GENERAL CHEMISTRY

Principles and Modern Applications

TENTH EDITION

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6

Gases

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Gases

CONTENTS

Properties of Gases:

Gases

- expand to fill their containers
- assume the shapes of their containers.
- they diffuse into one another and mix in all proportions.
- we cannot see individual particles of a gas, although we can see the bulk gas if it is colored (Fig. 6-1).
- Some gases, such as hydrogen and methane, are combustible; whereas others, such as helium and neon, are chemically unreactive.

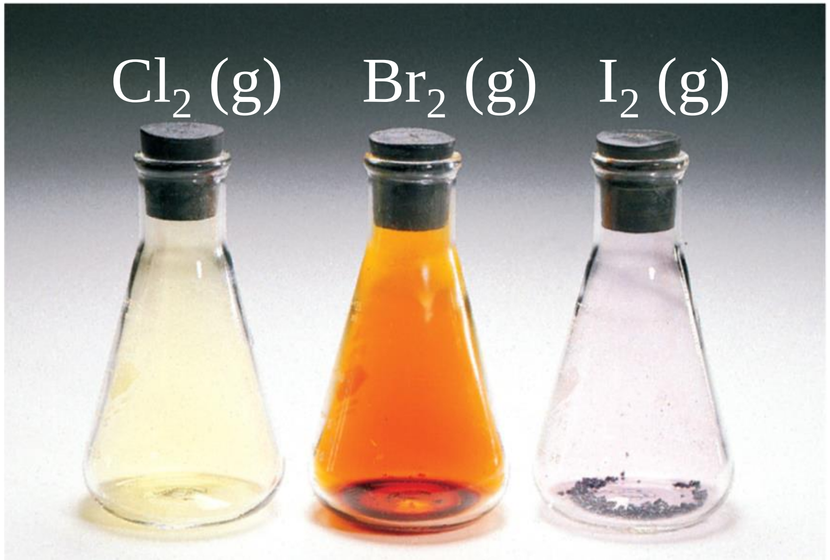


FIGURE 6-1

The gaseous state of three halogens (group 17)

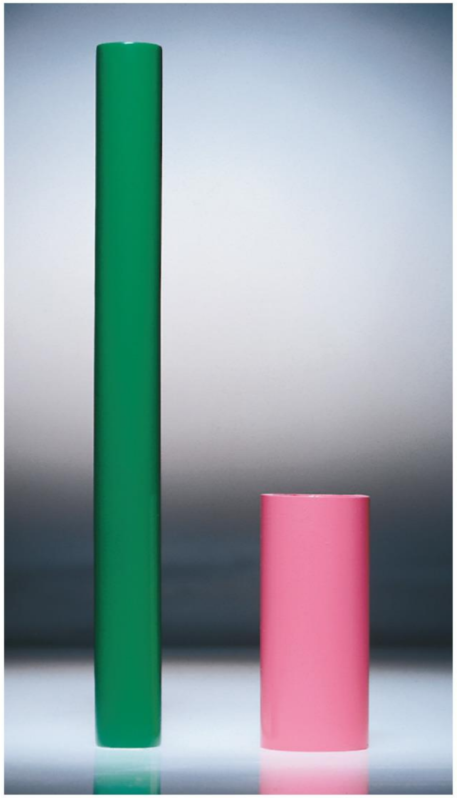
Physical Behaviour of Gases:

Four properties determine the physical behavior of a gas

1) the amount (in moles)
2) the volume,
3) temperature, and
4) pressure

If we know any three of these, we can usually calculate the value of the remaining one by using a mathematical equation called an equation of state (such as the ideal gas equation).

The concept of pressure:



Illustrating the pressure exerted by a solid

The two cylinders have the same mass and exert the same force on the supporting surface . F=gxm
The tall, thin one has a smaller area of contact, however, and exerts a greater pressure
P = F/A.

Pressure : force per unit area, that is, a force divided by the area over which the force is distributed.

Force

$$\text{Force (N)} = g\ (\text{m/s}^2) \times m\ (\text{kg})$$

Pressure

$$P\ (\text{Pa}) = \frac{F,\quad \text{Force (N)}}{A,\quad \text{Area (m}^2)}$$

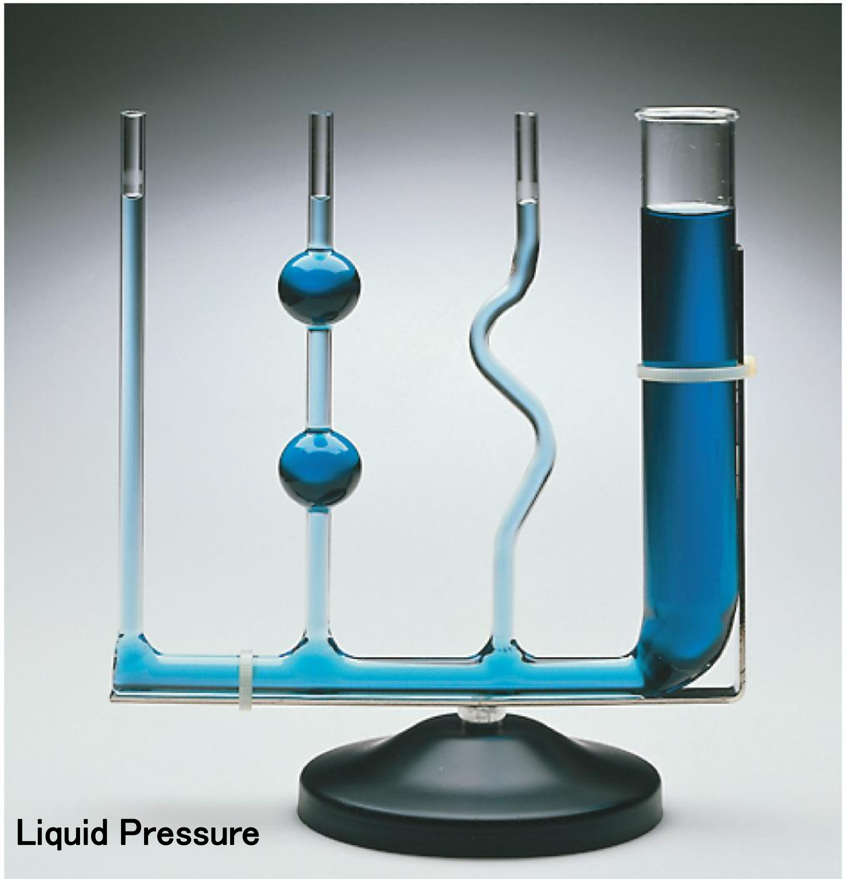
A pressure of one newton per square meter is defined as one pascal (Pa). kPa=kilopascal

Blaise Pascal (1623 - 1662), who studied pressure and its transmission through fluids- the basis of modern hydraulics.

Liquid pressure:

- It is difficult to measure the total force exerted by gas molecules,

- The pressure of a gas is usually measured indirectly, by comparing it with a liquid pressure.



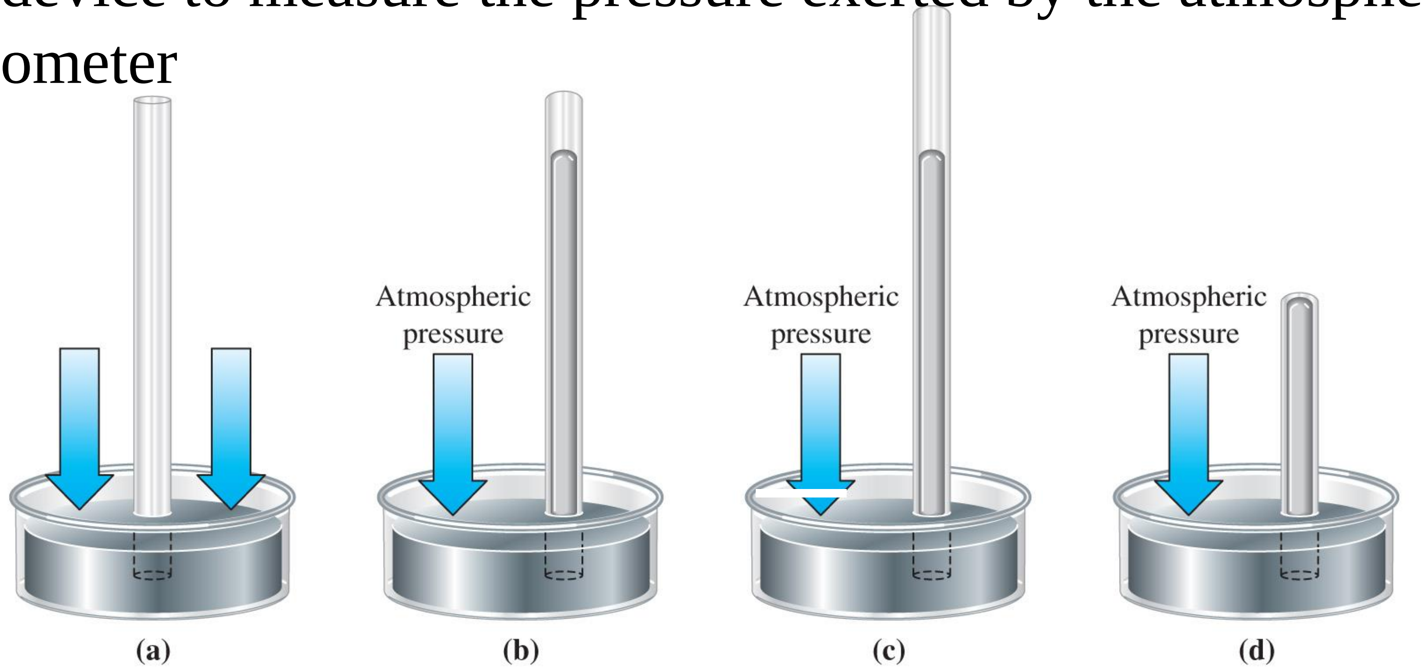
$$P\,(Pa) = \frac{F}{A} = \frac{W}{A} = \frac{g \times m}{A} = \frac{g \times V \times d}{A} = \frac{g \times h \times A \times d}{A} = g \times h \times d$$

liquid pressure is directly proportional to

▲- *the height of the liquid column and*
- *the liquid density*

Barometric Pressure: In 1643, Evangelista Torricelli

- A device to measure the pressure exerted by the atmosphere, Barometer



$$P = g \text{ x } h \text{ x } \delta = (9.80665 \text{ m s}^{-2})(0.760000 \text{ m})(1.35951\ 104 \text{ kg m}^{-3})$$
$$= 1.01325\text{x } 10^{5} \text{ kg m}^{-1} \text{ s}^{-2} = \text{Pa}$$

Standard Atmospheric Pressure=1.00 atm, 101.325 kPa, 1.01325 bar, 760 torr, ~760 mm Hg

Measurement of atmospheric pressure with a mercury barometer

EXAMPLE 6-1 Comparing Liquid Pressures

What is the height of a column of water that exerts the same pressure as a column of mercury 76.0 cm (760 mm) high?

Analyze

Equation (6.2) shows that, for a given liquid pressure, the column height is inversely proportional to the liquid density. The lower the liquid density, the greater the height of the liquid column. Mercury is 13.6 times as dense as water (13.6 g/cm^3 versus 1.00 g/cm^3). If columns of water and mercury exert the same pressure, then the column of water is 13.6 times as high as the column of mercury.

Solve

Although we have already reasoned out the answer, we can arrive at the same conclusion by applying equation (6.2) twice, and then setting the two pressures equal to each other. Equation (6.2) can be used to describe the pressure of the mercury column of known height and the pressure of the water column of unknown height. Then we can set the two pressures equal to each other.

$$\text{pressure of Hg column} = g \times h_{\text{Hg}} \times d_{\text{Hg}} = g \times 76.0 \text{ cm} \times 13.6 \text{ g/cm}^3$$

$$\text{pressure of H}_2\text{O column} = g \times h_{\text{H}_2\text{O}} \times d_{\text{H}_2\text{O}} = g \times h_{\text{H}_2\text{O}} \times 1.00 \text{ g/cm}^3$$

$$\cancel{g} \times h_{\text{H}_2\text{O}} \times 1.00 \text{ g/cm}^3 = \cancel{g} \times 76.0 \text{ cm} \times 13.6 \text{ g/cm}^3$$

$$h_{\text{H}_2\text{O}} = 76.0 \text{ cm} \times \frac{13.6 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} = 1.03 \times 10^3 \text{ cm} = 10.3 \text{ m}$$

Assess

We can think about equation (6.2) in another way. For a column of liquid of fixed height, the greater the density of the liquid, the greater the pressure exerted by the liquid column. A column of mercury that is 760 mm high will exert a pressure 13.6 times as great as a column of water that is 760 mm high.

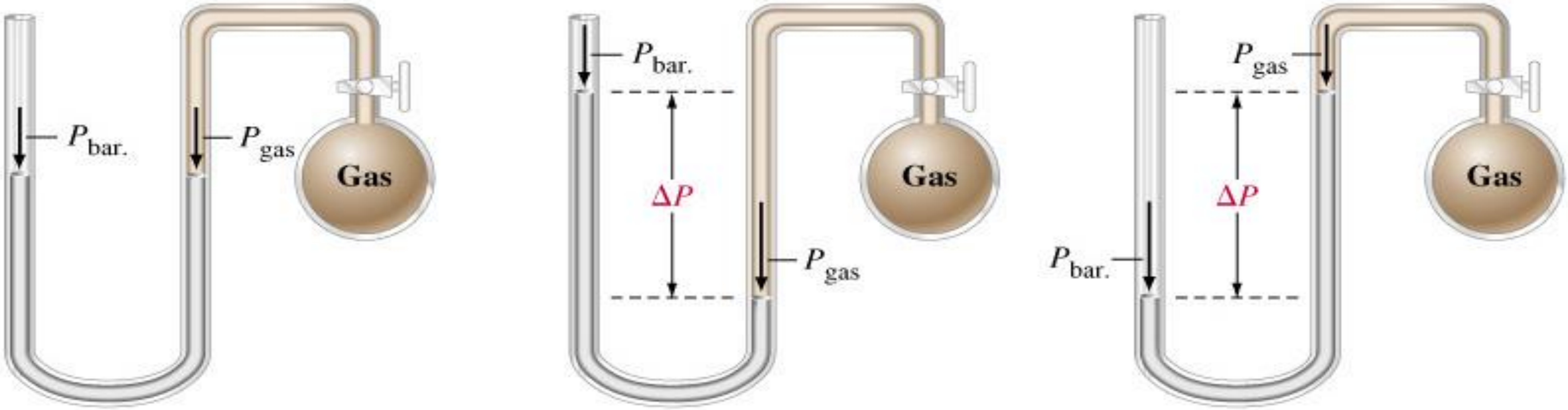
PRACTICE EXAMPLE A: A barometer is filled with diethylene glycol ($d = 1.118 \text{ g/cm}^3$). The liquid height is found to be 9.25 m. What is the barometric (atmospheric) pressure expressed in millimeters of mercury?

PRACTICE EXAMPLE B: A barometer is filled with triethylene glycol. The liquid height is found to be 9.14 m when the atmospheric pressure is 757 mmHg. What is the density of triethylene glycol?

Manometers

Difficult to place a barometer inside a gas to be measured.

Manometers compare gas pressure and barometric pressure.



$P_{gas} = P_{bar.}$

(a) Gas pressure equal to barometric pressure

$P_{gas} = P_{bar.} + \Delta P$
$(\Delta P > 0)$

(b) Gas pressure greater than barometric pressure

$P_{gas} = P_{bar.} + \Delta P$
$(\Delta P < 0)$

(c) Gas pressure less than barometric pressure

EXAMPLE 6-2 Using a Manometer to Measure Gas Pressure

When the manometer in Figure 6-5(c) is filled with liquid mercury ($d = 13.6\ \text{g/cm}^3$), the barometric pressure is 748.2 mmHg, and the difference in mercury levels is 8.6 mmHg. What is the gas pressure P_{gas}?

Analyze

We must first establish which is greater: the barometric pressure or the gas pressure. In Figure 6-5(c), the barometric pressure forces liquid mercury down the tube toward the gas sample. The barometric pressure is greater than the gas pressure. Thus, $\Delta P = P_{\text{gas}} - P_{\text{bar.}} < 0$.

Solve

The gas pressure is less than the barometric pressure. Therefore, we subtract 8.6 mmHg from the barometric pressure to obtain the gas pressure.

$$P_{\text{gas}} = P_{\text{bar.}} + \Delta P = 748.2\ \text{mmHg} - 8.6\ \text{mmHg} = 739.6\ \text{mmHg}$$

Assess

Because all pressures are expressed in millimeters of mercury, the pressure difference (ΔP) is numerically equal to the difference in mercury levels. Thus, the density of mercury does not enter into the calculation.

