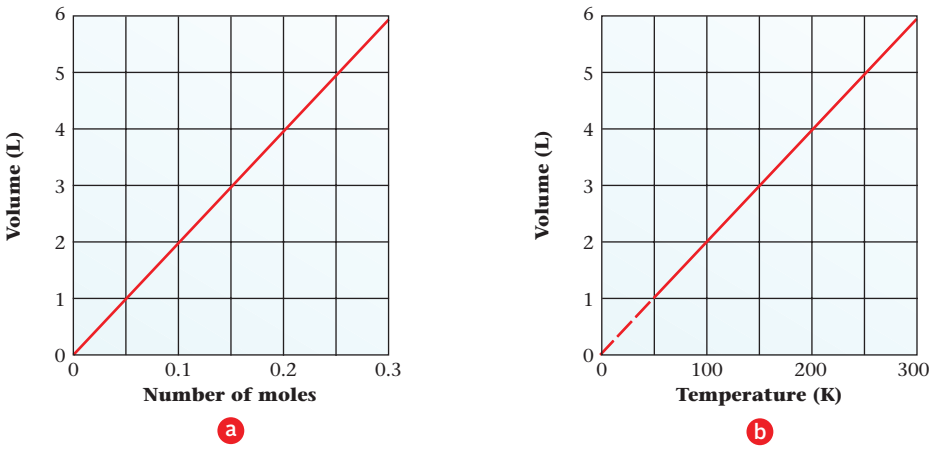


Figure 5.3 Relation of gas volume (V) to number of moles (n) and temperature (T) at constant pressure (P). The volume of a gas at constant pressure is directly proportional to (a) the number of moles of gas and (b) the absolute temperature. The volume-temperature plot must be extrapolated to reach zero because most gases liquefy at low temperatures well above 0 K.

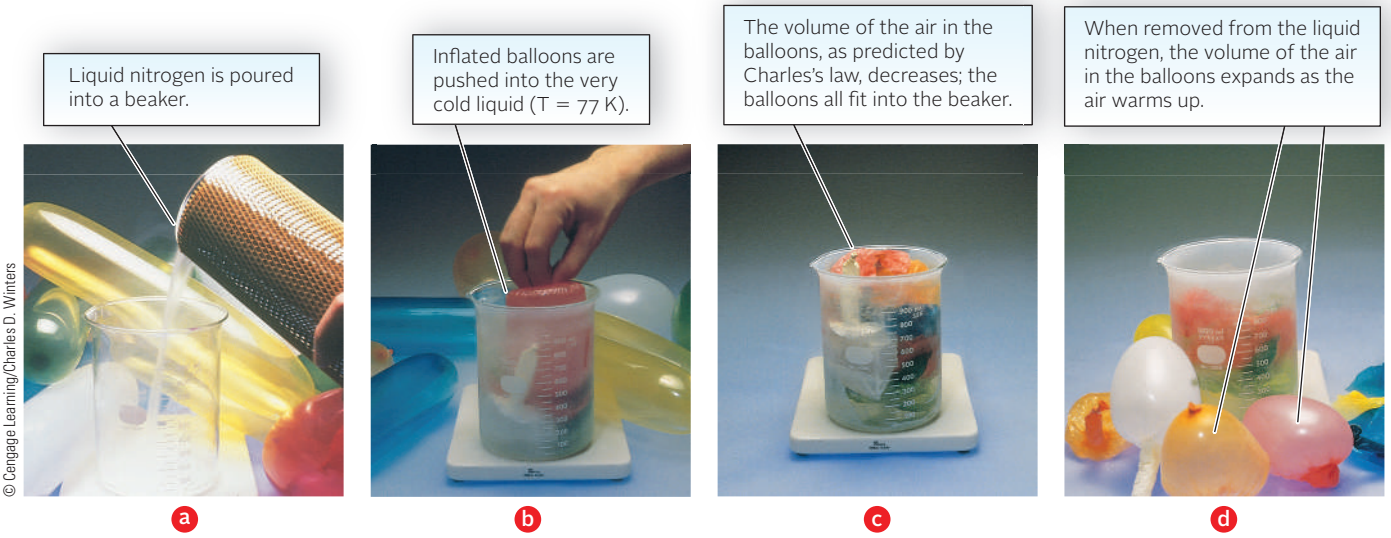


Figure 5.4 An illustration of Charles's law.

Hence it is often referred to as **Charles's and Gay-Lussac's law** or, more simply, as *Charles's law* (Figure 5.4).

3. *Volume is inversely proportional to pressure.* Figure 5.5 shows a typical plot of volume (V) versus pressure (P). Notice that V decreases as P increases. The graph is a hyperbola. The general relation between the two variables is

$$V = \frac{k_3}{P} \qquad \text{(constant } n, T\text{)}$$

The quantity k_3, like k_1 and k_2, is a constant. This is the equation of an inverse proportionality. The fact that volume is inversely proportional to pressure was first established in 1660 by Robert Boyle (1627–1691), an Irish experimental scientist. The equation above is one form of **Boyle's law**.

The three equations relating the volume, pressure, temperature, and amount of a gas can be combined into a single equation. Because V is directly proportional to both n and T,

$$V = k_1 n \qquad V = k_2 T$$

and inversely proportional to P,

$$V = \frac{k_3}{P}$$

it follows that

$$V = \text{constant} \times \frac{n \times T}{P}$$

We can evaluate the constant ($k_1 k_2 k_3$) in this equation by taking advantage of *Avogadro's law,* which states that equal volumes of all gases at the same temperature and pressure contain the same number of moles. For this law to hold, the constant must be the same for all gases. Ordinarily it is represented by the symbol R. Both sides of the equation are multiplied by P to give the **ideal gas law**

$$PV = nRT \qquad (5.1)$$

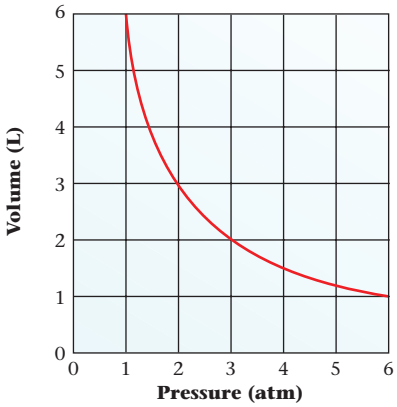


Figure 5.5 Relation of gas volume (V) to pressure (P) at constant temperature (T). The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure. In this case, the volume decreases from 6 L to 1 L when the pressure increases from 1 atm to 6 atm.

R is a constant, independent of *P*, *V*, *n*, and *T*, but its numerical value depends on the units used.

Table 5.1 Values of *R* in Different Units

Value	Where Used	How Obtained
$0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$	Gas law problems with *V* in liters, *P* in atm	From known values of *P*, *V*, *T*, *n*
$8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}$	Equations involving energy in joules	$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$
$8.31 \times 10^3 \frac{\text{g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}$	Calculation of molecular speed (page 115)	$1 \text{ J} = 10^3 \frac{\text{g} \cdot \text{m}^2}{\text{s}^2}$

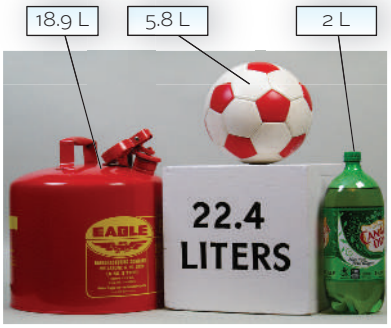


Figure 5.6 Molar volume. The cube has a volume of 22.4 L, which is the volume of one mole of an ideal gas at STP.

where *P* is the pressure, *V* the volume, *n* the number of moles, and *T* the Kelvin temperature. Experimentally, it is found that the ideal gas law predicts remarkably well the experimental behavior of real gases (e.g., H_2, N_2, O_2 . . .) at ordinary temperatures and pressures.

The value of the **gas constant** (*R*) can be calculated from experimental values of *P*, *V*, *n*, and *T*. Consider, for example, the situation that applies at 0°C and 1 atm. These conditions are often referred to as **standard temperature and pressure (STP)** for a gas. At STP, one mole of any gas occupies a volume of 22.4 L (Figure 5.6). Solving the ideal gas law for *R*,

$$R = \frac{PV}{nT}$$

Substituting $P = 1.00$ atm, $V = 22.4$ L, $n = 1.00$ mol, and $T = 0 + 273 = 273$ K,

$$R = \frac{1.00 \text{ atm} \times 22.4 \text{ L}}{1.00 \text{ mol} \times 273 \text{ K}} = 0.0821 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K})$$

Notice that *R* has the units of atmospheres, liters, moles, and K. These units must be used for pressure, volume, amount, and temperature in any problem in which this value of *R* is used.

Throughout most of this chapter, we will use $0.0821 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K})$ as the value of *R*. For certain purposes, however, *R* must be expressed in different units (Table 5.1).

5-3 Gas Law Calculations

The ideal gas law can be used to solve a variety of problems. We will show how you can use it to find

- the final state of a gas, knowing its initial state and the changes in *P*, *V*, *n*, or *T* that occur.
- one of the four variables, *P*, *V*, *n*, or *T*, given the values of the other three.
- the molar mass or density of a gas.

Final and Initial State Problems

A gas commonly undergoes a change from an initial to a final state. Typically, you are asked to determine the effect on *V*, *P*, *n*, or *T* of a change in one or more of these variables. For example, starting with a sample of gas at 25°C and 1.00 atm, you might be asked to calculate the pressure developed when the sample is heated to 95°C at constant volume.

The ideal gas law is readily applied to problems of this type. A relationship between the variables involved is derived from this law. In this case, pressure and temperature change, while n and V remain constant.

$$\text{initial state:} \quad P_1V = nRT_1$$
$$\text{final state:} \quad P_2V = nRT_2$$

Dividing the second equation by the first cancels V, n, and R, leaving the relation

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \qquad \text{(constant } n, V\text{)}$$

Applying this general relation to the problem just described,

$$P_2 = P_1 \times \frac{T_2}{T_1} = 1.00 \text{ atm} \times \frac{368 \text{ K}}{298 \text{ K}} = 1.23 \text{ atm}$$

Similar "two-point" equations can be derived from the ideal gas law to solve any problem of this type.

To obtain a two-point equation, write the gas law twice and divide to eliminate constants.

EXAMPLE 5.2

A sealed 15.0-L steel tank is used to deliver propane (C_3H_8) gas. It is fitted with a pressure gauge and a valve. The valve automatically opens to release gas when the pressure in the tank goes above 1.200 atm. The tank is filled with 24.7 g of propane at 25°C. The pressure gauge registers 0.915 atm.

a If the tank is heated to 55°C, will the valve open to release propane? (Assume that the expansion of steel from an increase in temperature is negligible.)

ANALYSIS

Information given:	V(15.0 L); P(0.915 atm); T(25°C); mass of propane (24.7 g) T(55°C)
Information implied:	2 sets of conditions for temperature
Asked for:	Will the valve release gas?

STRATEGY

1. Given two sets of conditions, you need to use the formula for initial state–final state conditions.
2. A sealed steel tank implies that the number of moles and the volume are kept constant.
3. Make sure all temperatures are in K.
4. Find P and compare with 1.200 atm.

SOLUTION

P_2	$\frac{V_1P_1}{n_1T_1} = \frac{V_2P_2}{n_2T_2} \rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \frac{0.915}{25 + 273} = \frac{P_2}{55 + 273} \rightarrow P_2 = 1.01 \text{ atm}$
Will the valve open?	No. 1.01 atm < 1.200 atm

b The temperature in the tank is increased to 200°C. The valve opens and releases propane. How many grams of propane are released?

ANALYSIS

Information given:	Before T increase: V (15.0 L); P (0.915 atm); T (25°C); mass of propane (24.7 g) After T increase: V (15.0 L); P (1.200 atm); T (200°C); mass of propane (24.7 g)
Information implied:	molar mass of propane
Asked for:	mass of propane released

continued

STRATEGY

1. Convert °C to K and mass of propane to mol propane.
2. Given two sets of conditions, you need to use the formula for initial state–final state conditions.
3. Find n_2.
4. Convert n_2 to mass of propane in the tank at 200°C and find the mass released by difference.

SOLUTION

1. T	°C → K; 25 + 273 = 298; 200 + 273 = 473 K
mol C_3H_8 initially (n_1)	$24.7\ \text{g} \times \frac{1\ \text{mol}}{44.1\ \text{g}} = 0.560\ \text{mol}$
2. Initial conditions	$P_1 = 0.915$ atm; $T_1 = 298$ K; $n_1 = 0.560$ mol; $V_1 = 15.0$ L
Final conditions	$P_2 = 1.200$ atm; $T_2 = 473$ K; $n_2 = ?$; $V_2 = 15.0$ L
3. n_2	$\frac{V_1P_1}{n_1T_1} = \frac{V_2P_2}{n_2T_2} \rightarrow \frac{0.915}{0.560 \times 298} = \frac{1.200}{n_2 \times 473}$; $n_2 = 0.463$ mol
mass C_3H_8 in the tank	(0.463 mol)(44.1 g/mol) = 20.4 g
mass to be released	24.7 − 20.5 = 4.3 g

END POINT

Note that the volume of the tank is never used in the calculations. It is important not only to read the problem carefully but also to visualize the description of the gas container. If the gas were in a balloon, instead of in a steel tank, the calculations would be different.