PRACTICE EXAMPLE A: Suppose that the mercury level in Example 6-2 is 7.8 mm higher in the arm open to the atmosphere than in the closed arm. What would be the value of P_{gas}?

PRACTICE EXAMPLE B: Suppose $P_{\text{bar.}}$ and P_{gas} are those described in Example 6-2, but the manometer is filled with liquid glycerol ($d = 1.26\ \text{g/cm}^3$) instead of mercury. What would be the difference in the two levels of the liquid?

EXAMPLE 6-3 Using SI Units of Pressure

The 1.000 kg red cylinder in Figure 6-2 has a diameter of 4.10 cm. What pressure, expressed in Torr, does this cylinder exert on the surface beneath it?

Analyze

We must apply equation (6.2). It is best to use SI units and obtain a pressure in SI units (Pa), and then convert the pressure to the required units (Torr).

Solve

Expression (6.1) defines pressure as force divided by area.

$$P = \frac{F}{A}$$

The force exerted by the cylinder is its weight.

$$F = W = m \times g$$

The mass is 1.000 kg, and g (the acceleration due to gravity) is $9.81\ \mathrm{m\,s^{-2}}$. The product of these two terms is the force in newtons.

$$F = m \times g = 1.000\ \mathrm{kg} \times 9.81\ \mathrm{m\,s^{-2}} = 9.81\ \mathrm{N}$$

The force is exerted on the area of contact between the cylinder and the underlying surface. This circular area is calculated by using the radius of the cylinder—one-half the 4.10 cm diameter, expressed in meters.

$$A = \pi r^2 = 3.1416 \times \left(2.05\ \mathrm{cm} \times \frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)^2 = 1.32 \times 10^{-3}\ \mathrm{m}^2$$

The force divided by the area (in square meters) gives the pressure in pascals.

$$P = \frac{F}{A} = \frac{9.81\ \mathrm{N}}{1.32 \times 10^{-3}\ \mathrm{m}^2} = 7.43 \times 10^3\ \mathrm{Pa}$$

The relationship between the units Torr and pascal (Table 6.1) is used for the final conversion.

$$P = 7.43 \times 10^3\ \mathrm{Pa} \times \frac{760\ \mathrm{Torr}}{101{,}325\ \mathrm{Pa}} = 55.7\ \mathrm{Torr}$$

Assess

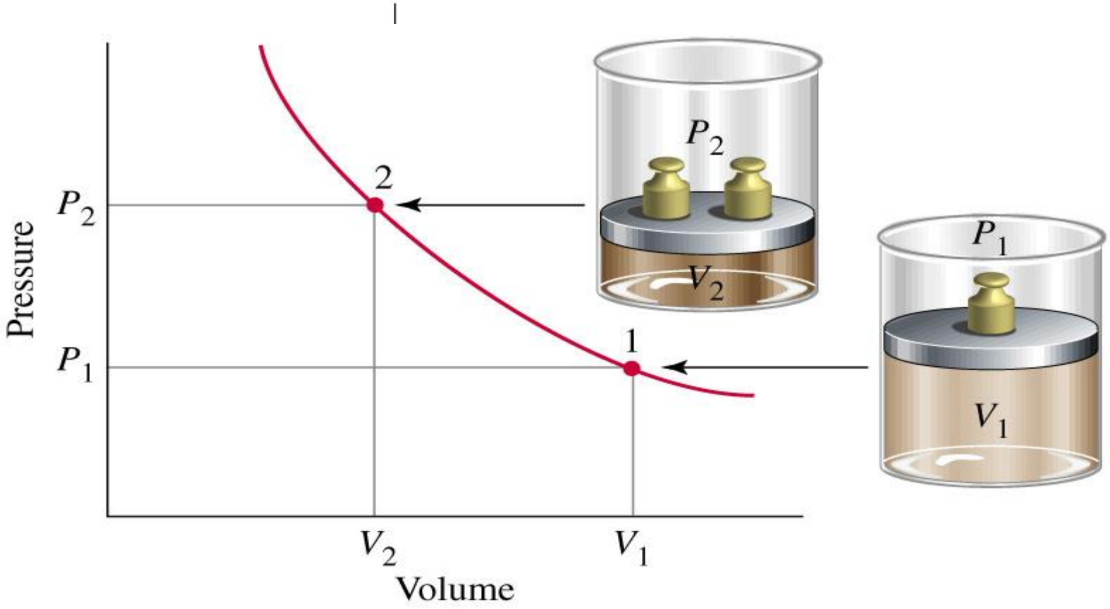
It's difficult to tell at a glance whether this is a reasonable result. To check our result, let us focus instead on a cylindrical column of mercury that is 55.7 mm high and has a diameter of 4.10 cm. This column of mercury also exerts a pressure of 55.7 mmHg = 55.7 Torr. The volume of mercury in this column is $V = \pi r^2 h = \pi \times (2.05\ \mathrm{cm})^2$

6-2 Simple Gas Laws

Boyle 1662

$$P \alpha \frac{1}{V}$$

PV = constant



6-2 CONCEPT ASSESSMENT

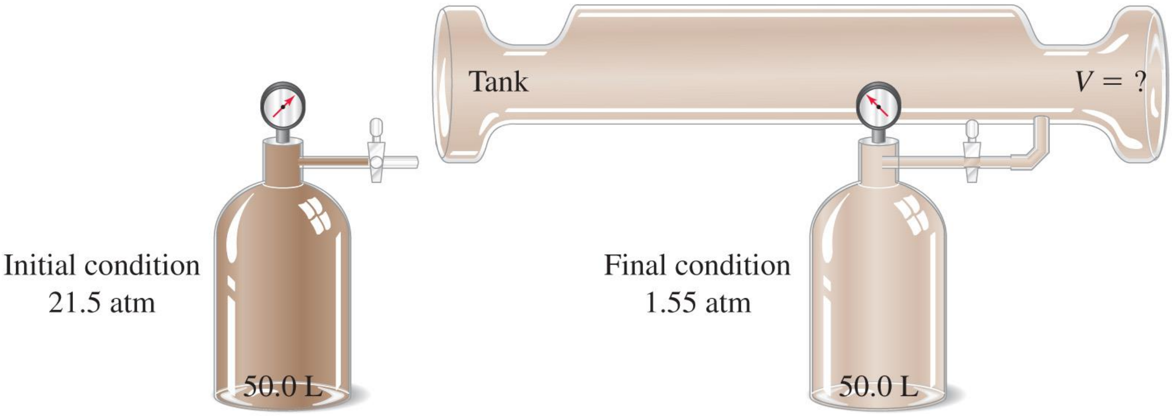
A 50.0 L cylinder contains nitrogen gas at a pressure of 21.5 atm. The contents of the cylinder are emptied into an evacuated tank of unknown volume. If the final pressure in the tank is 1.55 atm, then what is the volume of the tank?

(a) (21.5/1.55) x 50.0 L

(b) (1.55/21.5) x 50.0 L

(b) (c) v21./(1.55 x 50.0) L

(d) (1.55/(21.5 x 50.0) L

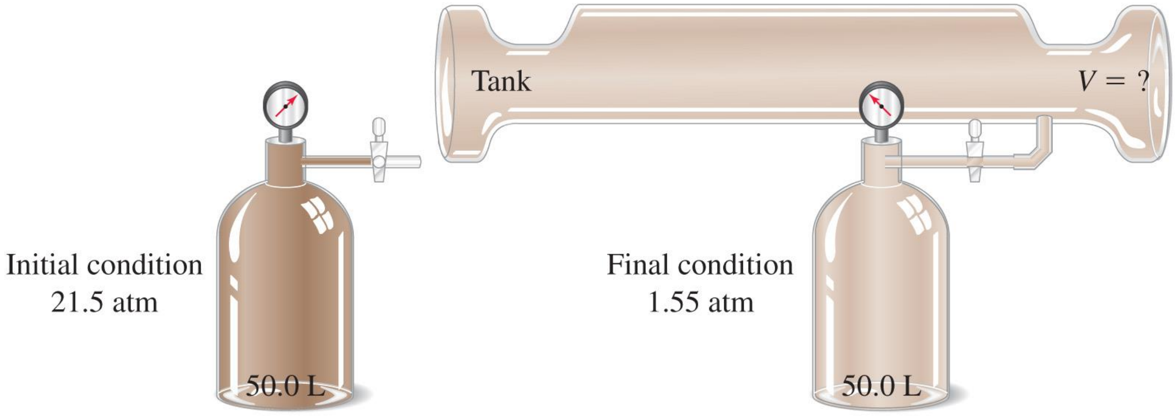


6-2 CONCEPT ASSESSMENT (CONTINUED)

Use Boyle's Law

$P_1V_1 = P_2V_2 \quad V_2 = \dfrac{P_1V_1}{P_2}$ therefore (a) is the answer

Calculation shows that $V_{tank} = 644$ L

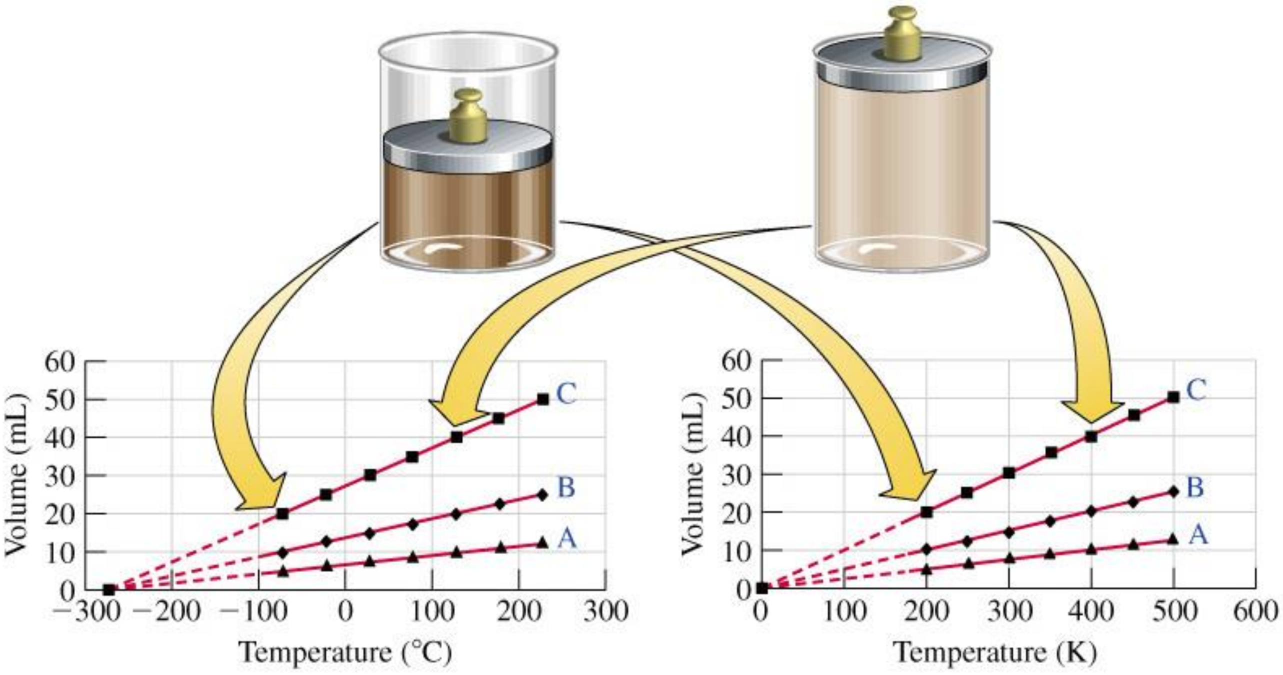


Charles's Law

Charles 1787, Gay-Lussac 1802

$V \alpha T$

$V = b T$



Three different gases show this behavior with temperature.
Temperature at which the volume of a hypothetical gas becomes 0 is the *absolute zero* of temperature.
The hypothetical gas has mass, but no volume, and does not condense into a liquid or solid.

Standard Temperature and Pressure

- Gas properties depend on conditions.
- IUPAC defines standard conditions of temperature and pressure (STP).

$$P = 1 \text{ Bar} = 10^5 \text{ Pa}$$
$$T = 0^\circ \text{ C} = 273.15 \text{ K}$$

1.00 atm = 760 mm Hg = 760 torr = 101.325 kPa = 1.01325 bar

= 1013.25 mbar

Avogadro’s Law

Gay-Lussac 1808

Small volumes of gases react in the ratio of small whole numbers.

Avogadro 1811

1. Equal volumes of different gases compared at the same temperature and pressure contain equal numbers of molecules.
2. Equal numbers of molecules of different gases compared at the same temperature and pressure occupy equal volumes.

At a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas.

At fixed T and P

$V \propto n$ or $V = c\,n$

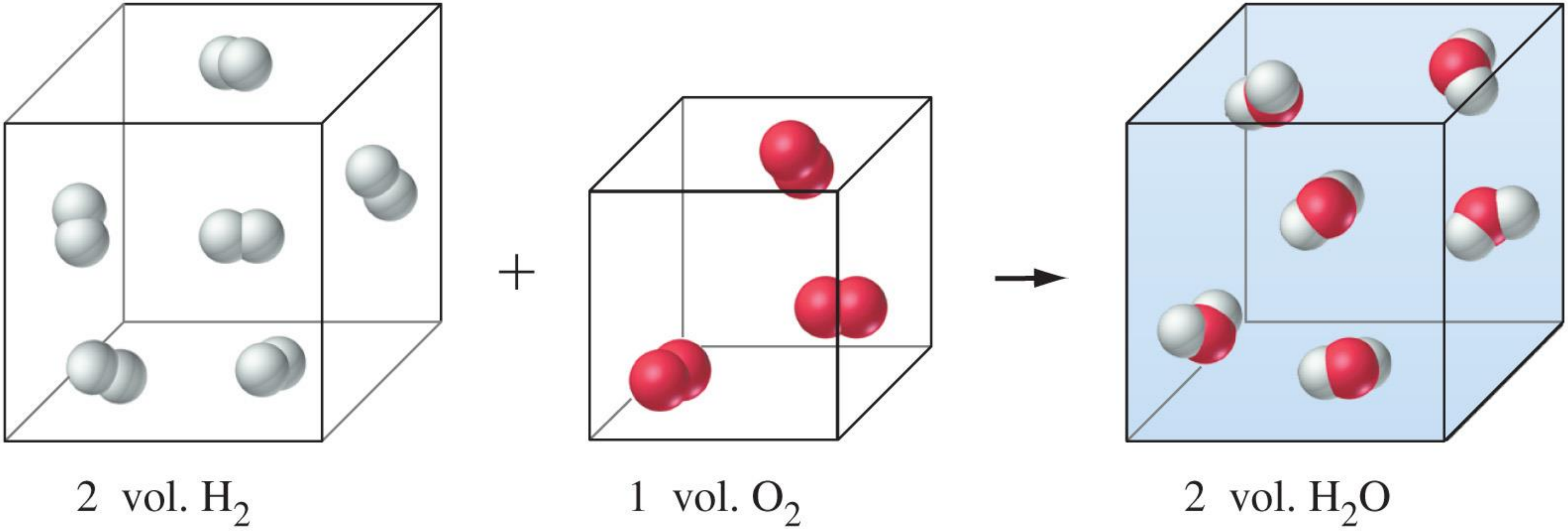
1 mol gas

= 22.414 L (at 0 C°, 1 atm)

= 22.711 L (at STP)

▲ FIGURE 6-9

Molar volume of a gas visualized



▲ FIGURE 6-8

Formation of Water – actual observation and Avogadro' s hypothesis

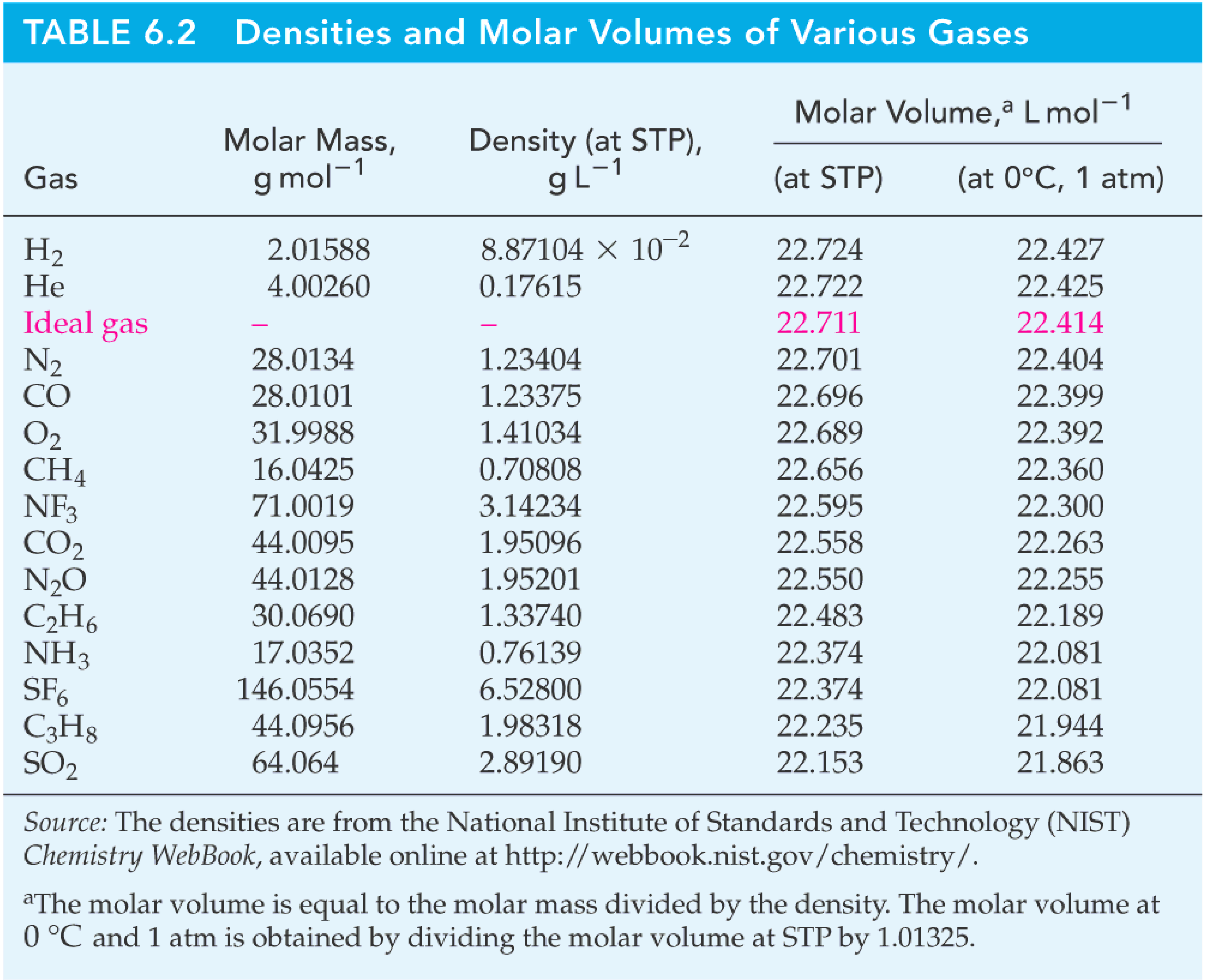


TABLE 6.2 Densities and Molar Volumes of Various Gases

Gas	Molar Mass, g mol^{-1}	Density (at STP), g L^{-1}	Molar Volume,[a] L mol^{-1}	
			(at STP)	(at 0°C, 1 atm)
H_2	2.01588	8.87104×10^{-2}	22.724	22.427
He	4.00260	0.17615	22.722	22.425
Ideal gas	–	–	22.711	22.414
N_2	28.0134	1.23404	22.701	22.404
CO	28.0101	1.23375	22.696	22.399
O_2	31.9988	1.41034	22.689	22.392
CH_4	16.0425	0.70808	22.656	22.360
NF_3	71.0019	3.14234	22.595	22.300
CO_2	44.0095	1.95096	22.558	22.263
N_2O	44.0128	1.95201	22.550	22.255
C_2H_6	30.0690	1.33740	22.483	22.189
NH_3	17.0352	0.76139	22.374	22.081
SF_6	146.0554	6.52800	22.374	22.081
C_3H_8	44.0956	1.98318	22.235	21.944
SO_2	64.064	2.89190	22.153	21.863

Source: The densities are from the National Institute of Standards and Technology (NIST) *Chemistry WebBook*, available online at http://webbook.nist.gov/chemistry/.

[a] The molar volume is equal to the molar mass divided by the density. The molar volume at 0 °C and 1 atm is obtained by dividing the molar volume at STP by 1.01325.

6-3 Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

$$\left.\begin{array}{ll} \text{Boyle's law} & V \propto 1/P \\ \text{Charles's law} & V \propto T \\ \text{Avogadro's law} & V \propto n \end{array}\right\} \quad V \propto \frac{nT}{P}$$

The Ideal Gas Equation

$$PV = nRT$$

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

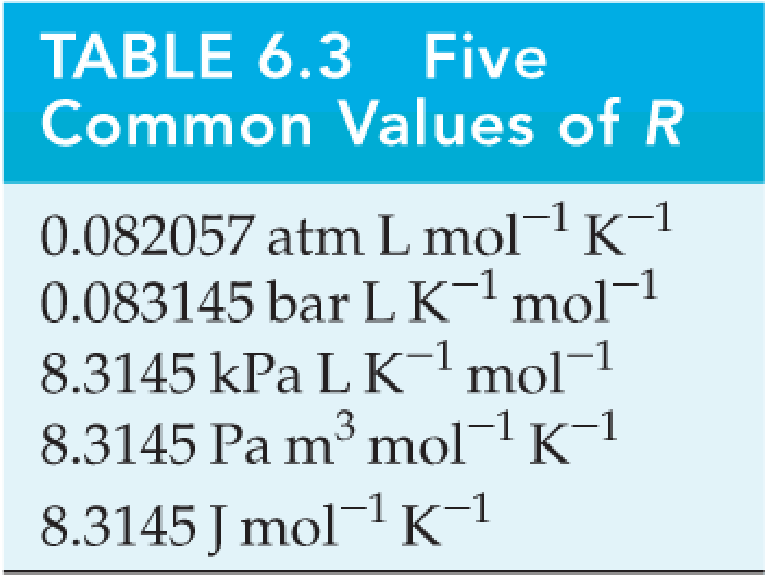
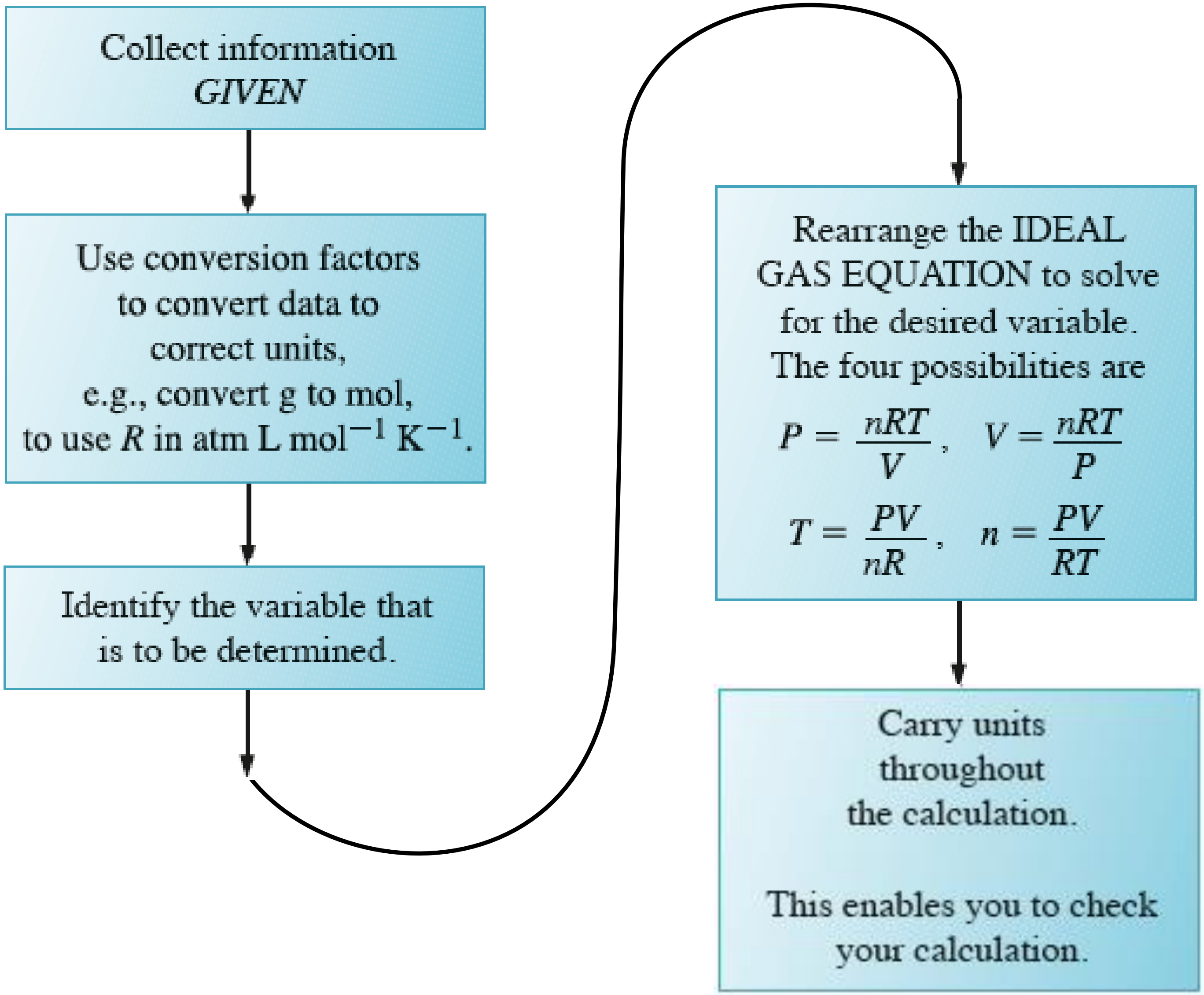


TABLE 6.3 Five Common Values of *R*

0.082057 atm L mol^{-1} K^{-1}
0.083145 bar L K^{-1} mol^{-1}
8.3145 kPa L K^{-1} mol^{-1}
8.3145 Pa m^3 mol^{-1} K^{-1}
8.3145 J mol^{-1} K^{-1}

Applying the ideal gas equation



Collect information *GIVEN*

Use conversion factors to convert data to correct units, e.g., convert g to mol, to use R in atm L mol^{-1} K^{-1}.

Identify the variable that is to be determined.

Rearrange the IDEAL GAS EQUATION to solve for the desired variable. The four possibilities are

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

$$T = \frac{PV}{nR}, \quad n = \frac{PV}{RT}$$

Carry units throughout the calculation.

This enables you to check your calculation.

The General Gas Equation

$$R = \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

If we hold the amount and volume constant:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

EXAMPLE 6-4 Calculating a Gas Volume with the Ideal Gas Equation

What is the volume occupied by 13.7 g $Cl_2(g)$ at 45 °C and 745 mmHg?

Analyze

This is a relatively straightforward application of the ideal gas equation. We are given an amount of gas (in grams), a pressure (in mmHg), and a temperature (in °C). Before using the ideal gas equation, we must express the amount in moles, the pressure in atmospheres, and the temperature in Kelvin. Include units throughout the calculation to ensure that the final result has acceptable units.

Solve

$$
\begin{aligned}
P &= 745\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.980\ \text{atm} \\
V &= ? \\
n &= 13.7\ \text{g}\ \text{Cl}_2 \times \frac{1\ \text{mol Cl}_2}{70.91\ \text{g Cl}_2} = 0.193\ \text{mol Cl}_2 \\
R &= 0.08206\ \text{atm L mol}^{-1}\ \text{K}^{-1} \\
T &= 45\ ^\circ\text{C} + 273 = 318\ \text{K}
\end{aligned}
$$

Divide both sides of the ideal gas equation by P to solve for V.

$$\frac{\cancel{P}V}{\cancel{P}} = \frac{nRT}{P} \quad \text{and} \quad V = \frac{nRT}{P}$$

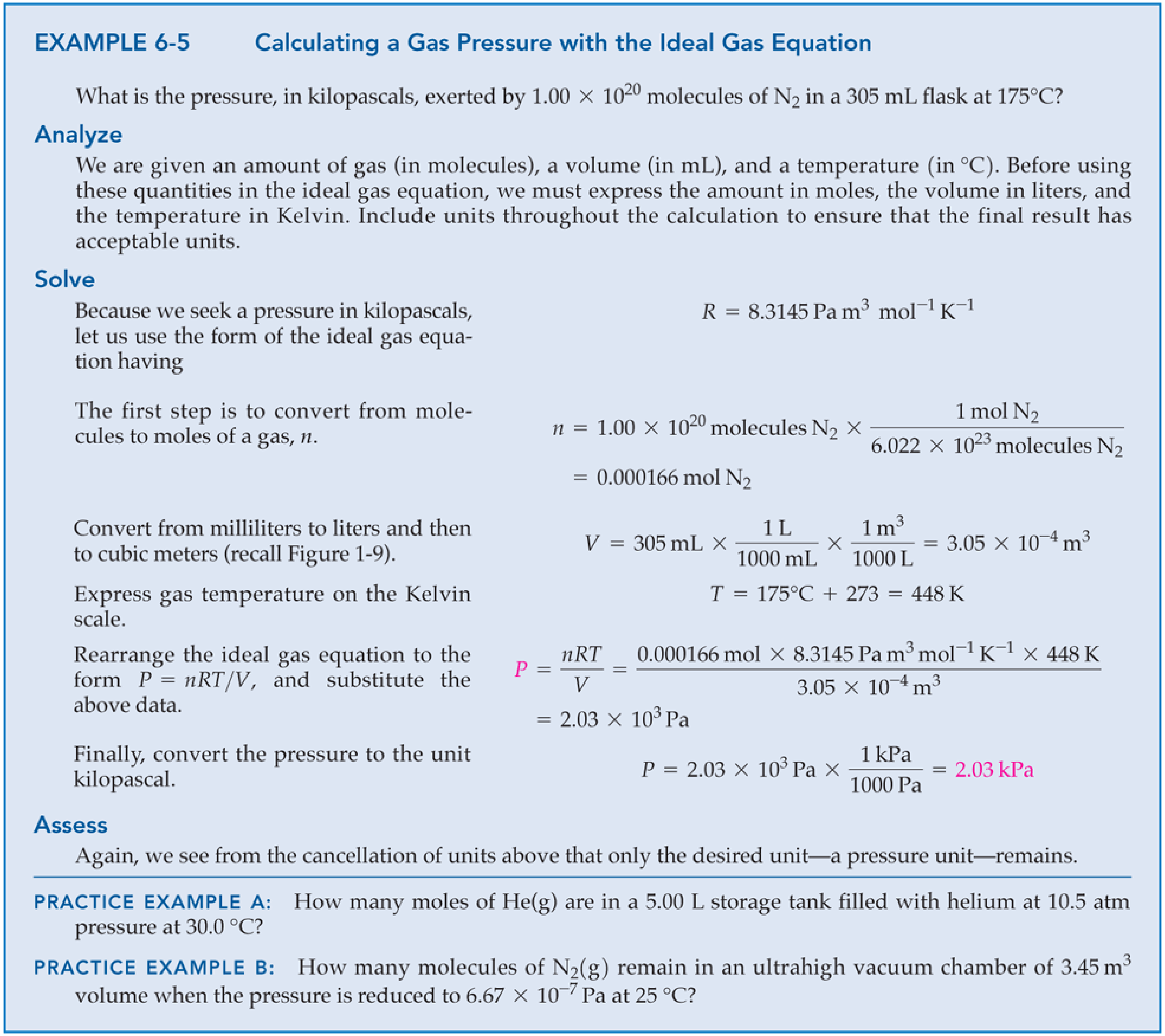
$$V = \frac{nRT}{P} = \frac{0.193\ \cancel{\text{mol}} \times 0.08206\ \cancel{\text{atm}}\ \text{L}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 318\ \cancel{\text{K}}}{0.980\ \cancel{\text{atm}}} = 5.14\ \text{L}$$

Assess

A useful check of the calculated result is to make certain the units cancel properly. In the setup above, all units cancel except for L, a unit of volume. Keep in mind that when canceling units, such a unit as mol^{-1} is the same as 1/mol. Thus, $\text{mol} \times \text{mol}^{-1} = 1$ and $\text{K} \times \text{K}^{-1} = 1$.

PRACTICE EXAMPLE A: What is the volume occupied by 20.2 g $NH_3(g)$ at −25°C and 752 mmHg?

PRACTICE EXAMPLE B: At what temperature will a 13.7 g Cl_2 sample exert a pressure of 0.993 bar when confined in a 7.50 L container?



EXAMPLE 6-5 Calculating a Gas Pressure with the Ideal Gas Equation

What is the pressure, in kilopascals, exerted by 1.00×10^{20} molecules of N_2 in a 305 mL flask at 175°C?