Calculation of *P, V, n,* or *T*

Frequently, values are known for three of these quantities (perhaps V, n, and T); the other one (P) must be calculated. This is readily done by direct substitution into the ideal gas law.

EXAMPLE 5.3

Sulfur hexafluoride is a gas used as a long-term tamponade (plug) for a retinal hole to repair detached retinas in the eye. If 2.50 g of this compound is introduced into an evacuated 500.0-mL container at 83°C, what pressure in atmospheres is developed?

ANALYSIS

Information given:	V(500.0 mL); T(83°C); mass of SF_6 (2.50 g)
Information implied:	molar mass of SF_6 ideal gas law (one state) value for R
Asked for:	pressure (P) in atm

STRATEGY

1. Change the given units to conform with the units for R (mL → L; °C → K).
2. You need to find n before you can use the ideal gas law to find P.
3. Substitute into the ideal gas law: $PV = nRT$.

continued

SOLUTION	
1. Change units.	$500.0\ \text{mL} = 0.5000\ \text{L} \qquad 83°\text{C} + 273\ \text{K} = 356\ \text{K}$
2. Find n.	$2.50\ \text{g} \times \dfrac{1\ \text{mol}}{146.07\ \text{g}} = 0.0171\ \text{mol}$
3. P	$P = \dfrac{nRT}{V} = \dfrac{0.0171\ \text{mol} \times 0.0821\ \text{L} \cdot \text{atm/(mol} \cdot \text{K)} \times 356\ \text{K}}{0.5000\ \text{L}} = 1.00\ \text{atm}$

Molar Mass and Density

The ideal gas law offers a simple approach to the experimental determination of the molar mass of a gas. Indeed, this approach can be applied to volatile liquids like acetone (Example 5.4). All you need to know is the mass of a sample confined to a container of fixed volume at a particular temperature and pressure.

EXAMPLE 5.4 GRADED

Acetone has a density of 1.96 g/L at 95°C and 1.02 atm.

a How many moles of acetone are there in a 1.00-L flask under these conditions?

ANALYSIS	
Information given:	volume of the flask (1.00 L); $T = 95°\text{C} + 273 = 368\ \text{K}$; density = 1.96 g/L
Information implied:	mass of acetone (1.96 g)
Asked for:	moles of acetone

STRATEGY

1. A gas occupies the volume of the flask; volume of acetone = volume of flask

2. Find n using the ideal gas law.

SOLUTION	
n	$n = \dfrac{PV}{RT} = \dfrac{1.02 \times 1.00}{0.0821 \times 368} = 0.0338\ \text{mol}$

b What is the molar mass of the acetone?

ANALYSIS	
Information given:	from part (a): $n = 0.0338\ \text{mol}$
Information implied:	mass of acetone (1.96 g)
Asked for:	molar mass

SOLUTION	
molar mass	$\text{MM} = \dfrac{\text{mass}}{\text{moles}} = \dfrac{1.96\ \text{g}}{0.0338\ \text{mol}} = 58.0\ \text{g/mol}$

continued

c Acetone contains the three elements, C, H, and O. When 1.000 g of acetone is burned, 2.27 g of CO_2 and 0.932 g of H_2O are formed. What is the molecular formula of the acetone?

ANALYSIS

Information given:	from part (b), molar mass of acetone (58.1 g/mol) The combustion of 1.00 g of sample yields 2.27 g CO_2 and 0.932 g H_2O.
Information implied:	mass of C, H, and O in 1.00-g sample
Asked for:	molecular formula of acetone

STRATEGY

1. Recall from Section 3.2 how to convert the mass of the product of combustion to the mass of the element.
2. Follow Figure 3.7 to obtain the simplest formula for the compound.
3. Compare the simplest formula's molar mass to the molar mass obtained in part (b).

SOLUTION

Mass of each element	mass C: $2.27\text{ g } CO_2 \times \dfrac{12.01\text{ g C}}{44.01\text{ g } CO_2} = 0.619\text{ g}$ mass H: $0.932\text{ g } H_2O \times \dfrac{2(1.008)\text{ g H}}{18.02\text{ g } H_2O} = 0.104\text{ g}$ mass O = mass sample − (mass C + mass H) $= 1.000\text{ g} - (0.619 + 0.104)\text{ g} = 0.277\text{ g}$
moles of each element	C: $\dfrac{0.619\text{ g}}{12.01\text{ g/mol}} = 0.0515\text{ mol}$; H: $\dfrac{0.104\text{ g}}{1.008\text{ g/mol}} = 0.103\text{ mol}$; O: $\dfrac{0.277\text{ g}}{16.00\text{ g/mol}} = 0.0173\text{ mol}$
Atomic ratios	C: $\dfrac{0.0515}{0.0173} = 3$; H: $\dfrac{0.104}{0.0173} = 6$; O: $\dfrac{0.0173}{0.0173} = 1$
Simplest formula	C_3H_6O
MM of simplest formula	$3(12.01) + 6(1.008) + 16.00 = 58.08$ g/mol
MM of vapor (from part (b))	58.1 g/mol
Molecular formula	C_3H_6O (simplest formula = molecular formula)

One way to calculate gas density is to use the ideal gas law where $\dfrac{\text{mass}}{\text{MM}}$ is substituted for n.

$$PV = \frac{\text{mass}}{\text{MM}}RT$$

Since density $= \dfrac{\text{mass}}{V}$ the general relation

$$\text{density} = MM\left(\frac{P}{RT}\right) \qquad (5.2)$$

results.

From this equation we see that the density of a gas is dependent (Figure 5.7) on

- *pressure*. Compressing a gas increases its density.
- *temperature*. Hot air rises because a gas becomes less dense when its temperature is increased. Hot air balloons are filled with air at a temperature higher

Figure 5.7 Density of a gas.

than that of the atmosphere, making the air inside less dense than that outside. First used in France in the eighteenth century, they are now seen in balloon races and other sporting events. Heat is supplied on demand by a propane burner.

- *molar mass*. Hydrogen (MM = 2.016 g/mol) has the lowest molar mass and the lowest density (at a given P and T) of all gases. Hence it has the greatest lifting power in "lighter-than-air" balloons. However, hydrogen has not been used in balloons carrying passengers since 1937, when the *Hindenburg*, a hydrogen-filled airship, exploded and burned. Helium (MM = 4.003 g/mol) is slightly less effective than hydrogen but a lot safer to work with because it is nonflammable. It is used in a variety of balloons, ranging from the small ones used at parties to meteorological balloons with volumes of a billion liters.

Very light gases, notably hydrogen and helium, tend to escape from the earth's atmosphere. The hydrogen you generate in the laboratory today is well on its way into outer space tomorrow. A similar situation holds with helium, which is found in very limited quantities mixed with natural gas in wells below the earth's surface. If helium is allowed to escape, it is gone forever, and our supply of this very useful gaseous element is depleted.

5-4 Stoichiometry of Gaseous Reactions

As pointed out in Chapter 3, a balanced equation can be used to relate moles or grams of substances taking part in a reaction. Where gases are involved, these relations can be extended to include volumes. To do this, we use the ideal gas law and modify Figures 3.11 and 4.6 as shown in Figure 5.8 (page 106). Note that the ideal gas law equation can be used only for gaseous reactants and products.

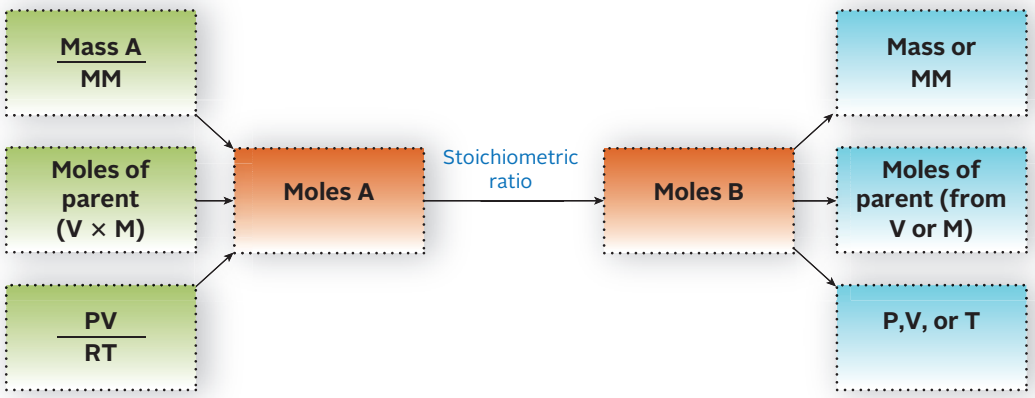


Figure 5.8 Flowchart for stoichiometry calculations involving gases.

EXAMPLE 5.5

Hydrogen peroxide, H_2O_2, is a common bleaching agent. It decomposes quickly to water and oxygen gas at high temperatures.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

How many liters of oxygen are produced at 78°C and 0.934 atm when 1.27 L of H_2O_2 (d = 1.00 g/mL) decompose?

ANALYSIS

Information given:	temperature (78°C); pressure (0.934 atm) H_2O_2: volume (1.27 L); density (1.00 g/mL)
Information implied:	mass and molar mass of H_2O_2 stoichiometric ratio of O_2 to H_2O_2 (2 H_2O_2/1 O_2)
Asked for:	volume of oxygen

STRATEGY

1. Change °C to K and L of H_2O_2 to mL. (Density is given in g/mL.)
2. Find the mass of H_2O_2. Note that you cannot directly use the volume of H_2O_2 to calculate the volume of O_2 because H_2O_2 is NOT a gas.
3. Follow Figure 5.8.

$$\text{mass } H_2O_2 \xrightarrow{\text{MM}} \text{mol } H_2O_2 \xrightarrow[\text{ratio}]{\text{stoichiometric}} \text{moles } O_2 \xrightarrow{nRT/P} \text{volume of oxygen}$$

SOLUTION

Mass H_2O_2	$\text{mass} = (\text{density})(\text{volume}) = (1.00\ \text{g/mL})(1.27 \times 10^3\ \text{mL}) = 1.27 \times 10^3\ \text{g}$
Mol O_2	$1.27 \times 10^3\ \text{g} \times \dfrac{1\ \text{mol } H_2O_2}{34.02\ \text{g}} \times \dfrac{1\ \text{mol } O_2}{2\ \text{mol } H_2O_2} = 18.7\ \text{mol}$
Volume O_2	$V = \dfrac{nRT}{P} = \dfrac{(18.7\ \text{mol})(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(78 + 273)\text{K}}{0.934\ \text{atm}} = 576\ \text{L}$

EXAMPLE 5.6 GRADED

Sodium bicarbonate (baking soda) is widely used to absorb odors inside refrigerators. When acid is added to baking soda, the following reaction occurs:

$$NaHCO_3(s) + H^+(aq) \longrightarrow Na^+(aq) + CO_2(g) + H_2O$$

All experiments here are performed with 2.45 *M* HCl and 12.75 g of $NaHCO_3$ at 732 mm Hg and 38°C.

a If an excess of HCl is used, what volume of CO_2 is obtained?

ANALYSIS

Information given:	pressure (732 mm Hg); temperature (38°C); mass of $NaHCO_3$ (12.75 g)
Information implied:	molar mass of $NaHCO_3$ stoichiometric ratio: 1 $NaHCO_3$ /1 CO_2
Asked for:	volume of CO_2 produced

STRATEGY

1. Follow the flowchart in Figure 5.8.
2. Convert to appropriate units of pressure and temperature.

$$\text{mass}_{NaHCO_3} \xrightarrow{\text{MM}} n_{NaHCO_3} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{CO_2} \xrightarrow{PV = nRT} V_{CO_2}$$

SOLUTION

mol CO_2 (n)

$$12.75 \text{ g } NaHCO_3 \times \frac{1 \text{ mol}}{84.01 \text{ g}} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } NaHCO_3} = 0.1518$$

volume CO_2 (V)

$$V = \frac{0.1518 \text{ mol} \times 0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times (273 + 38)\text{K}}{(732/760)\text{atm}} = 4.02 \text{ L}$$

b If $NaHCO_3$ is in excess, what volume of HCl is required to produce 2.65 L of CO_2?

ANALYSIS

Information given:	pressure (732 mm Hg); temperature (38°C); volume of CO_2 produced (2.65 L); molarity of HCl (2.45 *M*)
Information implied:	H^+ is the reacting species. HCl is the parent compound. stoichiometric ratio: 1 H^+/1 CO_2

STRATEGY

Follow the flowchart in Figure 5.8.

$$V_{CO_2} \xrightarrow{PV = nRT} n_{CO_2} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{H^+} \xrightarrow[\text{ratio}]{\text{atom}} n_{HCl} \xrightarrow{M} V_{HCl}$$

SOLUTION

mol CO_2

$$n = \frac{2.65 \text{ L} \times (732/760)\text{atm}}{0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times (273 + 38)\text{K}} = 0.100$$

mol HCl

$$0.100 \text{ mol } CO_2 \times \frac{1 \text{ mol } H^+}{1 \text{ mol } CO_2} \times \frac{1 \text{ mol HCl}}{1 \text{ mol } H^+} = 0.100$$

Volume HCl

$$\frac{0.100 \text{ mol HCl}}{2.45 \text{ mol/L}} = 0.0408 \text{ L} = 40.8 \text{ mL}$$

continued

c What volume of CO_2 is produced when all the $NaHCO_3$ is made to react with 50.0 mL of HCl?

ANALYSIS

Information given:	molarity of HCl (2.45 *M*); volume of HCl (50.0 mL); pressure (732 mm Hg); temperature (38°C)
Information implied:	H^+ is the reacting species. HCl is the parent compound. stoichiometric ratios: 1 H^+/1 CO_2; 1 $NaHCO_3$/1 CO_2 from part (a): mol $NaHCO_3$

STRATEGY

1. The presence of enough given data to calculate the number of moles of each reactant tells you that part (c) is a limiting reactant problem.
2. Follow the flowchart in Figure 5.8 to determine the number of moles of CO_2 obtained if HCl is limiting. You can obtain the moles of CO_2 if $NaHCO_3$ is limiting from part (a).
3. Compare the moles of CO_2 obtained using H^+ as the limiting reactant to the moles of CO_2 obtained using $NaHCO_3$ as the limiting reactant. Choose the smaller number of moles of CO_2.
4. Use the ideal gas law to convert mol CO_2 to the volume of CO_2.

SOLUTION

mol CO_2: $NaHCO_3$ limiting	from part (a): $0.1518 \text{ mol } NaHCO_3 \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } NaHCO_3} = 0.1518$
mol CO_2: HCl limiting	$(0.0500 \text{ L} \times 2.45 \text{ mol/L}) \text{ mol HCl} \times \frac{1 \text{ mol } H^+}{1 \text{ mol HCl}} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } H^+} = 0.122 \text{ mol}$
Theoretical yield of CO_2	$0.122 < 0.1518$; 0.122 mol CO_2 obtained
Volume CO_2	$V = \frac{0.122 \text{ mol} \times 0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times (273 + 38)\text{K}}{(732/760)\text{atm}} = 3.25 \text{ L}$

END POINTS

1. When a problem comes in several parts, you may not need to use all the given information for each part.
2. You should also check to see whether you can use information that you obtained from the preceding parts for subsequent questions.

Figure 5.9 Electrolysis of water (H_2O). The volume of hydrogen (H_2) formed in the tube at the right is twice the volume of oxygen (O_2) formed in the tube at the left, in accordance with the equation $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$.

Perhaps the first stoichiometric relationship to be discovered was the *law of combining volumes,* proposed by Gay-Lussac in 1808: ***The volume ratio of any two gases in a reaction at constant temperature and pressure is the same as the reacting mole ratio.***

To illustrate the law, consider the reaction

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

As you can see from Figure 5.9, the volume of hydrogen produced is twice that of the other gaseous product, oxygen.

The law of combining volumes, like so many relationships involving gases, is readily explained by the ideal gas law. At constant temperature and pressure, volume is directly proportional to number of moles ($V = k_1 n$). It follows that for gaseous species involved in reactions, the volume ratio must be the same as the mole ratio given by the coefficients of the balanced equation.

CHEMISTRY THE **HUMAN** SIDE

Avogadro's law (page 99) was proposed in 1811 by an Italian physicist at the University of Turin with the improbable name of Lorenzo Romano Amadeo Carlo Avogadro di Quarequa e di Cerreto (1776–1856).

Avogadro suggested this relationship to explain the law of combining volumes. Today it seems obvious. For example, in the reaction

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

the volume of hydrogen, like the number of moles, is twice that of oxygen. Hence, equal volumes of these gases must contain the same number of moles or molecules. This was by no means obvious to Avogadro's contemporaries. Berzelius, among others, dismissed Avogadro's ideas because he did not believe diatomic molecules composed of identical atoms (H_2, O_2) could exist. Dalton went a step further; he refused to accept the law of combining volumes because he thought it implied splitting atoms.

As a result of arguments like these, Avogadro's ideas lay dormant for nearly half a century. They were revived by another Italian scientist, Stanislao Cannizzaro, professor of chemistry at the University of Genoa. At a conference held in Karlsruhe in 1860, he persuaded the chemistry community of the validity of Avogadro's law and showed how it could be used to determine molar and atomic masses.


Bettmann/Corbis

Amadeo Avogadro
(1776–1856)

The quantity now called "Avogadro's number" (6.02×10^{23}/mol) was first estimated in 1865, nine years after Avogadro died. Not until well into the twentieth century did it acquire its present name. It seems appropriate to honor Avogadro in this way for the contributions he made to chemical theory.

EXAMPLE 5.7 GRADED

Consider the reaction between hydrogen and oxygen to form water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

One liter of oxygen is used and the reactant gases are maintained at 25°C and 1.00 atm. The density of water under the conditions of the experiment is 0.997 g/mL.

a What volume of $H_2(g)$ at 25°C and 1.00 atm is required to react with 1.00 L of $O_2(g)$?

ANALYSIS

Information given:	volume O_2 (1.00 L); pressure (1.00 atm); temperature (25°C)
Information implied:	stoichiometric ratio: 1 mol O_2/2 mol H_2 Conditions of temperature and pressure are constant.
Asked for:	Volume of H_2 at constant T and P that reacts with O_2

STRATEGY

Use the law of combining volumes (T and P are constant).

$$V_{O_2} \xrightarrow{\text{stoichiometric ratio}} V_{H_2}$$

SOLUTION

volume of H_2

$$1.00 \text{ L } O_2 \times \frac{2 \text{ L } H_2}{1 \text{ L } O_2} = 2.00 \text{ L } H_2$$

b What volume of $H_2O(l)$ is formed from the reaction?

ANALYSIS

Information given:	volume of $O_2(g)$ (1.00 L); pressure (1.00 atm); temperature (25°C); density of water (0.997 g/mL)
Asked for:	Volume of water obtained

continued

STRATEGY

The law of combining volumes cannot be used here because water is a liquid.

1. Use the ideal gas law to calculate the number of moles of O_2.
2. Follow the flowchart in Figure 5.8 to calculate the mass of water obtained.
3. Use the density of water to calculate its volume.

SOLUTION

1. Moles of O_2	$n_{O_2} = \dfrac{PV}{RT} = \dfrac{(1.00\text{ L})(1.00\text{ atm})}{(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(273+25)\text{K}} = 0.0409$
2. Mass of water	$0.0409\text{ mol } O_2 \times \dfrac{2\text{ mol } H_2O}{1\text{ mol } O_2} \times \dfrac{18.02\text{ g } H_2O}{1\text{ mol}} = 1.47\text{ g}$
3. Volume of water	$V = \dfrac{\text{mass}}{\text{density}} = \dfrac{1.47\text{ g}}{0.997\text{ g/mL}} = 1.48\text{ mL}$

c What mass of $H_2O(l)$ is formed, assuming a yield of 85.2%?

ANALYSIS

Information given:	% yield (85.2%)
Information implied:	theoretical yield
Asked for:	mass of water obtained (actual yield)

STRATEGY

1. The mass obtained in part (b) is the theoretical yield.
2. Calculate actual yield from percent yield.

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

SOLUTION

Actual yield	$\text{actual yield} = \dfrac{\%\text{ yield}}{100\%} \times \text{theoretical yield} = \dfrac{85.2\%}{100\%} \times 1.47\text{ g} = 1.25\text{ g}$

5-5 Gas Mixtures: Partial Pressures and Mole Fractions

Because the ideal gas law applies to all gases, you might expect it to apply to gas mixtures. Indeed it does. For a mixture of two gases A and B, the total pressure is given by the expression

$$P_{tot} = n_{tot}\frac{RT}{V} = (n_A + n_B)\frac{RT}{V}$$

Separating the two terms on the right,

$$P_{tot} = n_A\frac{RT}{V} + n_B\frac{RT}{V}$$

The terms n_ART/V and n_BRT/V are, according to the ideal gas law, the pressures that gases A and B would exert if they were alone. Each quantity is referred to as having a **partial pressure,** P_A and P_B.

Partial pressure is the pressure a gas would exert if it occupied the entire volume by itself.

$$P_A = \text{partial pressure A} = n_ART/V$$
$$P_B = \text{partial pressure B} = n_BRT/V$$

a

b

Figure 5.10 Collecting a gas by water displacement. (a) Hydrogen gas is being generated in the flask by an acidic solution dripping onto a metal. (b) When a gas is collected by displacing water, it becomes saturated with water vapor. The partial pressure of $H_2O(g)$ in the collecting flask is equal to the vapor pressure of liquid water at the temperature of the system.

Substituting P_A and P_B for $n_A RT/V$ and $n_B RT/V$ in the equation for P_{tot},

$$P_{tot} = P_A + P_B \tag{5.3}$$

The relation just derived was first proposed by John Dalton in 1801; it is often referred to as **Dalton's law** of partial pressures:

The total pressure of a gas mixture is the sum of the partial pressures of the components of the mixture.

To illustrate Dalton's law, consider a gaseous mixture of hydrogen and helium in which

$$P_{H_2} = 2.46 \text{ atm} \qquad P_{He} = 3.69 \text{ atm}$$

It follows from Dalton's law that

$$P_{tot} = 2.46 \text{ atm} + 3.69 \text{ atm} = 6.15 \text{ atm}$$

Wet Gases; Partial Pressure of Water

When a gas such as hydrogen is collected by bubbling through water (Figure 5.10), it picks up water vapor; molecules of H_2O escape from the liquid and enter the gas phase. Dalton's law can be applied to the resulting gas mixture:

$$P_{tot} = P_{H_2O} + P_{H_2}$$

In this case, P_{tot} is the measured pressure. The partial pressure of water vapor, P_{H_2O}, is equal to the **vapor pressure** of liquid water. It has a fixed value at a given temperature (see Appendix 1). The partial pressure of hydrogen, P_{H_2}, can be calculated by subtraction. The number of moles of hydrogen in the wet gas, n_{H_2}, can then be determined using the ideal gas law.

EXAMPLE 5.8

A student prepares a sample of hydrogen gas by electrolyzing water at 25°C. She collects 152 mL of H_2 at a total pressure of 758 mm Hg. Using Appendix 1 to find the vapor pressure of water at 25°C, calculate

(a) the partial pressure of hydrogen.

(b) the number of moles of hydrogen collected.

continued

ANALYSIS	
Information given:	V_{H_2} (152 mL); pressure (758 mm Hg); temperature (25°C)
Information implied:	vapor pressure of water at 25°C (Appendix 1) Volume and temperature are constant.
Asked for:	(a) P_{H_2} (b) n_{H_2}
STRATEGY	
(a) Recall that H_2 and $H_2O(g)$ contribute to the total pressure P_{tot}. Use Dalton's law: $P_{tot} = P_1 + P_2 + \ldots$ (b) Use the ideal gas law to calculate n_{H_2} at P_{H_2}.	
SOLUTION	
(a) P_{H_2}	$P_{tot} = P_{H_2} + P_{H_2O}$ $P_{H_2} = 758 \text{ mm Hg} - 23.76 \text{ mm Hg} = 734 \text{ mm Hg}$
(b) n_{H_2}	$n_{H_2} = \dfrac{P_{H_2} V}{RT} = \dfrac{[(734/760)\text{atm}](0.152 \text{ L})}{(298 \text{ K})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})} = 0.00600 \text{ mol}$

Vapor pressure, like density and solubility, is an intensive physical property that is characteristic of a particular substance. The vapor pressure of water at 25°C is 23.76 mm Hg, independent of volume or the presence of another gas. Like density and solubility, vapor pressure varies with temperature; for water it is 55.3 mm Hg at 40°C, 233.7 mm Hg at 70°C, and 760.0 mm Hg at 100°C. We will have more to say in Chapter 9 about the temperature dependence of vapor pressure.

Vapor pressure is further discussed in Chapter 9.

Partial Pressure and Mole Fraction

As pointed out earlier, the following relationship applies to a mixture containing gas A (and gas B):

$$P_A = \frac{n_A RT}{V} \qquad P_{tot} = \frac{n_{tot} RT}{V}$$

Dividing P_A by P_{tot} gives

$$\frac{P_A}{P_{tot}} = \frac{n_A}{n_{tot}}$$

The fraction n_A/n_{tot} is referred to as the **mole fraction** of A in the mixture. It is the fraction of the total number of moles that is accounted for by gas A. Using X_A to represent the mole fraction of A (i.e., $X_A = n_A/n_{tot}$),

$$P_A = X_A P_{tot} \tag{5.4}$$

In other words, ***the partial pressure of a gas in a mixture is equal to its mole fraction multiplied by the total pressure.*** This relation is commonly used to calculate partial pressures of gases in a mixture when the total pressure and the composition of the mixture are known (Example 5.9).

If a mixture contains equal numbers of A and B molecules, $X_A = X_B = 0.50$ and $P_A = P_B = \frac{1}{2}P_{tot}$.

EXAMPLE 5.9

When one mole of methane, CH_4, is heated with four moles of oxygen, the following reaction occurs:

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

Assuming all of the methane is converted to CO_2 and H_2O, what are the mole fractions of O_2, CO_2, and H_2O in the resulting mixture? If the total pressure of the mixture is 1.26 atm, what are the partial pressures?