Analyze

We are given an amount of gas (in molecules), a volume (in mL), and a temperature (in °C). Before using these quantities in the ideal gas equation, we must express the amount in moles, the volume in liters, and the temperature in Kelvin. Include units throughout the calculation to ensure that the final result has acceptable units.

Solve

Because we seek a pressure in kilopascals, let us use the form of the ideal gas equation having

$$R = 8.3145\ \text{Pa m}^3\ \text{mol}^{-1}\ \text{K}^{-1}$$

The first step is to convert from molecules to moles of a gas, n.

$$n = 1.00 \times 10^{20}\ \text{molecules N}_2 \times \frac{1\ \text{mol N}_2}{6.022 \times 10^{23}\ \text{molecules N}_2}$$
$$= 0.000166\ \text{mol N}_2$$

Convert from milliliters to liters and then to cubic meters (recall Figure 1-9).

$$V = 305\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{1\ \text{m}^3}{1000\ \text{L}} = 3.05 \times 10^{-4}\ \text{m}^3$$

Express gas temperature on the Kelvin scale.

$$T = 175°\text{C} + 273 = 448\ \text{K}$$

Rearrange the ideal gas equation to the form $P = nRT/V$, and substitute the above data.

$$P = \frac{nRT}{V} = \frac{0.000166\ \text{mol} \times 8.3145\ \text{Pa m}^3\ \text{mol}^{-1}\ \text{K}^{-1} \times 448\ \text{K}}{3.05 \times 10^{-4}\ \text{m}^3}$$
$$= 2.03 \times 10^3\ \text{Pa}$$

Finally, convert the pressure to the unit kilopascal.

$$P = 2.03 \times 10^3\ \text{Pa} \times \frac{1\ \text{kPa}}{1000\ \text{Pa}} = 2.03\ \text{kPa}$$

Assess

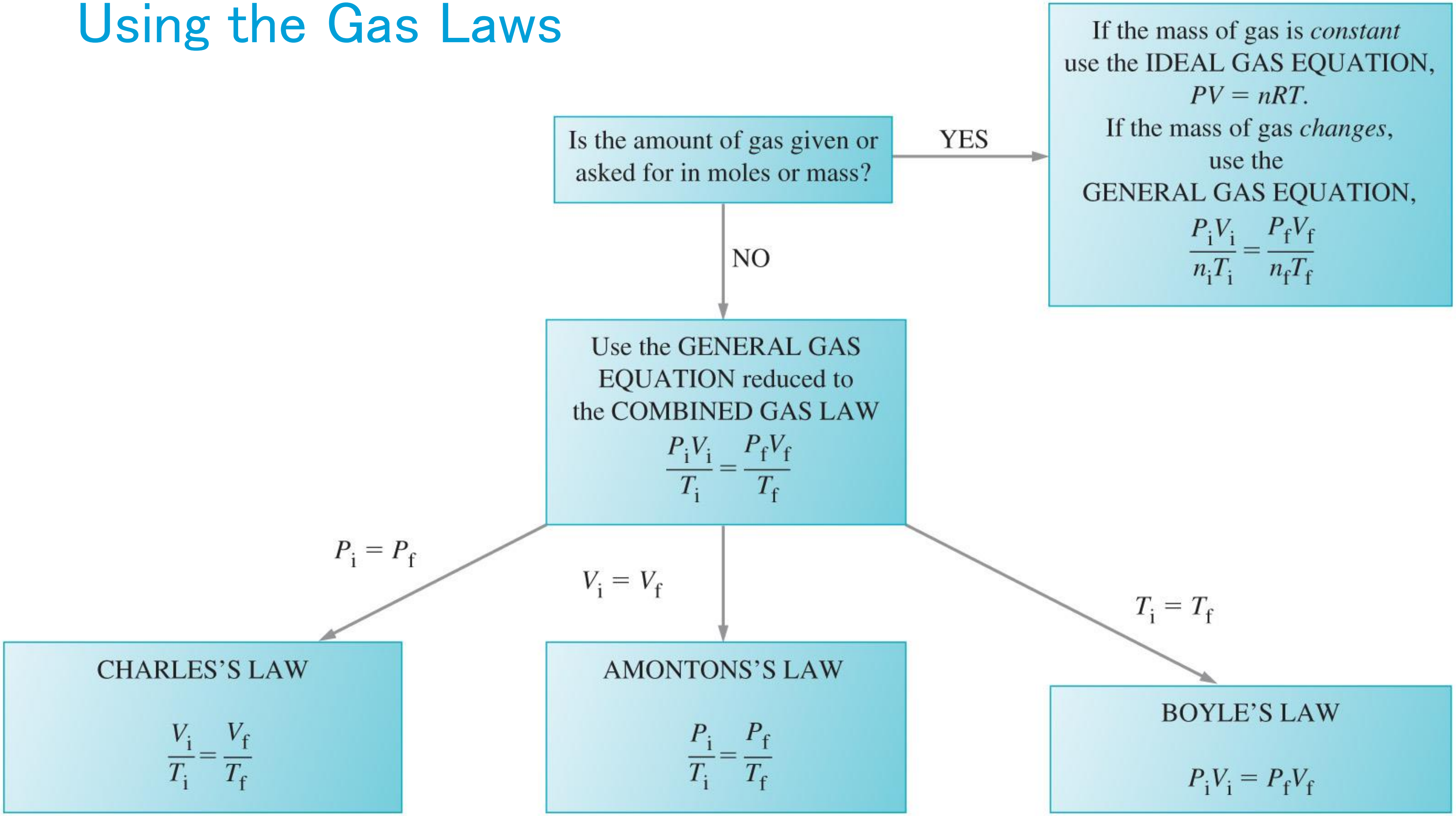
Again, we see from the cancellation of units above that only the desired unit—a pressure unit—remains.

PRACTICE EXAMPLE A: How many moles of He(g) are in a 5.00 L storage tank filled with helium at 10.5 atm pressure at 30.0 °C?

PRACTICE EXAMPLE B: How many molecules of $N_2(g)$ remain in an ultrahigh vacuum chamber of $3.45\ \text{m}^3$ volume when the pressure is reduced to 6.67×10^{-7} Pa at 25 °C?

anada Inc.

Using the Gas Laws



Is the amount of gas given or asked for in moles or mass?

YES

If the mass of gas is *constant* use the IDEAL GAS EQUATION,

$$PV = nRT.$$

If the mass of gas *changes*, use the GENERAL GAS EQUATION,

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$

NO

Use the GENERAL GAS EQUATION reduced to the COMBINED GAS LAW

$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$$

$P_i = P_f$

CHARLES'S LAW

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

$V_i = V_f$

AMONTONS'S LAW

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

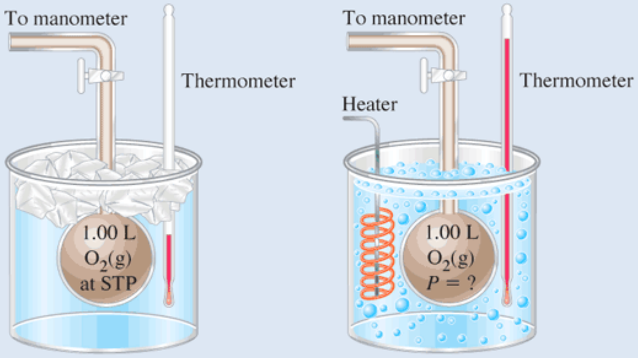
$T_i = T_f$

BOYLE'S LAW

$$P_iV_i = P_fV_f$$

EXAMPLE 6-6 Applying the General Gas Equation

The situation pictured in Figure 6-10(a) is changed to that in Figure 6-10(b). What is the gas pressure in Figure 6-10(b)?



(a) Ice bath **(b)** Boiling water

▲ FIGURE 6-10
Pressure of a gas as a function of temperature—Example 6-6 visualized
The amount of gas and volume are held constant. **(a)** 1.00 L $O_2(g)$ at STP; **(b)** 1.00 L $O_2(g)$ at 100 °C.

Analyze

Identify the quantities in the general gas equation that remain constant. Cancel out these quantities and solve the equation that remains.

Solve

In this case, the amount of O_2 is constant ($n_i = n_f$) and the volume is constant ($V_i = V_f$).

$$\frac{P_i \cancel{V_i}}{\cancel{n_i} T_i} = \frac{P_f \cancel{V_f}}{\cancel{n_f} T_f} \quad \text{and} \quad \frac{P_i}{T_i} = \frac{P_f}{T_f} \quad \text{and} \quad P_f = P_i \times \frac{T_f}{T_i}$$

Since $P_i = 1.00$ bar, $T_i = 273$ K, and $T_f = 373$ K, then

$$P_f = 1.00\text{ bar} \times \frac{373\text{ K}}{273\text{ K}} = 1.37\text{ bar}$$

Assess

We can base our check on a qualitative, intuitive understanding of what happens when a gas is heated in a closed container. Its pressure increases (possibly to the extent that the container bursts). If, by error, we had used the ratio of temperatures 273 K/373 K, the final pressure would have been less than 1.00 bar—an impossible result.

PRACTICE EXAMPLE A: A 1.00 mL sample of $N_2(g)$ at 36.2 °C and 2.14 atm is heated to 37.8 °C, and the pressure changed to 1.02 atm. What volume does the gas occupy at this final temperature and pressure?

PRACTICE EXAMPLE B: Suppose that in Figure 6-10 we want the pressure to remain at 1.00 bar when the $O_2(g)$ is heated to 100 °C. What mass of $O_2(g)$ must we release from the flask?

6-4 Applications of the Ideal Gas Equation

Molar Mass Determination

$$PV = nRT \qquad \text{and} \qquad n = \frac{m}{M}$$

$$PV = \frac{m}{M}\,RT$$

$$M = \frac{m\,RT}{PV}$$

EXAMPLE 6-7 Determining a Molar Mass with the Ideal Gas Equation

Propylene is an important commercial chemical (about ninth in the amount produced among manufactured chemicals) used in the synthesis of other organic chemicals and in production of plastics (polypropylene). A glass vessel weighs 40.1305 g when clean, dry, and evacuated; it weighs 138.2410 g when filled with water at 25.0 °C (density of water = 0.9970 g/mL) and 40.2959 g when filled with propylene gas at 740.3 mmHg and 24.0 °C. What is the molar mass of propylene?

Analyze

We are given a pressure (in mmHg), a temperature (in °C), and information that will enable us to determine the amount of gas (in grams) and the volume of the vessel. If we express these quantities in Kelvin, atmospheres, moles, and liters, respectively, then we can use equation (6.13), with $R = 0.08206 \text{ atm L K}^{-1} \text{ mol}^{-1}$, to calculate the molar mass of the gas.

Solve

First determine the mass of water required to fill the vessel.

$$\begin{aligned}\text{mass of water to fill vessel} &= 138.2410 \text{ g} - 40.1305 \text{ g}\\ &= 98.1105 \text{ g}\end{aligned}$$

Use the density of water in a conversion factor to obtain the volume of water (and hence, the volume of the glass vessel).

$$\begin{aligned}\text{volume of water (volume of vessel)} &= 98.1105 \text{ g H}_2\text{O} \times \frac{1 \text{ mL H}_2\text{O}}{0.9970 \text{ g H}_2\text{O}}\\ &= 98.41 \text{ mL} = 0.09841 \text{ L}\end{aligned}$$

The mass of the gas is the difference between the weight of the vessel filled with propylene gas and the weight of the empty vessel.

$$\text{mass of gas} = 40.2959 \text{ g} - 40.1305 \text{ g} = 0.1654 \text{ g}$$

The values of temperature and pressure are given.

$$T = 24.0 \text{ °C} + 273.15 = 297.2 \text{ K}$$

$$P = 740.3 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.9741 \text{ atm}$$

Substitute data into the rearranged version of equation (6.13).

$$\begin{aligned}M = \frac{mRT}{PV} &= \frac{0.1654 \text{ g} \times 0.08206 \ \cancel{\text{atm}}\ \cancel{\text{L}} \text{ mol}^{-1} \cancel{\text{K}^{-1}} \times 297.2 \ \cancel{\text{K}}}{0.9741 \ \cancel{\text{atm}} \times 0.09841 \ \cancel{\text{L}}}\\ &= 42.08 \text{ g mol}^{-1}\end{aligned}$$

Assess

Cancellations leave the units g and mol^{-1}. The unit g mol^{-1} or g/mol is that for molar mass, the quantity we are seeking. We can use another approach to solving this problem. We can substitute the pressure (0.9741 atm), temperature (297.2 K), and volume (0.09841 L) into the ideal gas equation to calculate the number of moles in the gas sample (0.003931 mol). Because the sample contains 0.003931 mol and has a mass of 0.165 g, the molar mass is $0.165 \text{ g}/0.003931 \text{ mol} = 42.0 \text{ g mol}^{-1}$. The advantage of this alternative approach is that it makes use of only the ideal gas equation; you do not have to memorize or derive equation (6.13) for the cases when you might need it.

PRACTICE EXAMPLE A: The same glass vessel used in Example 6-7 is filled with an unknown gas at 772 mmHg and 22.4 °C. The gas-filled vessel weighs 40.4868 g. What is the molar mass of the gas?

PRACTICE EXAMPLE B: A 1.27 g sample of an oxide of nitrogen, believed to be either NO or N_2O, occupies a volume of 1.07 L at 25 °C and 737 mmHg. Which oxide is it?

Gas Density

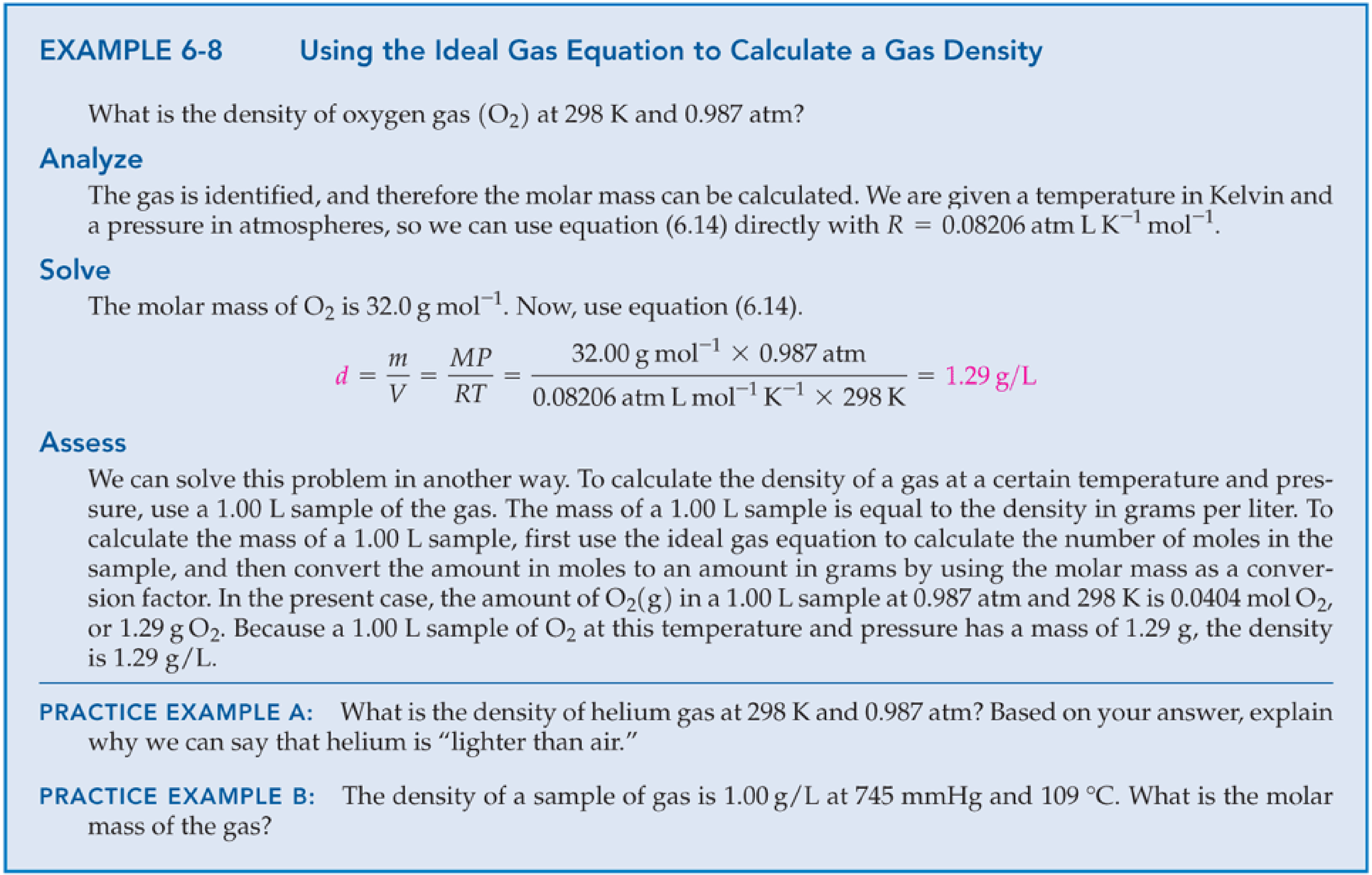
$$\delta = \frac{m}{V}$$

$$PV = \frac{m}{M}RT$$

$$\frac{m}{V} = \delta = \frac{MP}{RT}$$

KEEP IN MIND

that gas densities are typically much smaller than those of liquids and solids. Gas densities are usually expressed in grams per *liter* rather than grams per *milliliter.*



EXAMPLE 6-8 Using the Ideal Gas Equation to Calculate a Gas Density

What is the density of oxygen gas (O_2) at 298 K and 0.987 atm?