ANALYSIS

Information given:	P_{tot} (1.26 atm) Initial amounts of reactants (1.000 mol CH_4 and 4.000 mol O_2)
Information implied:	stoichiometric ratios: 2 mol O_2/1 mol CH_4/1 mol CO_2/2 mol H_2O limiting reactant (CH_4); reactant in excess (O_2)
Asked for:	mol fraction of each gas after reaction partial pressure of each gas after reaction

STRATEGY

1. Find the moles of reactants left after reaction. (Recall that CH_4 is limiting and thus is completely used up.)

   $$n_{CH_4} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{O_2}$$

   n_{O_2} after reaction = n_{O_2} initially − n_{O_2} used

2. Find the moles of products.

   $$n_{CH_4} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{CO_2} \quad \text{and} \quad n_{CH_4} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{H_2O}$$

3. Find n_{tot}.

   $$n_{tot} = n_{CH_4} + n_{O_2} + n_{CO_2} + n_{H_2O}$$

4. Find the mol fraction of each gas.

   $$X_A = \frac{n_A}{n_{tot}}$$

5. Find the partial pressure of each gas.

   $$P_A = (X_A)(P_{tot})$$

SOLUTION

1. mol CH_4	mol CH_4 = 0 (Problem states that CH_4 is completely used up.)
mol O_2 reacted	$1.000 \text{ mol } CH_4 \times \frac{2 \text{ mol } O_2}{1 \text{ mol } CH_4} = 2.000$
mol O_2 unreacted	4.000 mol O_2 initially − 2.000 mol reacted = 2.000 mol
2. mol CO_2	$1.000 \text{ mol } CH_4 \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4} = 1.000$ mol CO_2 are produced
mol H_2O	$1.000 \text{ mol } CH_4 \times \frac{2 \text{ mol } H_2O}{1 \text{ mol } CH_4} = 2.000$ mol H_2O are produced
3. n_{tot}	$n_{tot} = n_{CH_4} + n_{O_2} + n_{CO_2} + n_{H_2O} = 0 + 2.000 + 1.000 + 2.000 = 5.000$
4. X_{CH_4}	$X_{CH_4} = \frac{n_{CH_4}}{n_{tot}} = \frac{0}{5.000} = 0$
X_{O_2}	$X_{O_2} = \frac{n_{O_2}}{n_{tot}} = \frac{2.000}{5.000} = 0.4000$

continued

X_{CO_2}	$X_{CO_2} = \frac{n_{CO_2}}{n_{tot}} = \frac{1.000}{5.000} = 0.2000$
X_{H_2O}	$X_{H_2O} = \frac{n_{H_2O}}{n_{tot}} = \frac{2.000}{5.000} = 0.4000$
5. P_{CH_4}	$(X_{CH_4})(P_{tot}) = (0)(1.26) = 0$
P_{O_2}	$(X_{O_2})(P_{tot}) = (0.4000)(1.26) = 0.504$ atm
P_{CO_2}	$(X_{CO_2})(P_{tot}) = (0.2000)(1.26) = 0.252$ atm
P_{H_2O}	$(X_{H_2O})(P_{tot}) = (0.4000)(1.26) = 0.504$ atm

END POINT

The mole fractions of all the gases should add up to 1. All the partial pressures should add up to 1.26 atm. They do!

5-6 Kinetic Theory of Gases

The fact that the ideal gas law applies to all gases indicates that the gaseous state is a relatively simple one from a molecular standpoint. Gases must have certain common properties that cause them to follow the same natural law. Between about 1850 and 1880, James Maxwell (1831–1879), Rudolf Clausius (1822–1888), Ludwig Boltzmann (1844–1906), and others developed the **kinetic theory** of gases. They based it on the idea that all gases behave similarly as far as particle motion is concerned.

Molecular Model

By the use of the kinetic theory, it is possible to derive or explain the experimental behavior of gases. To do this we start with a simple molecular model, which assumes that

- ***gases are mostly empty space.*** The total volume of the molecules is negligibly small compared with that of the container to which they are confined.
- ***gas molecules are in constant, chaotic motion.*** They collide frequently with one another and with the container walls. As a result, their velocities are constantly changing.
- ***collisions are elastic.*** There are no attractive forces that would tend to make molecules "stick" to one another or to the container walls.
- ***gas pressure is caused by collisions of molecules with the walls of the container*** (Figure 5.11). As a result, pressure increases with the energy and frequency of these collisions.

In air, a molecule undergoes about 10 billion collisions per second.

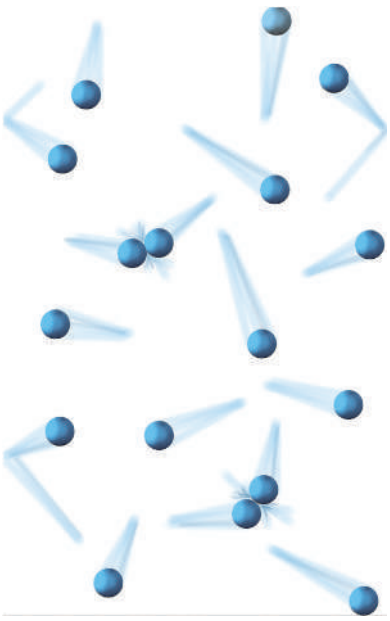


Figure 5.11 The kinetic molecular model of a gas. Gas molecules are in constant motion and their collisions are elastic. Collisions with the walls cause gas pressure.

Expression for Pressure, *P*

Applying the laws of physics to this simple model, it can be shown that the pressure (P) exerted by a gas in a container of volume V is

$$P = \frac{N(\text{mass})u^2}{3V}$$

where N is the number of molecules, and u is the average speed.* We will not attempt to derive this equation. However, it makes sense, at least qualitatively. In particular

- the ratio N/V expresses the concentration of gas molecules in the container. The more molecules there are in a given volume, the greater the collision frequency and so the greater the pressure.

*More rigorously, u^2 is the average of the squares of the speeds of all molecules.

- the product (mass)(u^2) is a measure of the energy of collision. (When a Cadillac traveling at 100 mph collides with a brick wall, the energy transferred is much greater than would be obtained with a bicycle at 5 mph.) Hence, as this equation predicts, pressure is directly related to (mass)(u^2).

Average Kinetic Energy of Translational Motion, E_t

The kinetic energy, E_t, of a gas molecule of a given mass moving at speed u is

$$E_t = \frac{(\text{mass})u^2}{2}$$

From the equation written above for P, we see that (mass) $u^2 = 3PV/N$. Hence

$$E_t = \frac{3PV}{2N}$$

But the ideal gas law tells us that $PV = nRT$, so

$$E_t = \frac{3nRT}{2N}$$

This equation can be simplified by noting that the number of molecules, N, in a gas sample is equal to the number of moles, n, multiplied by Avogadro's number, N_A, that is, $N = n \times N_A$. Making this substitution in the above equation and simplifying, we obtain the final expression for the *average translational kinetic energy* of a gas molecule:

$$E_t = \frac{3RT}{2N_A} \tag{5.5}$$

This equation contains three constants (3/2, R, N_A) and only one variable, the temperature T. It follows that

- ***at a given temperature, molecules of different gases*** **(e.g., H_2, O_2, . . .)** ***must all have the same average kinetic energy of translational motion.***
- ***the average translational kinetic energy of a gas molecule is directly proportional to the Kelvin temperature, T.***

A baseball in motion has translational energy.

Average Speed, u

By equating the first and last expressions written above for E_t, we see that

$$\frac{(\text{mass})u^2}{2} = \frac{3RT}{2N_A}$$

Solving this equation for u^2:

$$u^2 = \frac{3RT}{(\text{mass})N_A}$$

But the product (mass of a molecule) times N_A (the number of molecules in a mole) is simply the molar mass MM, so we can write

$$u^2 = \frac{3RT}{\text{MM}}$$

Taking the square root of both sides of this equation, we arrive at the final expression for the **average speed of gas molecules,** u,

$$u = \left(\frac{3RT}{\text{MM}}\right)^{1/2} \tag{5.6}$$

E_t depends only on T; u depends on both T and MM.

From this relation you can see that the average speed u is

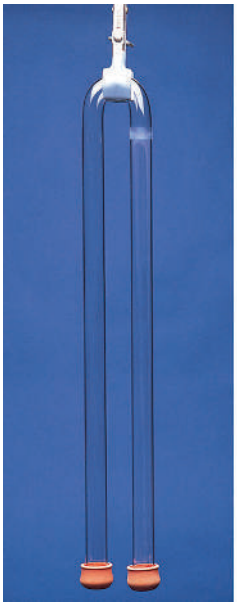


Figure 5.12 Relation of molecular speed to molar mass. When ammonia gas, which is injected into the left arm of the tube, comes in contact with hydrogen chloride, which is injected into the right arm of the tube, they react to form solid ammonium chloride: $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$. Because NH_3 (MM = 17 g/mol) moves faster than HCl (MM = 36.5 g/mol), the ammonium chloride forms closer to the HCl end of the tube.

- ***directly proportional to the square root of the absolute temperature.*** For a given gas at two different temperatures, T_2 and T_1, the quantity MM is constant, and we can write

$$\frac{u_2}{u_1} = \left(\frac{T_2}{T_1}\right)^{1/2}$$

- ***inversely proportional to the square root of molar mass*** (**MM**) (Figure 5.12). For two different gases A and B at the same temperature (T constant):

$$\frac{u_B}{u_A} = \left(\frac{MM_A}{MM_B}\right)^{1/2} \qquad (5.7)$$

EXAMPLE 5.10

Calculate the average speed, u, of an N_2 molecule at 25°C.

ANALYSIS

Information given:	temperature (25°C)
Information implied:	$R = 8.31 \times 10^3$ g · m²/s² · mol · K MM of N_2
Asked for:	average speed, u, of N_2 at 25°C

STRATEGY

1. Change T to the appropriate units.
2. Note the units of the constant R.
3. Substitute into the equation: $u = \left(\frac{3RT}{MM}\right)^{1/2}$

SOLUTION

Average speed

$$u = \left(\frac{3 \times 8.31 \times 10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K} \times 298\ K}{28.02 \frac{g}{mol}}\right)^{1/2} = 515\ m/s$$

continued

END POINT

Converting the speed of the nitrogen molecule obtained above to miles per hour:

$$515\ \frac{\text{m}}{\text{s}} \times \frac{1\ \text{mi}}{1.609 \times 10^3\ \text{m}} \times \frac{3600\ \text{s}}{1\ \text{h}} = 1.15 \times 10^3\ \text{mi/h}$$

Note that the average cruising speed of a Boeing 777 is about 580 mi/h and the speed of sound is 768 mi/h.

Effusion of Gases; Graham's Law

All of us are familiar with the process of gaseous diffusion, in which gas molecules move through space from a region of high concentration to one of low concentration. If your instructor momentarily opens a cylinder of chlorine gas at the lecture table, you will soon recognize the sharp odor of chlorine, particularly if you have a front-row seat in the classroom. On a more pleasant note, the odor associated with a freshly baked apple pie also reaches you via gaseous diffusion.

Diffusion is a relatively slow process; a sample of gas introduced at one location may take an hour or more to distribute itself uniformly throughout a room. At first glance this seems surprising, since as we saw in Example 5.10 gas molecules are moving very rapidly. However, molecules are constantly colliding with one another; at 25°C and 1 atm, an N_2 molecule undergoes more than a billion collisions per second with its neighbors. This slows down the net movement of gas molecules in any given direction.

Diffusion is slower than effusion for the same reason that boarding a subway car is slower at 5 P.M. than at 5 A.M.

As we have implied, diffusion is a rather complex process so far as molecular motion is concerned. **Effusion,** the flow of gas molecules at low pressures through tiny pores or pinholes, is easier to analyze using kinetic theory.

The relative rates of effusion of different gases depend on two factors: the pressures of the gases and the relative speeds of their particles. If two different gases A and B are compared at the same pressure, only their speeds are of concern, and

$$\frac{\text{rate of effusion B}}{\text{rate of effusion A}} = \frac{u_B}{u_A}$$

where u_A and u_B are average speeds. As pointed out earlier, at a given temperature,

$$\frac{u_B}{u_A} = \left(\frac{\text{MM}_A}{\text{MM}_B}\right)^{1/2}$$

It follows that, at constant pressure and temperature,

$$\frac{\text{rate of effusion B}}{\text{rate of effusion A}} = \left(\frac{\text{MM}_A}{\text{MM}_B}\right)^{1/2}$$

The time that a gas effuses can also be related to its molar mass. Since rate is inversely proportional to time, it follows that

$$\frac{\text{time}_A}{\text{time}_B} = \left(\frac{\text{MM}_A}{\text{MM}_B}\right)^{1/2}$$

This relation in a somewhat different form was discovered experimentally by the Scottish chemist Thomas Graham (1748–1843) in 1829. Graham was interested in a wide variety of chemical and physical problems, among them the separation of the components of air. **Graham's law** can be stated as

> ***At a given temperature and pressure, the rate of effusion of a gas, in moles per unit time, is inversely proportional to the square root of its molar mass.***

Graham's law tells us qualitatively that light molecules effuse more rapidly than heavier ones (Figure 5.13, page 119). In quantitative form, it allows us to determine molar masses of gases (Example 5.11).

EXAMPLE 5.11

In an effusion experiment, argon gas is allowed to expand through a tiny opening into an evacuated flask of volume 120 mL for 32.0 s, at which point the pressure in the flask is found to be 12.5 mm Hg. This experiment is repeated with a gas X of unknown molar mass at the same T and P. It is found that the pressure in the flask builds up to 12.5 mm Hg after 48.0 s. Calculate the molar mass of X.

ANALYSIS

Information given:	volume of both flasks (120 mL); pressure in both flasks (12.5 mm Hg); time for Ar effusion (32.0 s); time for gas (X) effusion (48.0 s)
Information implied:	Temperature, pressure, and volume are the same for both flasks. rate of effusion for each gas MM of argon
Asked for:	MM of X

STRATEGY

1. Since T, P, and V are the same for both gases, the number of moles of gas in both flasks is the same.

$$n_{Ar} = n_X = n$$

2. The rate of effusion is in mol/time.

$$\text{rate} = \frac{n_{Ar}}{\text{time}} = \frac{n_X}{\text{time}} = \frac{n}{\text{time}}$$

3. Substitute into Graham's law of effusion, where A = gas X and B = Ar.

$$\frac{\text{rate B}}{\text{rate A}} = \left(\frac{\text{MM}_A}{\text{MM}_B}\right)^{1/2} \longrightarrow \frac{\text{rate Ar}}{\text{rate X}} = \left(\frac{\text{MM}_X}{\text{MM}_{Ar}}\right)^{1/2}$$

SOLUTION

rates

$$\text{rate X} = \frac{n}{48.0\ \text{s}} \qquad \text{rate Ar} = \frac{n}{32.0\ \text{s}}$$

MM_X

$$\frac{\frac{n}{32.0\ \text{s}}}{\frac{n}{48.0\ \text{s}}} = \left(\frac{\text{MM}_X}{39.95\ \text{g/mol}}\right)^{1/2} \longrightarrow 1.50 = \left(\frac{\text{MM}_X}{39.95\ \text{g/mol}}\right)^{1/2}$$

$$(1.50)^2 = \left(\left(\frac{\text{MM}_X}{39.95\ \text{g/mol}}\right)^{1/2}\right)^2 \longrightarrow 2.25 = \frac{\text{MM}_X}{39.95\ \text{g/mol}} \rightarrow \text{MM}_X = 89.9\ \text{g/mol}$$

END POINT

Since the unknown gas takes longer to effuse, it should have a larger molar mass than argon. It does!

A practical application of Graham's law arose during World War II, when scientists were studying the fission of uranium atoms as a source of energy. It became necessary to separate $^{235}_{92}\text{U}$, which is fissionable, from the more abundant isotope of uranium, $^{238}_{92}\text{U}$, which is not fissionable. Because the two isotopes have almost identical chemical properties, chemical separation was not feasible. Instead, an effusion process was worked out using uranium hexafluoride, UF_6. This compound is a gas at room temperature and low pressures. Preliminary experiments indicated that $^{235}_{92}UF_6$ could indeed be separated from $^{238}_{92}UF_6$ by effusion.

The separation factor is very small because the rates of effusion of these two species are nearly equal:

$$\frac{\text{rate of effusion of } {}^{235}_{92}UF_6}{\text{rate of effusion of } {}^{238}_{92}UF_6} = \left(\frac{352.0}{349.0}\right)^{1/2} = 1.004$$

so a great many repetitive separations are necessary. An enormous plant was built for this purpose in Oak Ridge, Tennessee. In this process, UF_6 effuses many thousands of times through porous barriers. The lighter fractions move on to the next stage, while heavier fractions are recycled through earlier stages. Eventually, a nearly complete separation of the two isotopes is achieved.

Distribution of Molecular Speeds

As shown in Example 5.10, the average speed of an N_2 molecule at 25°C is 515 m/s; that of H_2 is even higher, 1920 m/s. However, not all molecules in these gases have these speeds. The motion of particles in a gas is utterly chaotic. In the course of a second, a particle undergoes millions of collisions with other particles. As a result, the speed and direction of motion of a particle are constantly changing. Over a period of time, the speed will vary from almost zero to some very high value, considerably above the average.

In 1860 James Clerk Maxwell, a Scottish physicist and one of the greatest theoreticians the world has ever known, showed that different possible speeds are distributed among particles in a definite way. Indeed, he developed a mathematical expression for this distribution (referred to today as the **Maxwell distribution**). His results are shown graphically in Figure 5.14 for O_2 at 25°C and 1000°C. On the graph, the relative number of molecules having a certain speed is plotted against that speed. At 25°C, this number increases rapidly with the speed, up to a maximum of about 400 m/s. This is the most probable speed of an oxygen molecule at 25°C. Above about 400 m/s, the number of molecules moving at any particular speed decreases. For speeds in excess of about 1600 m/s, the fraction of molecules drops off to nearly zero. In general, most molecules have speeds rather close to the average value.

As temperature increases, the speed of the molecules increases. The distribution curve for molecular speeds (Figure 5.14) shifts to the right and becomes broader. The chance of a molecule having a very high speed is much greater at 1000°C than at 25°C. Note, for example, that a large number of molecules has speeds greater than 1600 m/s at 1000°C; almost none have that speed at 25°C. The general

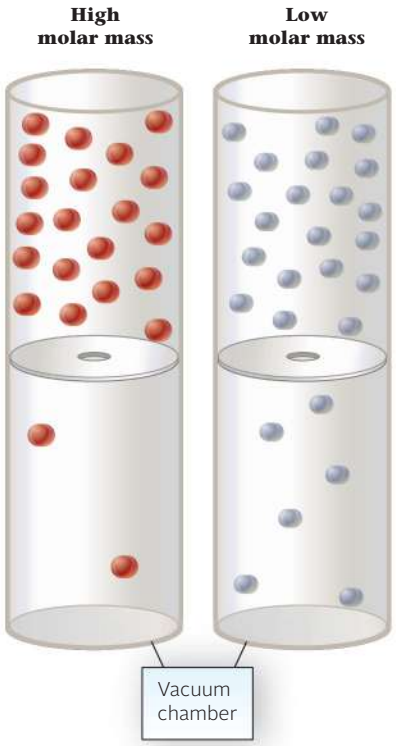


Figure 5.13 Effusion of gases. A gas with a higher molar mass (red molecules) effuses into a vacuum more slowly than a gas with a lower molar mass (gray molecules).

In a gas sample at any instant, gas molecules are moving at a variety of speeds.

Sort of like people—most of them go along with the crowd.

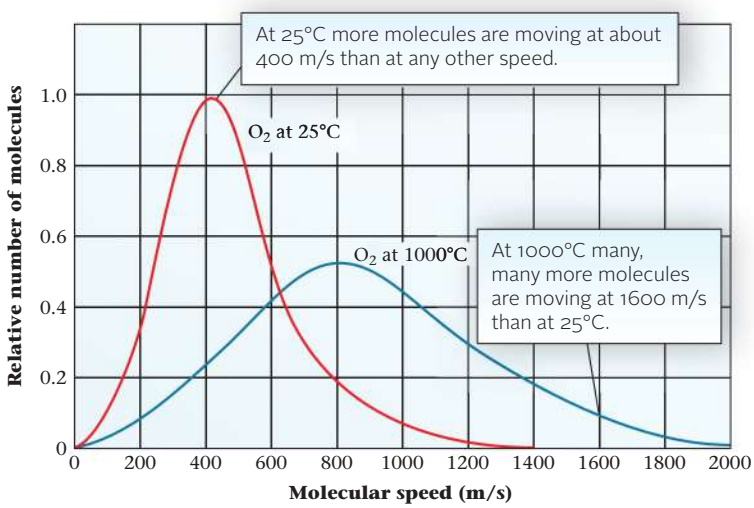
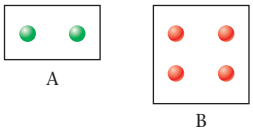


Figure 5.14 Distribution of molecular speeds of oxygen molecules at 25°C and 1000°C. At the higher temperature the fraction of molecules moving at very high speeds is greater.

principle here is one that we will find very useful when we look at the effect of temperature on reaction rate in Chapter 11.

EXAMPLE 5.12 CONCEPTUAL

Consider the two boxes A and B shown below. Box B has a volume exactly twice that of box A. The circles ● and ● represent one mole of HCl and He, respectively. The two boxes are at the same temperature.



(a) Compare the pressures of the gases in the two containers.

(b) Compare the densities of the two gases.

(c) Compare the number of atoms in the two boxes.

(d) If the HCl in box A were transferred to box B, what would be the mole fraction of HCl in the mixture?

(e) Which of the two gases effuses faster?

SOLUTION

(a) Since n/V and T are the same in both cases, $P = nRT/V$ is the same for the two gases.

(b) The mass of HCl is 2(36.5 g) = 73.0 g; that of He is 4(4.00 g) = 16.0 g. Since $73.0\ g/V > 16.0\ g/2V$, HCl has the higher density.

(c) Two moles of diatomic HCl contain the same number of atoms as four moles of He.

(d) $X_{HCl} = 2/6 = 1/3$

(e) Because HCl and He are at the same pressure, the lighter gas, He, effuses faster.

5-7 Real Gases

In this chapter, the ideal gas law has been used in all calculations, with the assumption that it applies exactly. Under ordinary conditions, this assumption is a good one; however, all real gases deviate at least slightly from the ideal gas law. Table 5.2 shows the extent to which two gases, O_2 and CO_2, deviate from ideality at different temperatures and pressures. The data compare the experimentally observed molar volume, V_m

$$\text{molar volume} = V_m = V/n$$

The molar volume is V when $n = 1$.

with the molar volume calculated from the ideal gas law V_m°:

$$V_m^\circ = RT/P$$

Table 5.2 Real Versus Ideal Gases, Percent Deviation* in Molar Volume

	O_2			CO_2		
P(atm)	50°C	0°C	−50°C	50°C	0°C	−50°C
1	−0.0%	−0.1%	−0.2%	−0.4%	−0.7%	−1.4%
10	−0.4%	−1.0%	−2.1%	−4.0%	−7.1%	
40	−1.4%	−3.7%	−8.5%	−17.9%		
70	−2.2%	−6.0%	−14.4%	−34.2%	Condenses to liquid	
100	−2.8%	−7.7%	−19.1%	−59.0%		

*Percent deviation $= \dfrac{(V_m - V_m^\circ)}{V_m^\circ} \times 100\%$

It should be obvious from Table 5.2 that deviations from ideality become larger at *high pressures and low temperatures*. Moreover, the deviations are larger for CO_2 than for O_2. All of these effects can be correlated in terms of a simple, common-sense observation:

In general, the closer a gas is to the liquid state, the more it will deviate from the ideal gas law.

A gas is liquefied by going to low temperatures and/or high pressures. Moreover, as you can see from Table 5.2, carbon dioxide is much easier to liquefy than oxygen.

From a molecular standpoint, deviations from the ideal gas law arise because it neglects two factors:

1. attractive forces between gas particles.
2. the finite volume of gas particles.

We will now consider in turn the effect of these two factors on the molar volumes of real gases.

Attractive Forces

Notice that in Table 5.2 all the deviations are negative; the observed molar volume is less than that predicted by the ideal gas law. This effect can be attributed to attractive forces between gas particles. These forces tend to pull the particles toward one another, reducing the space between them. As a result, the particles are crowded into a smaller volume, just as if an additional external pressure were applied. The observed molar volume, V_m, becomes less than V_m°, and the deviation from ideality is *negative:*

Attractive forces make the molar volume smaller than expected.

$$\frac{V_m - V_m^\circ}{V_m^\circ} < 0$$

The magnitude of this effect depends on the strength of the attractive forces and hence on the nature of the gas. Intermolecular attractive forces are stronger in CO_2 than they are in O_2, which explains why the deviation from ideality of V_m is greater with carbon dioxide and why carbon dioxide is more readily condensed to a liquid than is oxygen.

Particle Volume

Figure 5.15 shows a plot of V_m/V_m° versus pressure for methane at 25°C. Up to about 150 atm, methane shows a steadily increasing negative deviation from ideality, as might be expected on the basis of attractive forces. At 150 atm, V_m is only about 70% of V_m°.

At very high pressures, methane behaves quite differently. Above 150 atm, the ratio V_m/V_m° *increases,* becoming 1 at about 350 atm. Above that pressure, methane shows a *positive* deviation from the ideal gas law:

$$\frac{V_m - V_m^\circ}{V_m^\circ} > 0$$

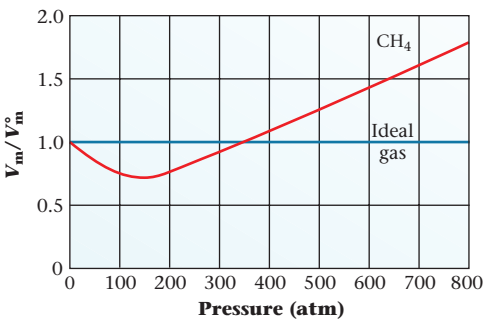


Figure 5.15 Deviation of methane gas from ideal gas behavior. Below about 350 atm, attractive forces between methane (CH_4) molecules cause the observed molar volume at 25°C to be less than that calculated from the ideal gas law. At 350 atm, the effect of the attractive forces is just balanced by that of the finite volume of CH_4 molecules, and the gas appears to behave ideally. Above 350 atm, the effect of finite molecular volume predominates and $V_m > V_m^\circ$.

This effect is by no means unique to methane; it is observed with all gases. If the data in Table 5.2 are extended to very high pressures, oxygen and carbon dioxide behave like methane; V_m becomes larger than V_m°.

An increase in molar volume above that predicted by the ideal gas law is related to the finite volume of gas particles. These particles contribute to the observed volume, making V_m greater than V_m°. Ordinarily, this effect becomes evident only at high pressures, where the particles are quite close to one another.

CHEMISTRY **BEYOND** THE CLASSROOM

Measurement of Blood Pressure

One of the first things that a nurse does when you visit your doctor is take your blood pressure with a *sphygmomanometer*. A condition of elevated blood pressure is called *hypertension* and can be a major factor in heart attacks and strokes. How does a sphygmomanometer work?

When the heart contracts and relaxes, it pumps blood through the arteries in the body. The pressure exerted by the blood on the walls of the artery can be measured in the same way as the pressure of a column of air or water.