Analyze

The gas is identified, and therefore the molar mass can be calculated. We are given a temperature in Kelvin and a pressure in atmospheres, so we can use equation (6.14) directly with $R = 0.08206 \text{ atm L K}^{-1} \text{ mol}^{-1}$.

Solve

The molar mass of O_2 is 32.0 g mol^{-1}. Now, use equation (6.14).

$$d = \frac{m}{V} = \frac{MP}{RT} = \frac{32.00 \text{ g mol}^{-1} \times 0.987 \text{ atm}}{0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 1.29 \text{ g/L}$$

Assess

We can solve this problem in another way. To calculate the density of a gas at a certain temperature and pressure, use a 1.00 L sample of the gas. The mass of a 1.00 L sample is equal to the density in grams per liter. To calculate the mass of a 1.00 L sample, first use the ideal gas equation to calculate the number of moles in the sample, and then convert the amount in moles to an amount in grams by using the molar mass as a conversion factor. In the present case, the amount of O_2(g) in a 1.00 L sample at 0.987 atm and 298 K is 0.0404 mol O_2, or 1.29 g O_2. Because a 1.00 L sample of O_2 at this temperature and pressure has a mass of 1.29 g, the density is 1.29 g/L.

PRACTICE EXAMPLE A: What is the density of helium gas at 298 K and 0.987 atm? Based on your answer, explain why we can say that helium is "lighter than air."

PRACTICE EXAMPLE B: The density of a sample of gas is 1.00 g/L at 745 mmHg and 109 °C. What is the molar mass of the gas?

6-5 Gases in Chemical Reactions

Stoichiometric factors relate gas quantities to quantities of other reactants or products.

Ideal gas equation relates the amount of a gas to volume, temperature and pressure.

Law of Combining Volumes can be developed using the gas law.

EXAMPLE 6-9 Using the Ideal Gas Equation in Reaction Stoichiometry Calculations

What volume of N_2, measured at 735 mmHg and 26 °C, is produced when 75.0 g NaN_3 is decomposed?

$$2\,NaN_3(s) \xrightarrow{\Delta} 2\,Na(l) + 3\,N_2(g)$$

Analyze

The following conversions are required.

$$g\,NaN_3 \longrightarrow mol\,NaN_3 \longrightarrow mol\,N_2 \longrightarrow L\,N_2$$

The molar mass of NaN_3 is used for the first conversion. The second conversion makes use of a stoichiometric factor constructed from the coefficients of the chemical equation. The ideal gas equation is used to complete the final conversion.

Solve

$$?\,mol\,N_2 = 75.0\,g\,NaN_3 \times \frac{1\,mol\,NaN_3}{65.01\,g\,NaN_3} \times \frac{3\,mol\,N_2}{2\,mol\,NaN_3} = 1.73\,mol\,N_2$$

$$P = 735\,mmHg \times \frac{1\,atm}{760\,mmHg} = 0.967\,atm$$

$$V = ?$$

$$n = 1.73\,mol$$

$$R = 0.08206\,atm\,L\,mol^{-1}\,K^{-1}$$

$$T = 26\,°C + 273 = 299\,K$$

$$V = \frac{nRT}{P} = \frac{1.73\,mol \times 0.08206\,atm\,L\,mol^{-1}\,K^{-1} \times 299\,K}{0.967\,atm} = 43.9\,L$$

Assess

75.0 g NaN_3 is slightly more than one mole ($M \approx 65$ g/mol). From this amount of NaN_3 we should expect a little more than 1.5 mol $N_2(g)$. At 0 °C and 1 atm, 1.5 mol $N_2(g)$ would occupy a volume of $1.5 \times 22.4 = 33.6$ L. Because the temperature is higher than 0 °C and the pressure is lower than 1 atm, the sample should have a volume somewhat greater than 33.6 L.

EXAMPLE 6-10 Applying the Law of Combining Volumes

Zinc blende, ZnS, is the most important zinc ore. Roasting (strong heating) of ZnS in oxygen is the first step in the commercial production of zinc.

$$2\,\text{ZnS(s)} + 3\,\text{O}_2\text{(g)} \xrightarrow{\Delta} 2\,\text{ZnO(s)} + 2\,\text{SO}_2\text{(g)}$$

What volume of SO_2(g) can be obtained from 1.00 L O_2(g) and excess ZnS(s)? Both gases are measured at 25 °C and 745 mmHg.

Analyze

The reactant and product being compared are both gases, and both are at the same temperature and pressure. Therefore, we can use the law of combining volumes and treat the coefficients in the balanced chemical equation as if they had units of liters.

Solve

The stoichiometric factor (shown below in blue) converts from L O_2(g) to L SO_2(g).

$$?\,\text{L SO}_2\text{(g)} = 1.00\,\text{L O}_2\text{(g)} \times \frac{2\,\text{L SO}_2\text{(g)}}{3\,\text{L O}_2\text{(g)}} = 0.667\,\text{L SO}_2\text{(g)}$$

Assess

Some students would solve this problem by using the following sequence of conversions: L O_2 $\longrightarrow$ mol O_2 $\longrightarrow$ mol SO_2 $\longrightarrow$ L SO_2. This approach is acceptable but not as simple as the approach we used.

PRACTICE EXAMPLE A: The first step in making nitric acid is to convert ammonia to nitrogen monoxide. This is done under conditions of high temperature and in the presence of a platinum catalyst. What volume of O_2(g) is consumed per liter of NO(g) formed?

$$4\,\text{NH}_3\text{(g)} + 5\,\text{O}_2\text{(g)} \xrightarrow[850\,^\circ\text{C}]{\text{Pt}} 4\,\text{NO(g)} + 6\,\text{H}_2\text{O(g)}$$

PRACTICE EXAMPLE B: If all gases are measured at the same temperature and pressure, what volume of NH_3(g) is produced when 225 L H_2(g) are consumed in the reaction $N_2(g) + H_2(g) \longrightarrow NH_3(g)$ (not balanced)?

6-6 Mixtures of Gases

-the simple gas laws and the ideal gas equation apply to a *mixture of nonreactive gases as well as to individual gases*.

- Simplest approach is to use for the value of *n, the total number of moles of the gaseous mixture,* n_{total}

- consider a mixture of gases in a vessel of fixed volume *V at temperature T, the total pressure of the mixture*

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

(T constant, V constant)

- for fixed values of *T and P, the total volume of a mixture of gases*

$$V_{tot} = \frac{n_{tot}\,RT}{P}$$

(T constant, P constant)

EXAMPLE 6-11 Applying the Ideal Gas Equation to a Mixture of Gases

What is the pressure, in bar, exerted by a mixture of 1.0 g H_2 and 5.00 g He when the mixture is confined to a volume of 5.0 L at 20 °C?

Analyze

For fixed T and V, the total pressure of a mixture of gases is determined by the total number of moles of gas: $P_{\text{tot}} = n_{\text{tot}}RT/V$.

Solve

$$\begin{aligned} n_{\text{tot}} &= \left(1.0\,\text{g H}_2 \times \frac{1\,\text{mol H}_2}{2.02\,\text{g H}_2}\right) + \left(5.00\,\text{g He} \times \frac{1\,\text{mol He}}{4.003\,\text{g He}}\right) \\ &= 0.50\,\text{mol H}_2 + 1.25\,\text{mol He} = 1.75\,\text{mol gas} \\ P &= \frac{1.75\,\text{mol} \times 0.0831\,\text{bar L mol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}{5.0\,\text{L}} = 8.5\,\text{bar} \end{aligned}$$

Assess

It is also possible to solve this problem by starting from equation (6.12). Because 1 mol of ideal gas occupies 22.7 L at 0 °C and 1 bar, the pressure exerted by 1.75 mol of gas in a 5.0 L vessel at 293 K is $(1.75\,\text{mol}/1.00\,\text{mol}) \times (293\,\text{K}/273\,\text{K}) \times (22.7\,\text{L}/5.0\,\text{L}) \times 1.0\,\text{bar} = 8.5\,\text{bar}$.

PRACTICE EXAMPLE A: What will be the total gas pressure if 12.5 g Ne is added to the mixture of gases described in Example 6-11 and the temperature is then raised to 55 °C? [*Hint:* What is the new number of moles of gas? What effect does raising the temperature have on the pressure of a gas at constant volume?]

PRACTICE EXAMPLE B: 2.0 L of $O_2(g)$ and 8.0 L of $N_2(g)$, each at 0.00 °C and 1.00 atm, are mixed together. The nonreactive gaseous mixture is compressed to occupy 2.0 L at 298 K. What is the pressure exerted by this mixture?

Partial Pressure

- John Dalton made an important contribution to the study of gaseous mixtures. He proposed that in a mixture, each gas expands to fill the container and exerts the same pressure (called its partial pressure) that it would if it were alone in the container.

- Dalton s law of partial pressures states that the total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture,

$$P_{tot} = P_a + P_b + \ldots$$

- In a gaseous mixture of moles of A, moles of B, and so on, the volume each gas would individually occupy at a pressure equal to is

$$V_a = n_a RT/P_{tot} \qquad V_b = n_b RT/P_{tot} \qquad \text{and} \qquad V_{tot} = V_a + V_b + \ldots$$

- and the commonly used expression *percent by volume is*

$$\text{Volume \% A} = \frac{V_A}{V_{tot}} \text{ X100\%} \qquad \text{Volume \% B} = \frac{V_B}{V_{tot}} \text{ X100\%}$$

We can derive a particularly useful expression from the following ratios,

$$\frac{P_a}{P_{tot}} = \frac{n_a RT/V_{tot}}{n_{tot} RT/V_{tot}} = \frac{n_a}{n_{tot}}$$

and

$$\frac{V_a}{V_{tot}} = \frac{n_a RT/P_{tot}}{n_{tot} RT/P_{tot}} = \frac{n_a}{n_{tot}}$$

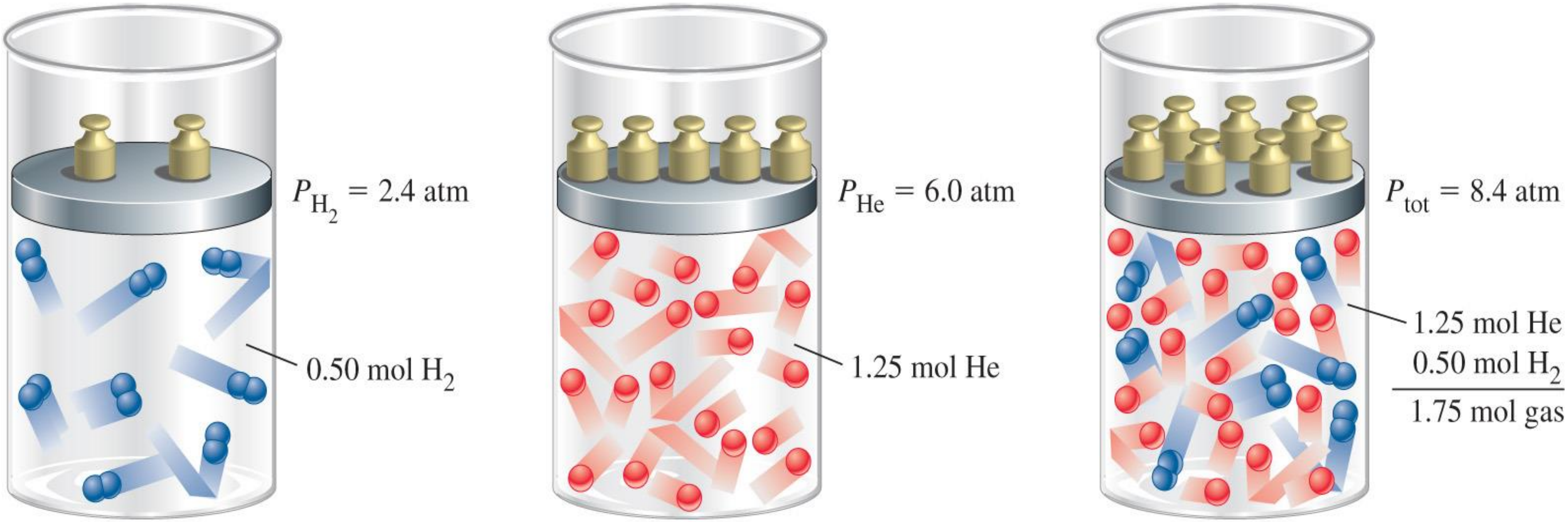
which means that

$$\frac{n_a}{n_{tot}} = \frac{P_a}{P_{tot}} = \frac{V_a}{V_{tot}} = \chi_a$$

- The mole fraction of a component A in a mixture , χ_a , is the fraction of all the molecules in the mixture contributed by that component.
- The sum of all the mole fractions in a mixture is one. $X_a + X_b = 1$

FIGURE 6-12

Dalton' s law of partial pressures illustrated



(a) 5.0 L at 20 °C **(b)** 5.0 L at 20 °C **(c)** 5.0 L at 20 °C

-The pressure of each gas is proportional to the number of moles of gas.

- The total pressure is the sum of the partial pressures of the individual gases.

EXAMPLE 6-12 Calculating the Partial Pressures in a Gaseous Mixture

What are the partial pressures of H_2 and He in the gaseous mixture described in Example 6-11?

Analyze

The ideal gas equation can be applied to each gas individually to obtain the partial pressure of each gas.