Blood pressure is measured by a special type of manometer called a sphygmomanometer. It consists of a cuff and a device that inflates an air bladder inside the cuff, which in turn restricts the flow of blood through an artery, together with a device that displays the pressure measured. Commonly, the cuff is placed at about heart level on the upper arm, just above the elbow, with the arm held in a relaxed position against a supporting table or bench. The cuff is inflated to a pressure above that of the blood being pumped by the heart, which cuts off the flow of blood through the artery. The pressure in the cuff is then slowly reduced.

As the cuff is deflated, a "whooshing" sound, called a Korotkoff sound, is detected by using a stethoscope pressed against the brachial artery (the artery that runs from your elbow to your shoulder). The sound results from the restoration of blood flow through the artery as the pressure opposing it in the cuff is relaxed. When two consecutive sounds are heard, the pressure reading is taken from the measuring device. This is called the systolic pressure reading. This reading corresponds to the cycle where the heart is contracting in response to an electrical stimulus.


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Figure A Aneroid sphygmomanometer.

Further deflation of the cuff leads to several more Korotkoff sounds, ultimately ending in silence as the pressure in the cuff drops below the diastolic blood pressure. The disappearance of sound determines the lower of the two readings that comprise a blood pressure measurement—the diastolic reading. The diastolic reading corresponds to the cycle where the heart is relaxing following its contraction.

The standard in sphygmomanometers uses a column of mercury, exactly as a mercury barometer does. It requires a separate stethoscope and a trained ear for proper operation. Another type of device is called an aneroid sphygmomanometer, which uses an analog gauge that is calibrated against a mercury column.

Even more common today are digital sphygmomanometers, which require no external listening device for the Korotkoff sounds. The cuff includes a microphone that is connected to a microprocessor and has an automatic inflator with a pressure sensor connected to an air pump. At the press of a button, the cuff inflates and deflates under computer control, and the reading is taken and processed by the computer chip. These devices measure the mean arterial pressure, which is then processed mathematically to give the systolic and diastolic readings. These are then displayed on a digital panel. Blood pressure readings are commonly reported as even numbers, and in units of millimeters of mercury. Although they are easy to use, digital sphygmomanometers are not suitable for all blood pressure measurements. Some conditions can render their readings significantly inaccurate.

Other types of sphygmomanometers include those that can be placed around a finger. They are easier to use but are less accurate than other types of blood pressure measuring devices.

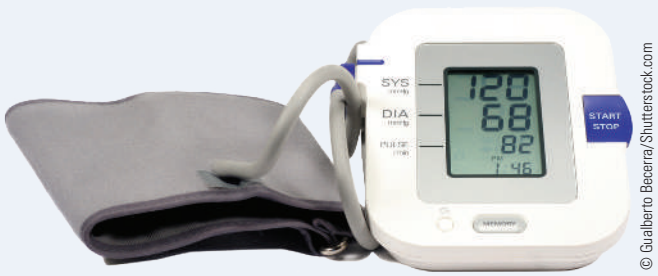

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Figure B Digital sphygmomanometer.

Key Concepts

1. Convert between units of P, V, T, and amount of gas. **(Example 5.1; Problems 1–4)**
2. Use the ideal gas law to
   - solve initial and final state problems. **(Example 5.2; Problems 5–14)**
   - calculate P, V, T or n. **(Example 5.3; Problems 15–20)**
   - calculate density or molar mass. **(Example 5.4; Problems 21–30)**
   - relate amounts and volumes of gases in reactions. **(Examples 5.5–5.7; Problems 31–40)**
3. Use Dalton's law. **(Examples 5.8, 5.9; Problems 41–52)**
4. Calculate the speeds of gas molecules. **(Example 5.10; Problems 53–56, 61, 62)**
5. Use Graham's law to relate rate of effusion to molar mass. **(Example 5.11; Problems 57–60)**

Key Equations

Ideal gas law	$PV = nRT$
Gas density	$d = (\text{MM}) \times P/RT$
Dalton's law	$P_{tot} = P_A + P_B$; $P_A = X_A \times P_{tot}$
Average translational kinetic energy	$E_t = 3RT/2N_A$
Average speed of gas molecules	$u = (3RT/\text{MM})^{1/2}$
Graham's law	$\text{rate}_B/\text{rate}_A = (\text{MM}_A/\text{MM}_B)^{1/2}$

Key Terms

atmosphere (atm)
bar
effusion
kinetic theory
millimeters of mercury (mm Hg)
mole fraction
partial pressure
gas constant
standard temperature and pressure (STP)
vapor pressure

Summary Problem

When aluminum foil is added to a solution of hydrochloric acid, the following reaction occurs:

$$2\text{Al}(s) + 6\text{H}^+(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{H}_2(g)$$

(a) Dry hydrogen gas is collected in a 250.0-mL flask at 22°C and 745 mm Hg. How many grams of hydrogen are in the flask?

(b) The hydrogen gas is transferred without loss from the 250.0-mL flask to a 100.0-mL flask at the same temperature (22°C). What is the pressure in the smaller flask?

(c) What is the density (in g/L) of the gas collected in part (a)?

(d) Suppose the hydrogen is collected over water in a 235-mL flask at 25°C. The total pressure in the flask is 756 mm Hg.

1. What is the partial pressure of the hydrogen gas?

2. What is the mass of the hydrogen gas?

3. What is the mole fraction of hydrogen in the wet gas?

(e) What mass of aluminum is required to generate 1.00 L of $H_2(g)$ at 25°C and 1.00 atm?

(f) How many liters of hydrogen at 25°C and 1.00 atm can be generated by adding 250.0 mL of 6.0 M HCl to an excess of aluminum foil?

(g) Compare the rate of effusion of H_2 to that of He.

(h) Compare the time required for an equal number of moles of H_2 and CO_2 to effuse out of identical pinholes.

(i) The average speed of a hydrogen molecule at 25°C is 1.92×10^3 m/s. What is the average speed of an ammonia molecule at that same temperature?

Answers

(a) **0.0204 g**
(b) **1.86×10^3 mm Hg**
(c) **0.0816 g/L**
(d) **(1) 732 mm Hg (2) 0.0187 g (3) 0.969**
(e) **0.735 g**
(f) **18 L**
(g) **1.41:1**
(h) **H_2 effuses 4.7 faster than CO_2**
(i) **661 m/s**

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

5-1 Measurements on Gases

1. A ten-gallon methane tank contains 1.243 mol of methane (CH_4) at 74°F. Express the volume of the tank in liters, the amount of methane in the tank in grams, and the temperature of the tank in Kelvin.

2. A 6.00-ft cylinder has a radius of 26 in. It contains 189 lb of helium at 25°C. Express the volume of the cylinder ($V = \pi r^2 h$) in liters, the amount of helium in moles, and the temperature in Kelvin.

3. Complete the following table of pressure conversions.

	mm Hg	atm	kPa	bar
(a)	396	_____	_____	_____
(b)	_____	1.15	_____	_____
(c)	_____	_____	97.1	_____
(d)	_____	_____	_____	1.00

4. Complete the following table of pressure conversions.

	mm Hg	atm	psi	kPa
(a)	_____	_____	_____	42.7
(b)	_____	_____	29.1	_____
(c)	_____	0.788	_____	_____
(d)	1216	_____	_____	_____

5-2 The Ideal Gas Law
5-3 Gas Law Calculations

5. A cylinder with a movable piston records a volume of 12.6 L when 3.0 mol of oxygen is added. The gas in the cylinder has a pressure of 5.83 atm. The cylinder develops a leak and the volume of the gas is now recorded to be 12.1 L at the same pressure. How many moles of oxygen are lost?

6. A tank is filled with gas to a pressure of 875 mm Hg at 25°C. The gas is transferred without loss to a tank twice the size of the original tank. If the pressure is to remain constant, at what temperature (in °C) should the tank be kept?

7. A sample of CO_2 gas at 22°C and 1.00 atm has a volume of 2.00 L. Determine the ratio of the original volume to the final volume when

(a) the pressure and amount of gas remain unchanged and the Celsius temperature is doubled.

(b) the pressure and amount of gas remain unchanged and the Kelvin temperature is doubled.

8. A sample of nitrogen gas has a pressure of 1.22 atm. If the amount of gas and the temperature are kept constant, what is the pressure if

(a) its volume is decreased by 38%?

(b) its volume is decreased to 38% of its original volume?

9. A bicycle owner's manual recommends that a tire have a gauge pressure of 73.0 psi at 75°F for a rider weighing 140 lbs. The bicycle is left overnight in the driveway, where the temperature in the tire is 27°F. What is the actual pressure in the tire? What is the gauge pressure? Gauge pressure is the pressure above atmospheric pressure (14.7 psi).

10. A tire is inflated to a gauge pressure of 28.0 psi at 71°F. Gauge pressure is the pressure above atmospheric pressure, which is 14.7 psi. After several hours of driving, the air in the tire has a temperature of 115°F. What is the gauge pressure of the air in the tire? What is the actual pressure of the air in the tire? Assume that the tire volume changes are negligible.

11. A 38.0-L gas tank at 35°C has nitrogen at a pressure of 4.65 atm. The contents of the tank are transferred without loss to an evacuated 55.0-L tank in a cold room where the temperature is 4°C. What is the pressure in the tank?

12. A sealed tank at room temperature, 25°C, has 22.0 g of CO_2. The gas has a pressure of 732 mm Hg. The tank is moved to a room kept at 12°C and an additional 10.0 g of CO_2 are added to the tank. What is the pressure in the tank? Assume no loss of gas when more CO_2 is added.

13. A balloon filled with helium has a volume of 1.28×10^3 L at sea level where the pressure is 0.998 atm and the temperature is 31°C. The balloon is taken to the top of a mountain where the pressure is 0.753 atm and the temperature is −25°C. What is the volume of the balloon at the top of the mountain?

14. A flask has 1.35 mol of hydrogen gas at 25°C and a pressure of 1.05 atm. Nitrogen gas is added to the flask at the same temperature until the pressure rises to 1.64 atm. How many moles of nitrogen gas are added?

15. A two-liter plastic bottle can withstand a pressure of 5 atm. Approximately 125 mL (about half a cup) of water (d = 1.00 g/mL) is poured into the flask. The bottle with water is placed in a water bath maintained at 101°C. Will the bottle explode? (Ignore the volume occupied by the water.)

16. A drum used to transport crude oil has a volume of 162 L. How many grams of water, as steam, are required to fill the drum at 1.00 atm and 108°C? When the temperature in the drum is decreased to 25°C, all the steam condenses. How many mL of water (d = 1.00 g/mL) can be collected?

17. A piece of dry ice ($CO_2(s)$) has a mass of 22.50 g. It is dropped into an evacuated 2.50-L flask. What is the pressure in the flask at −4°C?

18. A four-liter tank is filled with propane gas, C_3H_8. The mass of the tank filled with gas is 1236 g. The pressure in the tank is 2.68 atm. The temperature in the room is 37°C. The propane in the tank is used up under the same conditions of temperature and pressure. What is the mass of the empty tank?

19. Complete the following table for dinitrogen tetroxide gas.

	Pressure	Volume	Temperature	Moles	Grams
(a)	1.77 atm	4.98 L	43.1°C	_____	_____
(b)	673 mm Hg	488 mL	_____	0.783	_____
(c)	0.899 bar	_____	912°C	_____	6.25
(d)	_____	1.15 L	39°F	0.166	_____

20. Use the ideal gas law to complete the following table for propane (C_3H_8) gas.

	Pressure	Volume	Temperature	Moles	Grams
(a)	18.9 psi	0.886 L	22°C	_____	_____
(b)	633 mm Hg	1.993 L	_____	0.0844	_____
(c)	1.876 atm	_____	75°F	2.842	_____
(d)	_____	2244 mL	13°C	_____	47.25

21. Calculate the densities (in g/L) of the following gases at 78°F and 13.6 psi.

(a) xenon (b) methane (c) acetylene, C_2H_2

22. Calculate the densities (in grams per liter) of the following gases at 97°C and 755 mm Hg.

(a) hydrogen chloride (b) sulfur dioxide

(c) butane (C_4H_{10})

23. Helium-filled balloons rise in the air because the density of helium is less than the density of air.

(a) If air has an average molar mass of 29.0 g/mol, what is the density of air at 25°C and 770 mm Hg?

(b) What is the density of helium at the same temperature and pressure?

(c) Would a balloon filled with carbon dioxide at the same temperature and pressure rise?

24. Space probes to Mars have shown that its atmosphere consists mostly of carbon dioxide. The average temperature on the surface of Mars is −55°C with an average pressure of 0.00592 atm. Compare the density of CO_2 on Mars's surface with that on the earth's surface at 25°C and one atmosphere.

25. Cyclopropane mixed in the proper ratio with oxygen can be used as an anesthetic. At 755 mm Hg and 25°C, it has a density of 1.71 g/L.

(a) What is the molar mass of cyclopropane?

(b) Cyclopropane is made up of 85.7% C and 14.3% H. What is the molecular formula of cyclopropane?

26. Phosgene is a highly toxic gas made up of carbon, oxygen, and chlorine atoms. Its density at 1.05 atm and 25°C is 4.24 g/L.

(a) What is the molar mass of phosgene?

(b) Phosgene is made up of 12.1% C, 16.2% O, and 71.7% Cl. What is the molecular formula of phosgene?

27. The gas in the discharge cell of a laser contains (in mole percent) 11% CO_2, 5.3% N_2, and 84% He.

(a) What is the molar mass of this mixture?