Solve

One approach involves a direct application of Dalton's law in which we calculate the pressure that each gas would exert if it were alone in the container.

$$P_{H_2} = \frac{n_{H_2} \times RT}{V} = \frac{0.50\ \text{mol} \times 0.0821\ \text{atm L mol}^{-1}\ \text{K}^{-1} \times 293\ \text{K}}{5.0\ \text{L}} = 2.4\ \text{atm}$$

$$P_{He} = \frac{n_{He} \times RT}{V} = \frac{1.25\ \text{mol} \times 0.0821\ \text{atm L mol}^{-1}\ \text{K}^{-1} \times 293\ \text{K}}{5.0\ \text{L}} = 6.0\ \text{atm}$$

Expression (6.17) gives us a simpler way to answer the question because we already know the number of moles of each gas and the total pressure from Example 6-11 ($P_{tot} = 8.4$ atm).

$$P_{H_2} = \frac{n_{H_2}}{n_{tot}} \times P_{tot} = \frac{0.50}{1.75} \times 8.4\ \text{atm} = 2.4\ \text{atm}$$

$$P_{He} = \frac{n_{He}}{n_{tot}} \times P_{tot} = \frac{1.25}{1.75} \times 8.4\ \text{atm} = 6.0\ \text{atm}$$

Assess

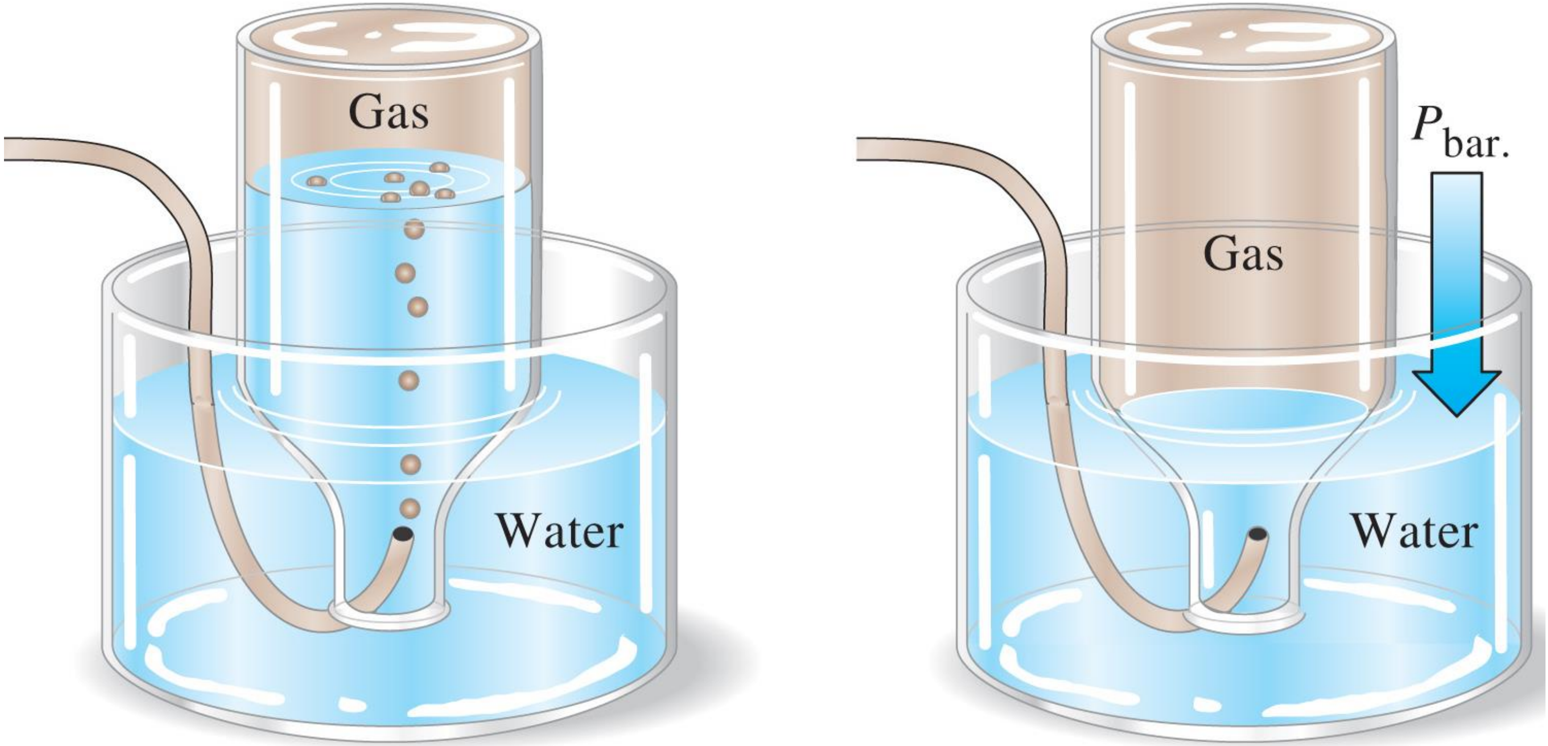
An effective way of checking an answer is to obtain the same answer when the problem is done in different ways, as was the case here.

PRACTICE EXAMPLE A: A mixture of 0.197 mol $CO_2(g)$ and 0.00278 mol $H_2O(g)$ is held at 30.0 °C and 2.50 atm. What is the partial pressure of each gas?

PRACTICE EXAMPLE B: The percent composition of air by volume is 78.08% N_2, 20.95% O_2, 0.93% Ar, and 0.036% CO_2. What are the partial pressures of these four gases in a sample of air at a barometric pressure of 748 mmHg?

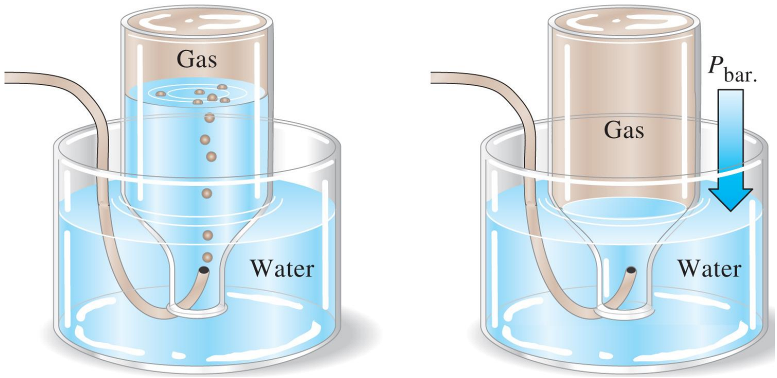
Collecting a gas over water -- a *pneumatic trough*

- Isolating gases in the early days of chemistry



- The method works, of course, only for gases that are insoluble in and do not react with the liquid being displaced, e.g N_2, H_2, O_2 are all essentially insoluble in and unreactive with water.

Collecting a gas over water -- a *pneumatic trough*



- A gas collected in a pneumatic trough filled with water is said to be *collected over water and is wet. It is a mixture of two gases- the desired gas and water* vapor.

-Total pressure of wet gas is equal to atmospheric pressure (P_{bar}) if the water level is the same inside and outside.

- The total pressure can be made equal to the prevailing pressure of the atmosphere (barometric pressure) by adjusting the position of the bottle; thus we can write

$$P_{tot} = P_{bar} = P_{gas} + P_{H_2O}$$

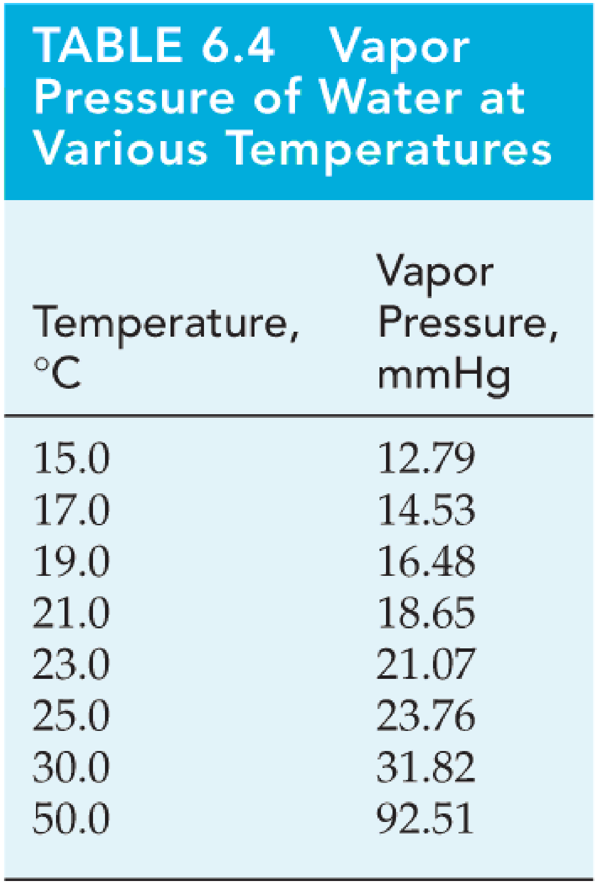


TABLE 6.4 Vapor Pressure of Water at Various Temperatures

Temperature, °C	Vapor Pressure, mmHg
15.0	12.79
17.0	14.53
19.0	16.48
21.0	18.65
23.0	21.07
25.0	23.76
30.0	31.82
50.0	92.51

The pressure of the water vapor depends only on the temperature of the water,

EXAMPLE 6-13 Collecting a Gas over a Liquid (Water)

In the following reaction, 81.2 mL of $O_2(g)$ is collected over water at 23 °C and barometric pressure 751 mmHg. What mass of $Ag_2O(s)$ decomposed? (The vapor pressure of water at 23 °C is 21.1 mmHg.)

$$2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$$

Analyze

The key concept is that the gas collected is wet, that is, a *mixture* of $O_2(g)$ and water vapor. Use $P_{bar.} = P_{O_2} + P_{H_2O}$ to calculate P_{O_2}, and then use the ideal gas equation to calculate the number of moles of O_2. The following conversions are used to complete the calculation: mol $O_2 \longrightarrow$ mol $Ag_2O \longrightarrow$ g Ag_2O.

Solve

$$P_{O_2} = P_{bar.} - P_{H_2O} = 751\text{ mmHg} - 21.1\text{ mmHg} = 730\text{ mmHg}$$

$$P_{O_2} = 730\text{ mmHg} \times \frac{1\text{ atm}}{760\text{ mmHg}} = 0.961\text{ atm}$$

$$V = 81.2\text{ mL} = 0.0812\text{ L}$$

$$n = ?$$

$$R = 0.08206\text{ atm L mol}^{-1}\text{ K}^{-1}$$

$$T = 23\text{ °C} + 273 = 296\text{ K}$$

$$n = \frac{PV}{RT} = \frac{0.961\text{ atm} \times 0.0812\text{ L}}{0.08206\text{ atm L mol}^{-1}\text{ K}^{-1} \times 296\text{ K}} = 0.00321\text{ mol}$$

From the chemical equation we obtain a factor to convert from moles of O_2 to moles of Ag_2O. The molar mass of Ag_2O provides the final factor.

$$?\text{ g }Ag_2O = 0.00321\text{ mol }O_2 \times \frac{2\text{ mol }Ag_2O}{1\text{ mol }O_2} \times \frac{231.7\text{ g }Ag_2O}{1\text{ mol }Ag_2O} = 1.49\text{ g }Ag_2O$$

Assess

The determination of the number of moles of O_2 in the sample is the key calculation. We can quickly estimate the number of moles of O_2 in the sample by using the fact that for typical conditions ($T \approx 298$ K, $P \approx 760$ mmHg), the molar volume of an ideal gas is about 24 L. The number of moles of gas (mostly O_2) in the sample is approximately $0.08\text{ L}/24\text{ L} \approx 0.003$ mol. This estimate is quite close to the value calculated above.

6–7 Kinetic Molecular Theory of Gases

- To explain the gas laws, we need a theory.
- One theory developed during the mid-nineteenth century is called the **kinetic-molecular theory of gases.**
- It is based on the model illustrated in Figure 6-14

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Visualizing molecular motion: Molecules of a gas are in constant motion and collide with one another and with the container wall.

6–7 Kinetic Molecular Theory of Gases

- A gas is composed of a very large number of extremely small particles (molecules or, in some cases, atoms) in constant, random, straight-line motion.

- Molecules of a gas are separated by great distances. The gas is mostly empty space. (The molecules are treated as so-called point masses, as though they have mass but no volume.)

- Molecules collide only fleetingly with one another and with the walls of their container, and most of the time molecules are not colliding.

- There are assumed to be no forces between molecules except very briefly during collisions. That is, each molecule acts independently of all the others and is unaffected by their presence, except during collisions.

- Individual molecules may gain or lose energy as a result of collisions. In a collection of molecules at constant temperature, however, *the total energy remains constant.*

Derivation of Boyle's Law

- kinetic-molecular theory of gases provides a satisfactory explanation of Boyle s law.

$PV = a$

Boyle s law.

-The value of ' *a* ' *depends on the*

- *number, N, of molecules in the sample*
- *and the* temperature, *T.*

-Because pressure is a force per unit area and for assessing the forces associated with molecules hitting the walls of the container let's focus on a molecule traveling along the *x direction toward a* wall perpendicular to its path.

- The speed of the molecule is denoted by u_x.
- The force exerted on the wall by the molecule depends on the following factors

Derivation of Boyle's Law

The force exerted on the wall by the molecule depends on;

1. The frequency of molecular collisions, $\nu \propto u \frac{N}{V}$

The higher this frequency, the greater the total force on the wall of the container. Collision frequency increases with the number of molecules per unit volume and with molecular speeds.

2. Impulse or momentum transfer, $I \propto mu$

When a molecule hits the wall of a vessel, momentum is transferred as the molecule reverses direction. This momentum transfer is called an *impulse*. *The magnitude of the impulse is* directly proportional to the mass, *m, of a molecule and its speed, u:*

The pressure of a gas (P) is the product of impulse and collision frequency

$$P \propto \frac{N}{V} m u^2$$

Derivation of Boyle's Law

- At any instant, however, the molecules in a gas sample are traveling at different speeds. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2 which is denoted by $\overline{u_x^2}$

- the overbar reminds us that we are referring to the average value of u_x^2

<u>the concept of the average of the squares of speeds,</u>

- five molecules with speeds 400, 450, 525, 585, and 600 m/s. We find the average of the squares of these speeds by squaring the speeds, adding the squares, and dividing by the number of particles, in this case five.

$$\overline{u^2} = \frac{(400m/s)^2 + (450m/s)^2 + (525m/s)^2 + (585m/s)^2 + (600m/s)^2}{5}$$

$$= 2.68 \text{ x}10^5 \text{ m}^2/\text{s}^2$$

Thus, pressure expression

$$P \propto \frac{N}{V} m\overline{u_x^2}$$

We have one final factor to consider !!!!!!!

There is absolutely nothing special about the *x direction, so we should expect that*

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2} \qquad \text{where } \overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$$

$\overline{u^2}$ is the average value of u^2 taking into account all the molecules, not just those moving in the *x direction*

$\overline{u^2}$ is called the mean square speed

$$P \propto \frac{N}{V} m\overline{u_x^2}$$

if we substitute $\frac{1}{3}\overline{u^2}$ for $\overline{u^2}$ the equation becomes

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2}$$

Basic equation of the kinetic–molecular theory of gases.

Distribution of molecular speeds

not all the molecules in a gas travel at the same speed. Because of the large number of molecules, we cannot know the speed of each molecule, but we can make a statistical prediction of how many molecules have a particular speed.

Fraction of molecules that have speed u, F(u); Maxwell Distribution of speeds:

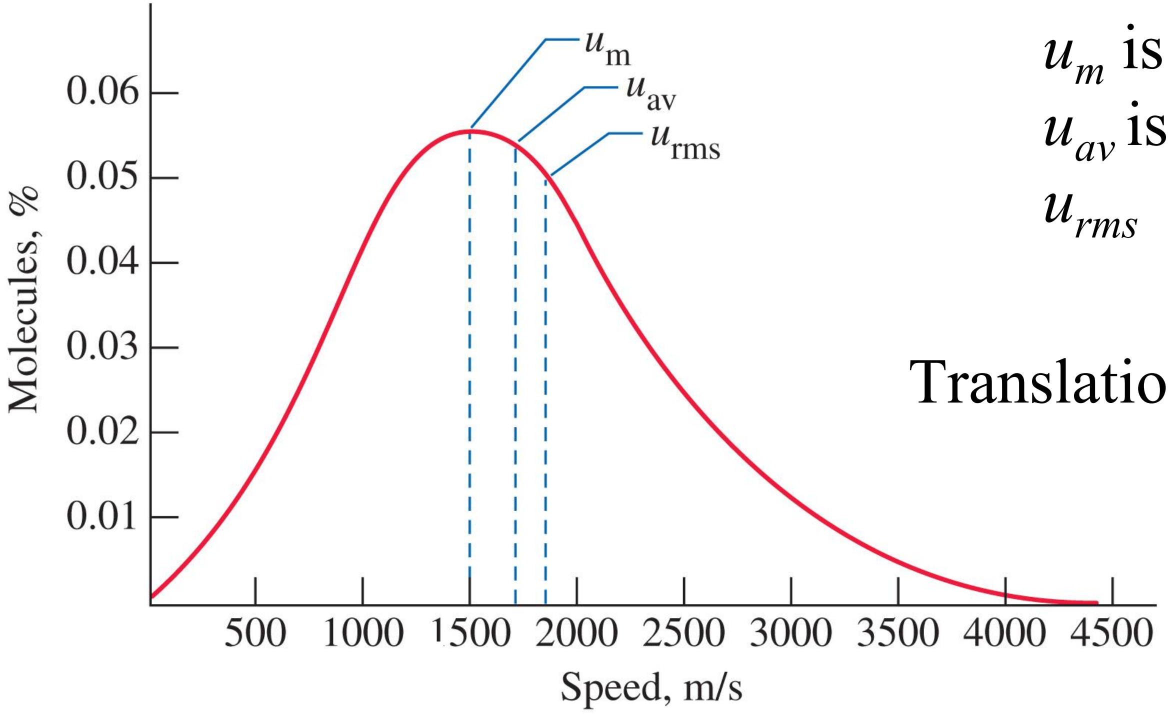

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FIGURE 6-15

Pressure and Molecular Speed

u_m is the modal speed

u_{av} is the simple average

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

Translational kinetic energy,

$$e_k \propto \frac{1}{2} mu^2$$

EXAMPLE 6-14 Calculating a Root-Mean-Square Speed

Which is the greater speed, that of a bullet fired from a high-powered M-16 rifle (2180 mi/h) or the root-mean-square speed of H_2 molecules at 25 °C?

Analyze

This is a straightforward application of equation (6.20). We must use SI units: $R = 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $M = 2.016 \times 10^{-3}\ \mathrm{kg\,mol^{-1}}$. Recall that $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$.