(b) Calculate the density of this gas mixture at 32°C and 758 mm Hg.

(c) What is the ratio of the density of this gas to that of air (MM = 29.0 g/mol) at the same conditions?

28. Exhaled air contains 74.5% N_2, 15.7% O_2, 3.6% CO_2, and 6.2% H_2O (mole percent).

(a) Calculate the molar mass of exhaled air.

(b) Calculate the density of exhaled air at 37°C and 757 mm Hg and compare the value you obtained with that of ordinary air (MM = 29.0 g/mol) under the same conditions.

29. A 1.58-g sample of $C_2H_3X_3(g)$ has a volume of 297 mL at 769 mm Hg and 35°C. Identify the element X.

30. A 0.750-g sample of the gas PX_3 is in a sealed 542-mL bulb at 26°C and 1.00 atm pressure. Identify the element X and name the gas.

5-4 Stoichiometry of Gaseous Reactions

31. Nitrogen oxide is a pollutant commonly found in smokestack emissions. One way to remove it is to react it with ammonia.

$$4NH_3(g) + 6NO(g) \longrightarrow 5N_2(g) + 6H_2O(l)$$

How many liters of ammonia are required to change 12.8 L of nitrogen oxide to nitrogen gas? Assume 100% yield and that all gases are measured at the same temperature and pressure.

32. Nitrogen trifluoride gas reacts with steam to produce the gases HF, NO, and NO_2.

(a) Write a balanced equation for the reaction.

(b) What volume of nitrogen oxide is formed when 5.22 L of nitrogen trifluoride are made to react with 5.22 L of steam? Assume 100% yield and constant temperature and pressure conditions throughout the reaction.

33. Dichlorine oxide is used as bactericide to purify water. It is produced by the chlorination of sulfur dioxide gas.

$$SO_2(g) + 2Cl_2(g) \longrightarrow SOCl_2(l) + Cl_2O(g)$$

How many liters of Cl_2O can be produced by mixing 5.85 L of SO_2 and 9.00 L of Cl_2? How many liters of the reactant in excess are present after reaction is complete? Assume 100% yield and that all the gases are measured at the same temperature and pressure.

34. Titanium(III) chloride is used in the manufacture of polyethylene. It is produced by the reaction (at high temperatures) between $TiCl_4$ gas and H_2.

$$2TiCl_4(g) + H_2(g) \longrightarrow 2TiCl_3(s) + 2HCl(g)$$

Assume 100% yield and constant temperature and pressure.

(a) How many liters of HCl gas can be produced by mixing 3.72 L of $TiCl_4$ and 4.50 L of H_2?

(b) How many liters of reactant in excess are present after the reaction is complete?

35. Nitric acid can be prepared by bubbling dinitrogen pentoxide into water.

$$N_2O_5(g) + H_2O \longrightarrow 2H^+(aq) + 2NO_3^-(aq)$$

(a) How many moles of H^+ are obtained when 1.50 L of N_2O_5 at 25°C and 1.00 atm pressure is bubbled into water?

(b) The solution obtained in (a) after reaction is complete has a volume of 437 mL. What is the molarity of the nitric acid obtained?

36. Potassium peroxide is used to absorb the CO_2 produced by the people in a space vehicle.

$$2K_2O_2(s) + 2CO_2(g) \longrightarrow 2K_2CO_3(s) + O_2(g)$$

If a person at rest exhales 3.0 L of air per minute and CO_2 is 3.4% (by volume) of exhaled air, how many grams of K_2O_2 are needed per person for a five-day trip. Assume a temperature of 25° and 728 mm Hg pressure.

37. Hydrogen cyanide (HCN) is a poisonous gas. It can be formed by the following reaction:

$$H^+(aq) + NaCN(s) \longrightarrow HCN(g) + Na^+(aq)$$

What volume of 6.00 *M* HCl is required to react with an excess of NaCN to produce enough HCN to fill a room $12 \times 11 \times 9$ feet at a pressure of 0.987 atm and 72°F?

38. When hydrogen peroxide decomposes, oxygen is produced:

$$2H_2O_2(aq) \longrightarrow 2H_2O + O_2(g)$$

What volume of oxygen gas at 25°C and 1.00 atm is produced from the decomposition of 25.00 mL of a 30.0% (by mass) solution of hydrogen peroxide (d = 1.05 g/mL)?

39. Ammonium nitrate can be used as an effective explosive because it decomposes into a large number of gaseous products. At a sufficiently high temperature, ammonium nitrate decomposes into nitrogen, oxygen, and steam.

(**a**) Write a balanced net ionic equation for the decomposition of ammonium nitrate.

(**b**) If 2.00 kg of ammonium nitrate are sealed in a 50.0-L steel drum and heated to 745°C, what is the resulting pressure in the drum after decomposition? (Assume 100% decomposition.)

40. Acetone peroxide, $C_9H_{18}O_6(s)$, is a powerful but highly unstable explosive that does not contain nitrogen. It can pass undetected through scanners designed to detect the presence of nitrogen in explosives like TNT (trinitrotoluene, $C_7H_5N_3O_6$), or ammonium nitrate.

(**a**) Write a balanced equation for the combustion (burning in oxygen) of acetone peroxide producing steam and carbon dioxide.

(**b**) What pressure is generated in a 2.00-L bottle when 5.00 g of acetone peroxide is ignited to 555°C and burned in air? Assume 100% combustion.

5-5 Gas Mixtures: Partial Pressures and Mole Fractions

41. A gaseous mixture is made up of 10.6 g of cyclopropane (C_3H_6), 12.2 g of chloroform ($CHCl_3$), and 5.23 g of methane. What pressure is exerted by the mixture in a 78.0-L tank at 20°C (two significant figures)? Which gas has the highest partial pressure?

42. A certain laser uses a gas mixture consisting of 9.00 g HCl, 2.00 g H_2, and 165.0 g of Ne. What pressure is exerted by the mixture in a 75.0-L tank at 22°C? Which gas has the smallest partial pressure?

43. A sample of a smoke stack emission was collected into a 1.25-L tank at 752 mm Hg and analyzed. The analysis showed 92% CO_2, 3.6% NO, 1.2% SO_2, and 4.1% H_2O by mass. What is the partial pressure exerted by each gas?

44. The contents of a tank of natural gas at 1.20 atm is analyzed. The analysis showed the following mole percents: 88.6% CH_4, 8.9% C_2H_6, and 2.5% C_3H_8. What is the partial pressure of each gas in the tank?

45. A sample of oxygen collected over water at 25°C (vapor pressure H_2O = 23.8 mm Hg). The wet gas occupies a volume of 7.28 L at a total pressure of 1.25 bar. If all the water is removed, what volume will the dry oxygen occupy at a pressure of 1.10 atm and a temperature of 27°C?

46. Hydrogen gas generated in laboratory experiments is usually collected over water. It is called a "wet gas" when collected in this manner because it contains water vapor. A sample of "wet" hydrogen at 25°C fills a 125-mL flask at a pressure of 769 mm Hg. If all the water is removed by heating, what volume will the dry hydrogen occupy at a pressure of 722 mm Hg and a temperature of 37°C? (The vapor pressure of water at 25°C is 23.8 mm Hg.)

47. Consider two bulbs separated by a valve. Both bulbs are maintained at the same temperature. Assume that when the valve between the two bulbs is closed, the gases are sealed in their respective bulbs. When the valve is closed, the following data apply:

	Bulb A	Bulb B
Gas	**Ne**	**CO**
V	2.50 L	2.00 L
P	1.09 atm	0.773 atm

Assuming no temperature change, determine the final pressure inside the system after the valve connecting the two bulbs is opened. Ignore the volume of the tube connecting the two bulbs.

48. Follow the instructions of Problem 47 for the following set of bulbs.

	Bulb X	Bulb Y
Gas	**CO_2**	**CH_4**
V	3.00 L	6.00 L
P	1.25 atm	2.66 atm

49. When acetylene, C_2H_2, is burned in oxygen, carbon dioxide and steam are formed. A sample of acetylene with a volume of 7.50 L and a pressure of 1.00 atm is burned in excess oxygen at 225°C. The products are transferred without loss to a 10.0-L flask at the same temperature.

(**a**) Write a balanced equation for the reaction.

(**b**) What is the total pressure of the products in the 10.0-L flask?

(**c**) What is the partial pressure of each of the products in the flask?

50. When ammonium nitrate decomposes at 722°C, nitrogen, oxygen, and steam are produced. A 25.0-g sample of ammonium nitrate decomposes, and the products are collected at 125°C into an evacuated flask with a volume of 15.0 L.

(**a**) Write a balanced equation for the reaction.

(**b**) What is the total pressure in the collecting flask after decomposition is complete?

(c) What is the partial pressure of each product in the flask?

51. A sample of oxygen is collected over water at 22°C and 752 mm Hg in a 125-mL flask. The vapor pressure of water at 22°C is 19.8 mm Hg.

(a) What is the partial pressure of oxygen?
(b) How many moles of dry gas are collected?
(c) How many moles of wet gas are in the flask?
(d) If 0.0250 g of $N_2(g)$ are added to the flask at the same temperature, what is the partial pressure of nitrogen in the flask?
(e) What is the total pressure in the flask after nitrogen is added?

52. Nitrogen gas can be obtained by decomposing ammonium nitrate at high temperatures. The nitrogen gas is collected over water in a 500-mL (three significant figures) flask at 19°C. The ambient pressure is 745 mm Hg. (Vapor pressure of water at 19°C is 16.48 mm Hg.)

(a) What is the partial pressure of nitrogen?
(b) How many moles of water are there in the wet gas?
(c) How many moles of dry gas are collected?
(d) If 0.128 g of Ne are added to the flask at the same temperature, what is the partial pressure of neon in the flask?
(e) What is the total pressure after Ne is added?

5-6 Kinetic Theory of Gases

53. Rank the following gases

$$NO \qquad Ar \qquad N_2 \qquad N_2O_5$$

in order of

(a) increasing speed of effusion through a tiny opening.
(b) increasing time of effusion.

54. Rank the gases Xe, CH_4, F_2, and CH_2F_2 in order of

(a) increasing speed of effusion through a pinhole.
(b) increasing time of effusion.

55. What is the ratio of the rate of effusion of the most abundant gas, nitrogen, to the lightest gas, hydrogen?

56. A balloon filled with nitrogen gas has a small leak. Another balloon filled with hydrogen gas has an identical leak. How much faster will the hydrogen balloon deflate?

57. A gas effuses 1.55 times faster than propane (C_3H_8) at the same temperature and pressure.

(a) Is the gas heavier or lighter than propane?
(b) What is the molar mass of the gas?

58. A gas effuses through an opening one-fifth as fast as helium gas effuses through the same opening.

(a) Is the gas heavier than helium?
(b) What is the molar mass of the gas?

59. If 0.0129 mol of N_2O_4 effuses through a pinhole in a certain amount of time, how much NO would effuse in that same amount of time under the same conditions?

60. At a certain temperature it takes 11.2 s for 1.78×10^{-3} mol of NH_3 gas to effuse through a pinhole. Under the same conditions, how long will it take for the same amount of phosphine gas, PH_3, to effuse through the same pinhole?

61. At what temperature will a molecule of uranium hexafluoride, the densest gas known, have the same average speed as a molecule of the lightest gas, hydrogen, at 37°C?

62. Calculate the average speed of a

(a) chlorine molecule at −32°C.
(b) UF_6 molecule at room temperature (25°C).

5-7 Real Gases

63. The normal boiling points of acetylene (C_2H_2) and NO_2 are −84°C and 21°C, respectively.

(a) At 25°C and 1 atm, which gas would you expect to have a molar volume closer to the ideal value?
(b) If you want to reduce the deviations from ideal behavior, in what direction would you change the temperature? The pressure?

64. A sample of methane gas (CH_4) is at 50°C and 20 atm. Would you expect it to behave more or less ideally if

(a) the pressure were reduced to 1 atm?
(b) the temperature were reduced to −50°C?

65. Using Figure 5.15

(a) estimate the density of methane gas at 200 atm.
(b) compare the value obtained in (a) with that calculated from the ideal gas law.

66. Using Figure 5.15

(a) estimate the density of methane gas at 100 atm.
(b) compare the value obtained in (a) with that calculated from the ideal gas law.
(c) determine the pressure at which the calculated density and the actual density of methane will be the same.

Unclassified

67. When air pollution is high, ozone (O_3) contents can reach 0.60 ppm (i.e., 0.60 mol ozone per million mol air). How many molecules of ozone are present per liter of polluted air if the barometric pressure is 755 mm Hg and the temperature is 79°F?

68. Assume that an automobile burns octane, C_8H_{18} (d = 0.692 g/mL).

(a) Write a balanced equation for the combustion of octane to carbon dioxide and water.
(b) A car has a fuel efficiency of 22 mi/gal of octane. What volume of carbon dioxide at 25°C and one atmosphere pressure is generated by the combustion when that car goes on a 75-mile trip.

69. A mixture of 3.5 mol of Kr and 3.9 mol of He occupies a 10.00-L container at 300 K. Which gas has the larger

(a) average translational energy?
(b) partial pressure?
(c) mole fraction?
(d) effusion rate?

70. Given that 1.00 mol of neon and 1.00 mol of hydrogen chloride gas are in separate containers at the same temperature and pressure, calculate each of the following ratios.