Solve

Determine u_{rms} of H_2 with equation (6.20).

$$u_{\mathrm{rms}} = \sqrt{\frac{3 \times 8.3145\ \mathrm{kg\,m^2\,s^{-2}\,mol^{-1}\,K^{-1}} \times 298\ \mathrm{K}}{2.016 \times 10^{-3}\ \mathrm{kg\,mol^{-1}}}}$$

$$= \sqrt{3.69 \times 10^{6}\ \mathrm{m^2/s^2}} = 1.92 \times 10^{3}\ \mathrm{m/s}$$

The remainder of the problem requires us either to convert 1.92×10^3 m/s to a speed in miles per hour, or 2180 mi/h to meters per second. Then we can compare the two speeds. When we do this, we find that 1.92×10^3 m/s corresponds to 4.29×10^3 mi/h. The root-mean-square speed of H_2 molecules at 25 °C is greater than the speed of the high-powered rifle bullet.

Assess

The cancellation of units yields a result for u_{rms} with the correct units (m/s). Also, Figure 6-15 shows that u_{rms} for H_2 is a bit greater than 1500 m/s at 273 K. At 298 K, u_{rms} should be slightly greater than it is at 273 K.

PRACTICE EXAMPLE A: Which has the greater root-mean-square speed at 25 °C, $NH_3(g)$ or $HCl(g)$? Calculate u_{rms} for the one with the greater speed.

PRACTICE EXAMPLE B: At what temperature are u_{rms} of H_2 and the speed of the M-16 rifle bullet given in Example 6-14 the same?

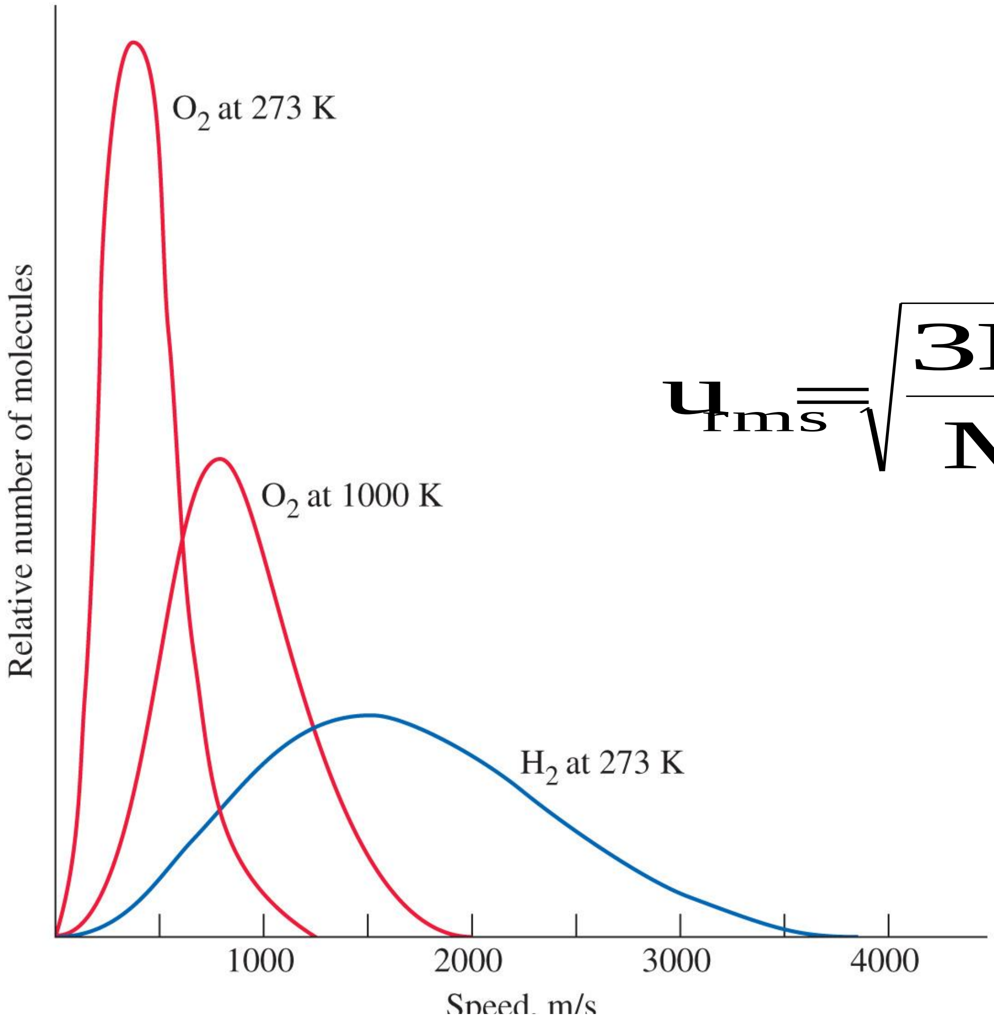
Pressure

Assume one mole: $PV = \frac{1}{3} N_A m \overline{u}^2$

PV=RT so: $3RT = N_A m \overline{u}^2$

$N_A m = M$: $3RT = M \overline{u}^2$

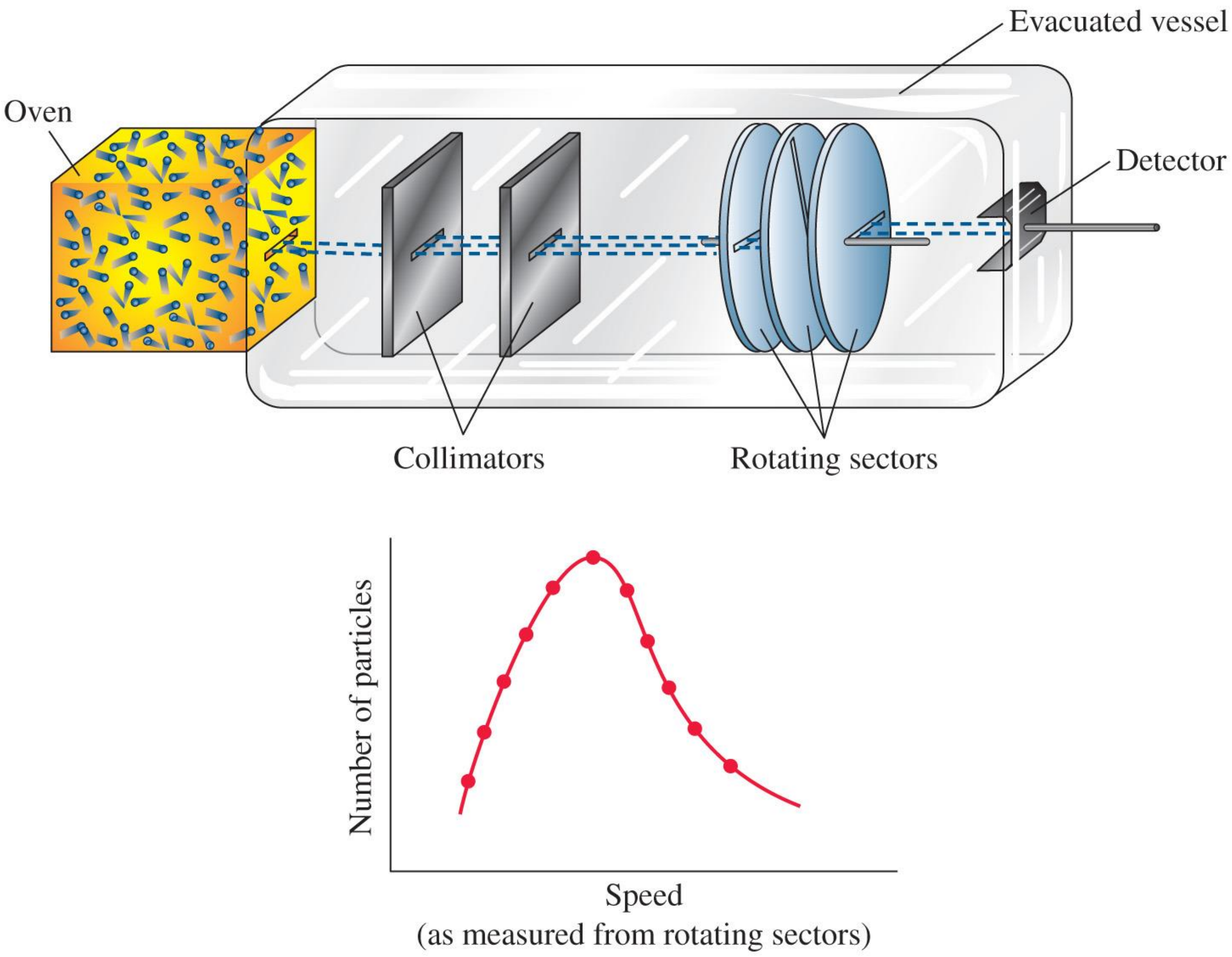
Rearrange: $u_{rms} = \sqrt{\frac{3RT}{M}}$



$$u_{rms} = \sqrt{\frac{3R}{M}}$$

▲ FIGURE 6-16

Distribution of Molecular Speeds – the effect of mass and temperature



▲ FIGURE 6-17

Distribution of molecular speeds – an experimental determination

Temperature

Modify: $$PV = \frac{1}{3} N_A m\overline{u^2} = \frac{2}{3} N_A \left(\frac{1}{2} m\overline{u^2}\right)$$

PV=RT so: $$RT = \frac{2}{3} N_A \overline{e}_k$$

Solve for $\overline{e}_k$: $$\overline{e}_k = \frac{3}{2} \frac{R}{N_A} (T)$$

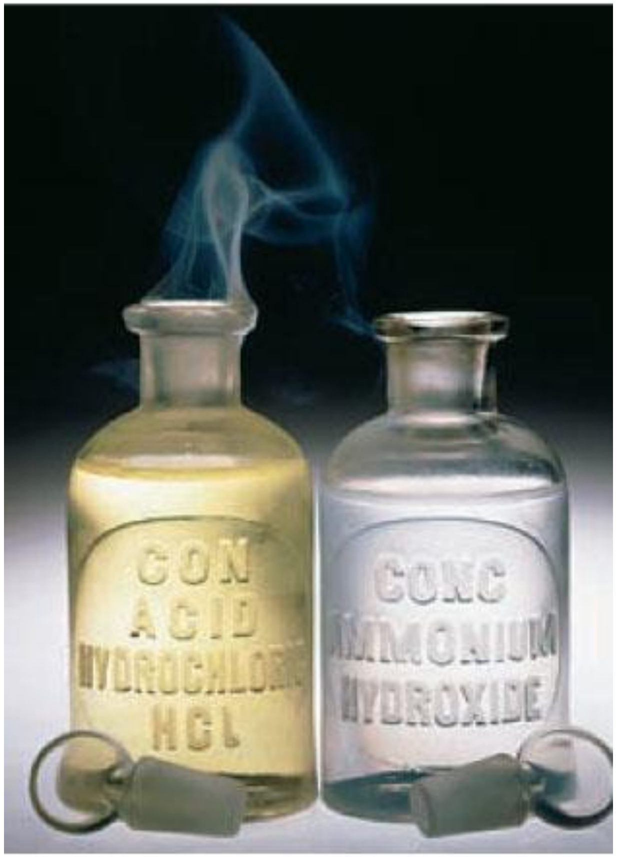
Average kinetic energy is directly proportional to temperature!

6-8 Gas Properties Relating to the Kinetic-Molecular Theory

Diffusion is the migration of molecules as a result of random molecular motion.

a common diffusion seen in a chemistry laboratory.

Diffusion of $NH_3(g)$ and $HCl(g)$



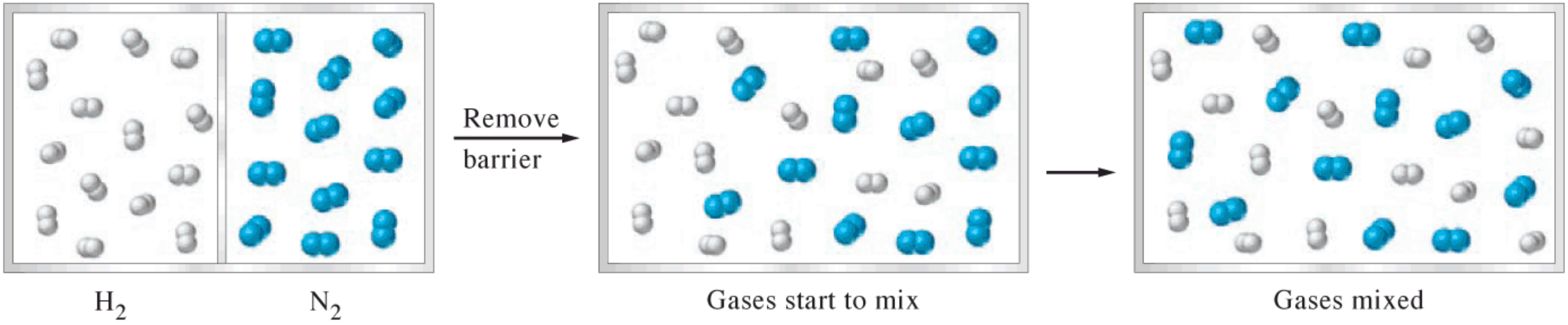
- NH_3 (g) escapes from NH_3 (aq) and HCl(g) escapes from HCl(aq).
- The gases diffuse toward each other, and, where they meet, a white cloud of ammonium chloride forms as a result of the following reaction:

$$NH_3(g) + HCl(g) \qquad\qquad NH_4Cl(s)$$

Because of their greater average speed, NH_3 molecules diffuse faster than HCl. As a result, the cloud forms close to the mouth of the HCl(aq) container.

Diffusion:

The diffusion of two or more gases results in an intermingling of the molecules and, in a closed container, soon produces a homogeneous mixture, as shown in Figure below,

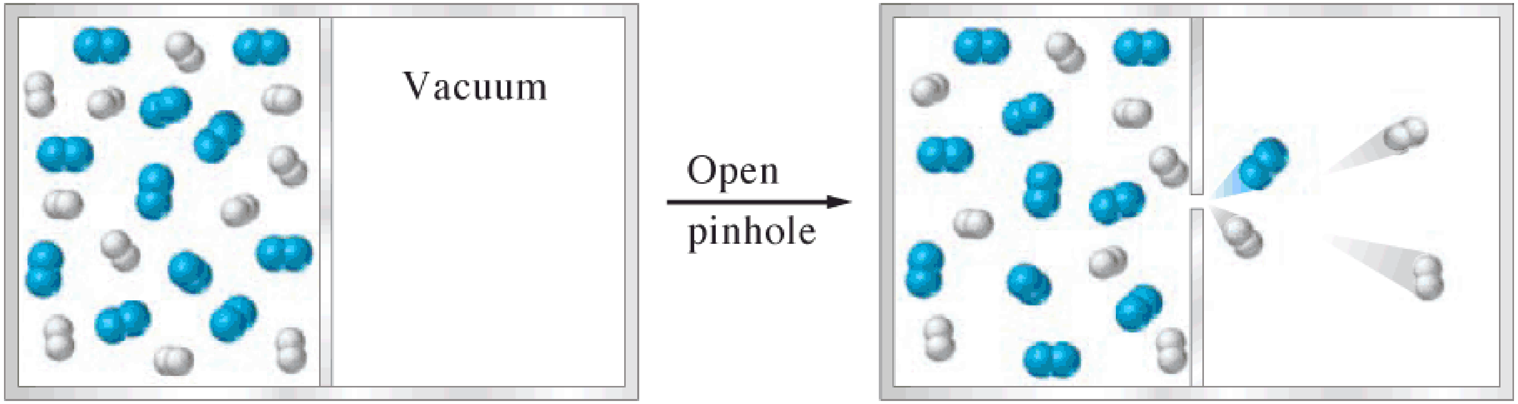


(a)

(a) Diffusion is the passage of one substance through another. In this case, the H_2 initially diffuses farther through the N_2 because it is lighter, although eventually a complete random mixing occurs. Net rate is proportional to molecular speed.

Effusion:

A related phenomenon, **effusion,** is the escape of gas molecules from their container through *a tiny orifice or pinhole*. The effusion of a hypothetical mixture of two gases is suggested by the Figure below



(b)

- Effusion is the passage of a substance through a pinhole or porous membrane into a vacuum. In this case, the lighter H_2 effuses faster across the empty space than does the N_2.

- The rate at which effusion occurs is directly proportional to molecular speeds. That is, molecules with high speeds effuse faster than molecules with low speeds.

Graham's Law, 1831

Let us consider the effusion of two different gases at the same temperature and pressure. We can first compare effusion rates with rootmean-square speeds and then substitute expression (6.20) for these speeds.

$$\frac{\textit{rate of effusion of A}}{\textit{rate of effusion of B}} = \frac{(u_{rms})_A}{(u_{rms})_B} ; \qquad u_{rms} = \sqrt{\frac{3R}{M}}$$

$$\frac{\textit{rate of effusion of A}}{\textit{rate of effusion of B}} = \frac{(u_{rms})_A}{(u_{rms})_B} = \sqrt{\frac{3RT/M_A}{3RT/MB}} = \sqrt{\frac{M_B}{M_A}}$$

The rate of effusion of a gas is inversely proportional to the square root of its molar mass.