(a) volume Ne/volume HCl (b) density Ne/density HCl
(c) average translational energy Ne/average translational energy HCl
(d) number of Ne atoms/number of HCl molecules

71. An intermediate reaction used in the production of nitrogen-containing fertilizers is that between ammonia and oxygen:

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

A 150.0-L reaction chamber is charged with reactants to the following partial pressures at 500°C: $P_{NH_3} = 1.3$ atm, $P_{O_2} = 1.5$ atm. What is the limiting reactant?

72. A student prepared 118.9 mL of CO_2 at a pressure of 758 mm Hg and a temperature of 22°C. He did this by adding 35.47 mL of a 0.1380 *M* solution of a strong acid (H^+) to Na_2CO_3.

$$Na_2CO_3(s) + 2H^+(aq) \longrightarrow 2Na^+(aq) + CO_2(g) + H_2O$$

Did the student use HCI or H_2SO_4 as the strong acid?

73. At 25°C and 380 mm Hg, the density of sulfur dioxide is 1.31 g/L. The rate of effusion of sulfur dioxide through an orifice is 4.48 mL/s. What is the density of a sample of gas that effuses through an identical orifice at the rate of 6.78 mL/s under the same conditions? What is the molar mass of the gas?

74. Glycine is an amino acid made up of carbon, hydrogen, oxygen, and nitrogen atoms. Combustion of a 0.2036-g sample gives 132.9 mL of CO_2 at 25°C and 1.00 atm and 0.122 g of water. What are the percentages of carbon and hydrogen in glycine? Another sample of glycine weighing 0.2500 g is treated in such a way that all the nitrogen atoms are converted to $N_2(g)$. This gas has a volume of 40.8 mL at 25°C and 1.00 atm. What is the percentage of nitrogen in glycine? What is the percentage of oxygen? What is the empirical formula of glycine?

Conceptual Questions

75. A 250.0-mL flask filled with nitrogen gas at 25°C and 1.10 atm is inverted into cold acetone. As the gas contracts, acetone is forced into the flask to maintain the same pressure of nitrogen. This required 88.7 mL of acetone. What is the final temperature of the nitrogen?

76. The Lamborghini Aventador engine has a 12-cylinder engine in which each cylinder has a volume of 542 cm^3. Each cylinder is full of air at 85°C and 1.00 atm.

(**a**) How many moles of oxygen are in each cylinder? (mole percent of O_2 in air = 21.0)

(**b**) Assume that the hydrocarbons in gasoline have an average molar mass of 1.0×10^2 g/mol and react with oxygen in a 1:12 mole ratio. How many grams of gasoline should be injected into the cylinder to react with the oxygen?

77. Consider two independent identical bulbs (A and B), each containing a gas. Bulb A has 2.00 moles of CH_4 and bulb B has 2.00 moles of SO_2. These bulbs have a valve that can open into a long tube that has no gas (a vacuum). The tubes for each bulb are identical in length.

(**a**) If both valves to bulbs A and B are opened simultaneously, which gas will reach the end of the tube first?

(**b**) If both gases are to reach the end of the tube simultaneously, how would you alter the contents of each bulb? (You may not alter the bulbs or the length of the tube.)

78. Consider two identical sealed steel tanks in a room maintained at a constant temperature. One tank (A) is filled with CO_2 , and the other (B) is filled with H_2 until the pressure gauges on both tanks register the same pressure.

(**a**) Which tank has the greater number of moles?

(**b**) Which gas has the higher density (g/L)?

(**c**) Which gas will take longer to effuse out of its tank?

(**d**) Which gas has a larger average translational energy?

(**e**) If one mole of helium is added to each tank, which gas (CO_2 or H_2) will have the larger partial pressure?

79. Consider three sealed tanks all at the same temperature, pressure, and volume.

Tank A contains SO_2 gas.
Tank B contains O_2 gas.
Tank C contains CH_4 gas.

Use **LT** (for "*is less than*"), **GT** (for "*is greater than*"), **EQ** (for "*is equal to*"), or **MI** (for "*more information required*") as answers to the blanks below.

(**a**) The mass of SO_2 in tank A _____ the mass of O_2 in tank B.

(**b**) The average translational energy of CH_4 in tank C _____ the average translational energy of SO_2 in tank A.

(**c**) It takes 20 s for all of the O_2 gas in tank B to effuse out of a pinhole in the tank. The time it takes for all of the SO_2 to effuse out of tank A from an identical pinhole _____ 40 s.

(**d**) The density of O_2 in tank B _____ the density of CH_4 in tank C.

(**e**) The temperature in tank A is increased from 150 K to 300 K. The temperature in tank B is kept at 150 K. The pressure in tank A is _____ half the pressure in tank B.

80. Consider two bulbs A and B, identical in volume and temperature. Bulb A contains 1.0 mol of N_2 and bulb B has 1.0 mol of NH_3. Both bulbs are connected by a tube with a valve that is closed.

(**a**) Which bulb has the higher pressure?

(**b**) Which bulb has the gas with the higher density?

(**c**) Which bulb has molecules with a higher average kinetic energy?

(**d**) Which bulb has a gas whose molecules move with a faster molecular speed?

(**e**) If the valve between the two bulbs is opened, how will the pressure change?

(**f**) If 2.0 mol of He are added while the valve is opened, what fraction of the total pressure will be due to helium?

81. Sketch a cylinder with ten molecules of helium (He) gas. The cylinder has a movable piston. Label this sketch *before*. Make an *after* sketch to represent

(**a**) a decrease in temperature at constant pressure.

(**b**) a decrease in pressure from 1000 mm Hg to 500 mm Hg at constant temperature.

(**c**) five molecules of H_2 gas added at constant temperature and pressure.

82. Tank A has SO_2 at 2 atm, whereas tank B has O_2 at 1 atm. Tanks A and B have the same volume. Compare the temperature (in K) in both tanks if

(**a**) tank A has twice as many moles of SO_2 as tank B has of O_2.

(**b**) tank A has the same number of moles of SO_2 as tank B has of O_2.

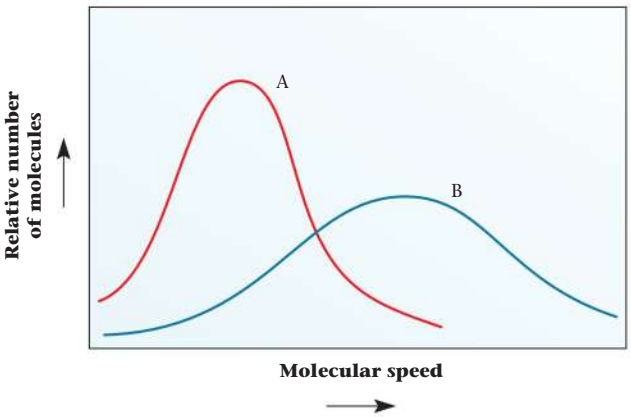
(**c**) tank A has twice as many grams of SO_2 as tank B has of O_2.

83. Two tanks (A and B) have the same volume and are kept at the same pressure. Compare the temperature in both tanks if

(**a**) tank A has 2.00 mol of methane and tank B has 2.00 mol of neon.

(**b**) tank A has 2.00 g of methane and tank B has 2.00 g of neon. (Try to do this without a calculator.)

84. The graph below shows the distribution of molecular speeds for helium and carbon dioxide at the same temperature.



(**a**) Which curve could represent the behavior of carbon dioxide?

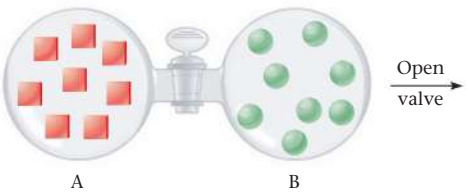
(**b**) Which curve represents the gas that would effuse more quickly?

(**c**) Which curve could represent the behavior of helium gas?

85. Consider the following sketch. Each square in bulb A represents a mole of atoms X. Each circle in bulb B represents a mole of atoms Y. The bulbs have the same volume, and the temperature is kept constant. When the valve is opened, atoms of X react with atoms of Y according to the following equation:

$$2X(g) + Y(g) \longrightarrow X_2Y(g)$$

The gaseous product is represented as □○□, and each □○□ represents one mole of product.

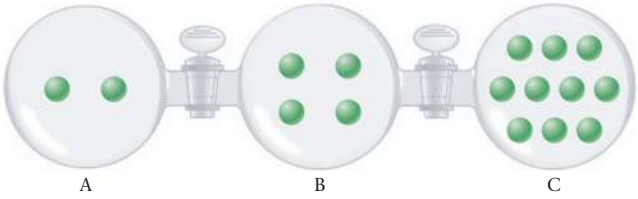


(**a**) If $P_A = 2.0$ atm, what is P_B before the valve is opened and the reaction is allowed to occur? What is $P_A + P_B$?

(**b**) Redraw the sketch to represent what happens after the valve is opened.

(**c**) What is P_A? What is P_B? What is $P_A + P_B$? Compare your answer with the answer in part (a).

86. The following figure shows three 1.00-L bulbs connected by valves. Each bulb contains argon gas with amounts proportional to the number of circles pictorially represented in the chamber. All three bulbs are maintained at the same temperature. Unless stated otherwise, assume that the valves connecting the bulbs are closed and seal the gases in their respective chambers. Assume also that the volume between each bulb is negligible.



(**a**) Which bulb has the highest pressure?

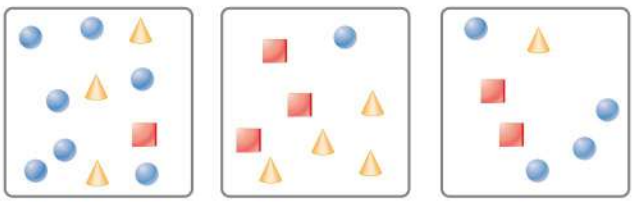
(**b**) If the pressure in bulb A is 0.500 atm, what is the pressure in bulb C?

(**c**) If the pressure in bulb A is 0.500 atm, what is the total pressure?

(**d**) If the pressure in bulb A is 0.500 atm, and the valve between bulbs A and B is opened, redraw the figure shown above to accurately represent the gas atoms in all three bulbs. What is $P_A + P_B + P_C$? Compare your answer in part (d) to that in part (c).

(**e**) Follow the instructions of part (d) but now open only the valve between bulbs B and C.

87. Consider three sealed steel tanks, labeled X, Y, and Z. Each tank has the same volume and the same temperature. In each tank, one mole of CH_4 is represented by a circle, one mole of oxygen by a square, and one mole of SO_2 by a triangle. Assume that no reaction takes place between these molecules.



(**a**) In which tank is the total pressure highest?

(**b**) In which tank is the partial pressure of SO_2 highest?

(**c**) In which tank is the mass of all three gases the same?

(**d**) Which tank has the heaviest contents?

Challenge Problems

88. Consider an ideal gas that exerts a pressure of 23.76 mm Hg at 25°C. Assuming n and V are held constant, what would its pressure be at 40°C? 70°C? 100°C? Compare the numbers you have just calculated with the vapor pressures of water at these temperatures. Can you suggest a reason why the two sets of numbers are so different?

89. Two 750-mL (three significant figures) tanks contain identical amounts of a gaseous mixture containing O_2, N_2, and CO_2. Each tank has a pressure of 1.38 atm and is kept at 25°C. The gas in the first tank is passed through a CO_2 absorber. After all the CO_2 is absorbed, the mass of the absorber increases by 0.114 g. All the nitrogen in the second tank is removed. The pressure in the tank without the nitrogen at 25°C is 1.11 atm. What is the composition (in mass percent) of the gaseous mixture in the tanks?

90. A tube 5.0 ft long is evacuated. Samples of NH_3 and HCl, at the same temperature and pressure, are introduced simultaneously through tiny openings at opposite ends of the tube. When the two gases meet, a white ring of $NH_4Cl(s)$ forms. How far from the end at which ammonia was introduced will the ring form?

91. Sulfur trioxide can be prepared by burning sulfur in oxygen.

$$2S(s) + 3O_2(g) \longrightarrow 2SO_3(g)$$

A 5.00-L flask containing 5.00 g of sulfur and oxygen at a pressure of 995 mm Hg and 25°C is heated. When the reaction is complete, the temperature in the flask is 138°C.

(**a**) What is the pressure of SO_3 in the flask?

(**b**) What is the total pressure in the flask?

(**c**) When water is added to SO_3, H_2SO_4 is formed. What is the molarity of the H_2SO_4 formed if 250.0 mL of water are added to the flask? (Assume that there is enough water to convert all the SO_3 to H_2SO_4.)

92. A 0.2500-g sample of an Al-Zn alloy reacts with HCl to form hydrogen gas:

$$Al(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + \tfrac{3}{2}H_2(g)$$
$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

The hydrogen produced has a volume of 0.147 L at 25°C and 755 mm Hg. What is the percentage of zinc in the alloy?

93. The buoyant force on a balloon is equal to the mass of air it displaces. The gravitational force on the balloon is equal to the sum of the masses of the balloon, the gas it contains, and the balloonist. If the balloon and the balloonist together weigh 168 kg, what would the diameter of a spherical hydrogen-filled balloon have to be (in meters) if the rig is to get off the ground at 22°C and 758 mm Hg? (Take $MM_{air} = 29.0$ g/mol.)

94. A mixture in which the mole ratio of hydrogen to oxygen is 2:1 is used to prepare water by the reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The total pressure in the container is 0.950 atm at 25°C before the reaction. What is the final pressure in the container at 125°C after the reaction, assuming an 88.0% yield and no volume change?