Limitations:

- Only for gases at low pressures, (natural escape, not a jet).
- Tiny orifice (no collisions occur)
- Does not apply to diffusion to make quantitative predictions about rates of diffusion

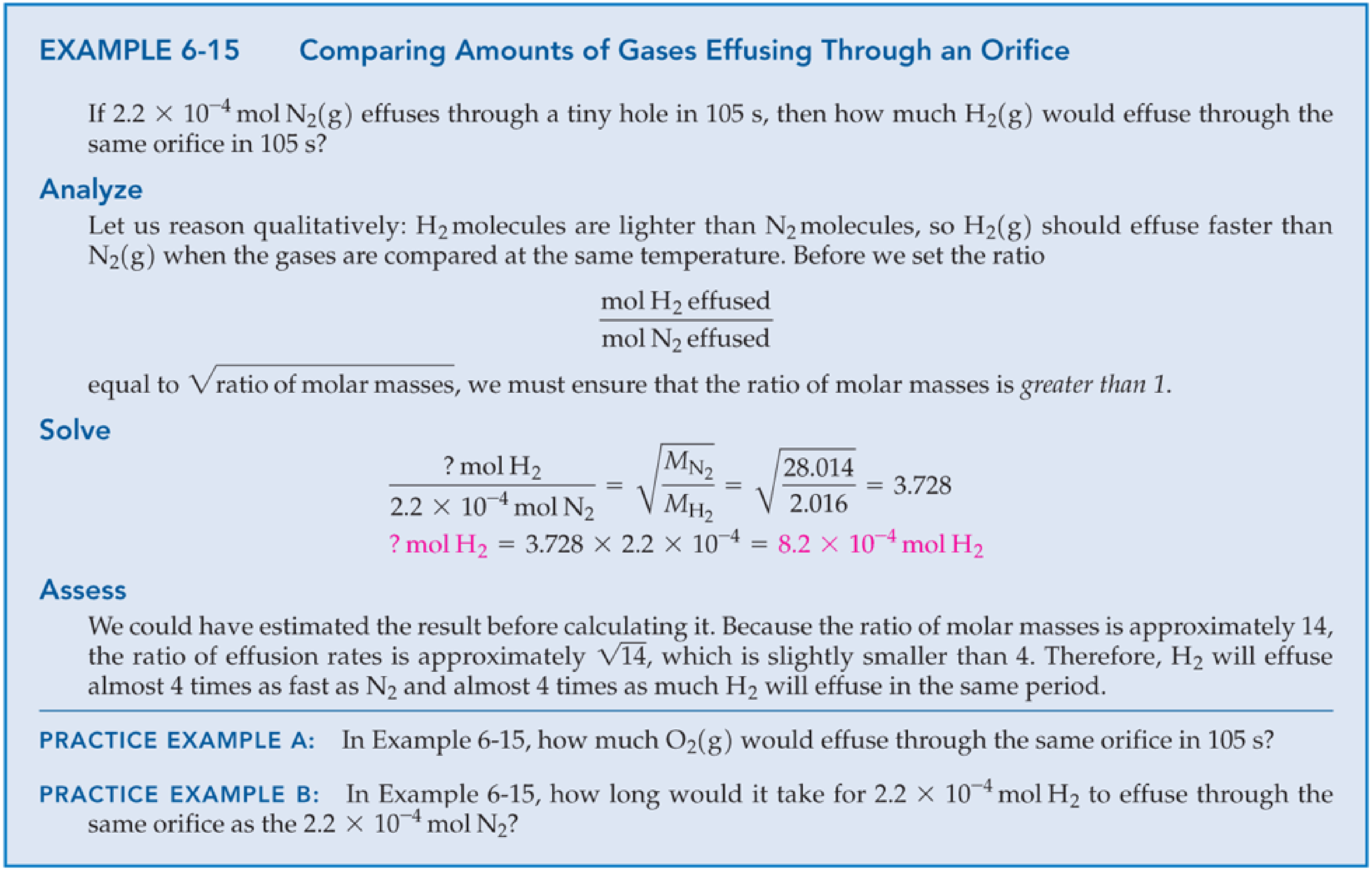
- When compared at the same temperature, two different gases have the same value of kinetic energy. $e_k \propto \frac{1}{2}mu^2$

- This means that molecules with a smaller mass (*m)* have a higher speed, (u_{rms})

Ratio of two molar masses can be used :

- Rate of effusion (as above)
- Molecular speeds
- Effusion times
- Distances traveled by molecules
- Amounts of gas effused.

When using equation (6.25), first reason qualitatively and work out whether the ratio of properties should be greater or less than one. Then set up the ratio of molar masses accordingly.



EXAMPLE 6-15 Comparing Amounts of Gases Effusing Through an Orifice

If 2.2×10^{-4} mol $N_2(g)$ effuses through a tiny hole in 105 s, then how much $H_2(g)$ would effuse through the same orifice in 105 s?

Analyze

Let us reason qualitatively: H_2 molecules are lighter than N_2 molecules, so $H_2(g)$ should effuse faster than $N_2(g)$ when the gases are compared at the same temperature. Before we set the ratio

$$\frac{\text{mol } H_2 \text{ effused}}{\text{mol } N_2 \text{ effused}}$$

equal to $\sqrt{\text{ratio of molar masses}}$, we must ensure that the ratio of molar masses is *greater than 1*.

Solve

$$\frac{?\ \text{mol } H_2}{2.2 \times 10^{-4}\ \text{mol } N_2} = \sqrt{\frac{M_{N_2}}{M_{H_2}}} = \sqrt{\frac{28.014}{2.016}} = 3.728$$

$$?\ \text{mol } H_2 = 3.728 \times 2.2 \times 10^{-4} = 8.2 \times 10^{-4}\ \text{mol } H_2$$

Assess

We could have estimated the result before calculating it. Because the ratio of molar masses is approximately 14, the ratio of effusion rates is approximately $\sqrt{14}$, which is slightly smaller than 4. Therefore, H_2 will effuse almost 4 times as fast as N_2 and almost 4 times as much H_2 will effuse in the same period.

PRACTICE EXAMPLE A: In Example 6-15, how much $O_2(g)$ would effuse through the same orifice in 105 s?

PRACTICE EXAMPLE B: In Example 6-15, how long would it take for 2.2×10^{-4} mol H_2 to effuse through the same orifice as the 2.2×10^{-4} mol N_2?

EXAMPLE 6-16 Relating Effusion Times and Molar Masses

A sample of Kr(g) escapes through a tiny hole in 87.3 s. The same amount of an unknown gas escapes in 42.9 s under identical conditions. What is the molar mass of the unknown gas?

Analyze

Because the unknown gas effuses faster, it must have a smaller molar mass than Kr. Before we set the ratio

$$\frac{\text{effusion time for unknown}}{\text{effusion time for Kr}}$$

equal to $\sqrt{\text{ratio of two molar masses}}$, we must make sure the ratio of molar masses is smaller than one. Thus, the ratio of molar masses must be written with the molar mass of the lighter gas (the unknown gas) in the numerator.

Solve

$$\frac{\text{effusion time for unknown}}{\text{effusion time for Kr}} = \frac{42.9\text{ s}}{87.3\text{ s}} = \sqrt{\frac{M_{\text{unk}}}{M_{\text{Kr}}}} = 0.491$$

$$M_{\text{unk}} = (0.491)^2 \times M_{\text{Kr}} = (0.491)^2 \times 83.80 = 20.2\text{ g/mol}$$

Assess

Use the final result and work backward. The molar mass of the unknown is about 4 times as small as that of Kr. Because *effusion rate* $\propto 1/\sqrt{M}$, the unknown will effuse about $\sqrt{4} = 2$ times as fast as Kr. The effusion times show that the unknown does indeed effuse 2 times as fast as Kr.

PRACTICE EXAMPLE A: Under the same conditions as in Example 6-16, another unknown gas requires 131.3 s to escape. What is the molar mass of this unknown gas?

PRACTICE EXAMPLE B: Given all the same conditions as in Example 6-16, how long would it take for a sample of ethane gas, C_2H_6, to effuse?

Applications of Diffusion

The diffusion of gases into one another has many practical applications.

- Natural gas and liquefied petroleum gas (LPG) are odorless; for commercial use, a small quantity of a gaseous organic sulfur compound, methyl mercaptan, CH_3SH, is added to them. The mercaptan has an odor that can be detected in parts per billion (ppb) or less. When a leak occurs, which can lead to asphyxiation or an explosion, we rely on the *diffusion of this odorous compound for a warning*.

- During World War II, the Manhattan Project (the secret, U.S. Government run program for developing the atomic bomb) used a method called gaseous diffusion to separate the desired isotope ^{235}U from the predominant ^{238}U. The method is based on the fact that uranium hexafluoride is one of the few compounds of uranium that can be obtained as a gas at moderate temperatures. When high-pressure $UF_6(g)$ is forced through a barrier having millions of submicroscopic holes per square centimeter, molecules containing the ^{235}U isotope pass through the barrier slightly faster than those containing ^{238}U just as expectd and therefore $UF_6(g)$ contains a slightly higher ratio of ^{235}U to ^{238}U than it did previously. The gas has become enriched in ^{235}U. Carrying this process through several thousand passes yields a product highly enriched in ^{235}U.

6-9 Nonideal (Real) Gases

A useful measure of how much a gas deviates from ideal gas behavior is found in its *compressibility factor*

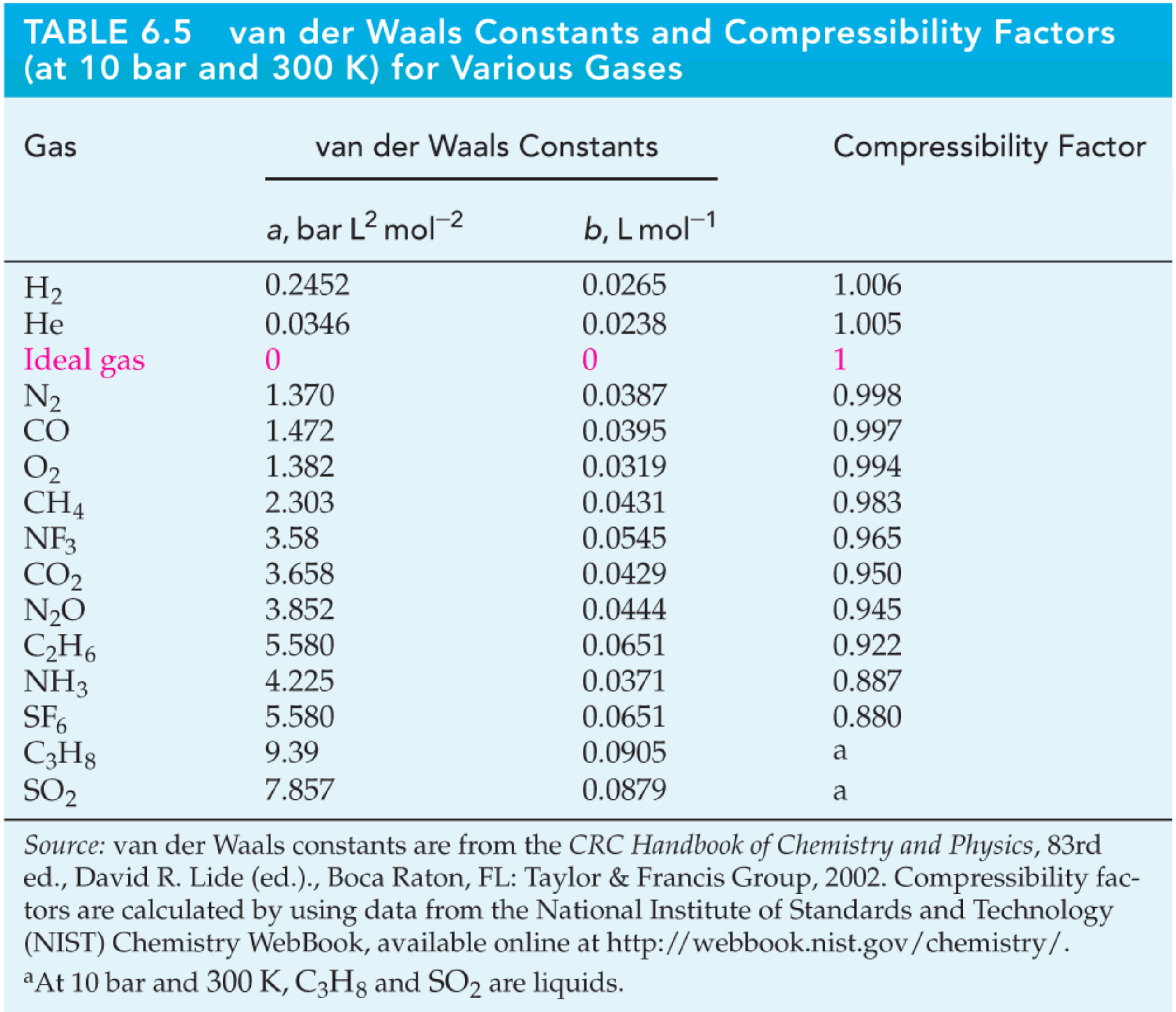


TABLE 6.5 van der Waals Constants and Compressibility Factors (at 10 bar and 300 K) for Various Gases

Gas	van der Waals Constants		Compressibility Factor
	a, bar L^2 mol^{-2}	b, L mol^{-1}	
H_2	0.2452	0.0265	1.006
He	0.0346	0.0238	1.005
Ideal gas	0	0	1
N_2	1.370	0.0387	0.998
CO	1.472	0.0395	0.997
O_2	1.382	0.0319	0.994
CH_4	2.303	0.0431	0.983
NF_3	3.58	0.0545	0.965
CO_2	3.658	0.0429	0.950
N_2O	3.852	0.0444	0.945
C_2H_6	5.580	0.0651	0.922
NH_3	4.225	0.0371	0.887
SF_6	5.580	0.0651	0.880
C_3H_8	9.39	0.0905	a
SO_2	7.857	0.0879	a

Source: van der Waals constants are from the *CRC Handbook of Chemistry and Physics*, 83rd ed., David R. Lide (ed.)., Boca Raton, FL: Taylor & Francis Group, 2002. Compressibility factors are calculated by using data from the National Institute of Standards and Technology (NIST) Chemistry WebBook, available online at http://webbook.nist.gov/chemistry/.

[a] At 10 bar and 300 K, C_3H_8 and SO_2 are liquids.

PV/nRT = 1

ideal gases-

PV/nRT >1 or <1

real gases

dependent on the gas

At 300 K and 10 bar,

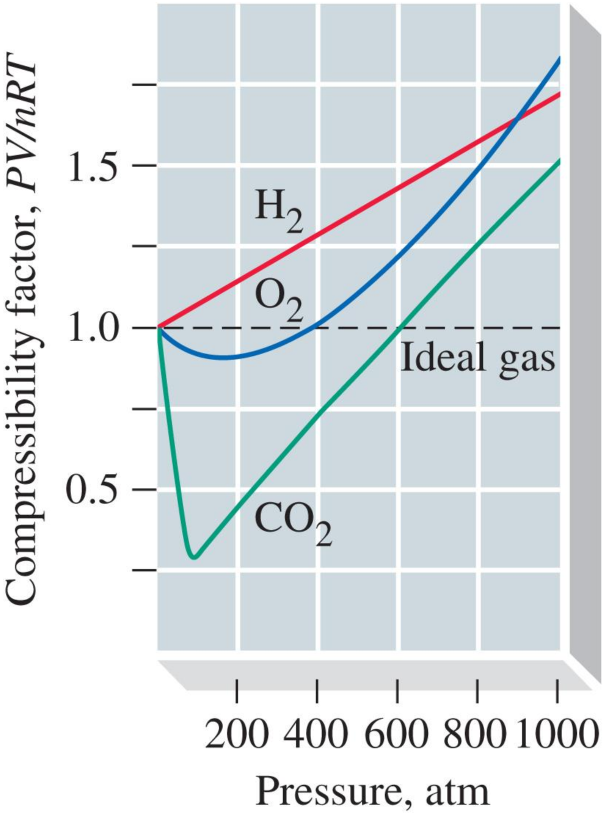
- He, H_2, CO, N_2, O_2 behave almost ideally.

PV/nRT ≅ 1

-But NH_3 and SF_6 do not.....

PV/nRT ≅ 0.88

The behavior of real gases compressibility factor as a function of pressure at 0 C.



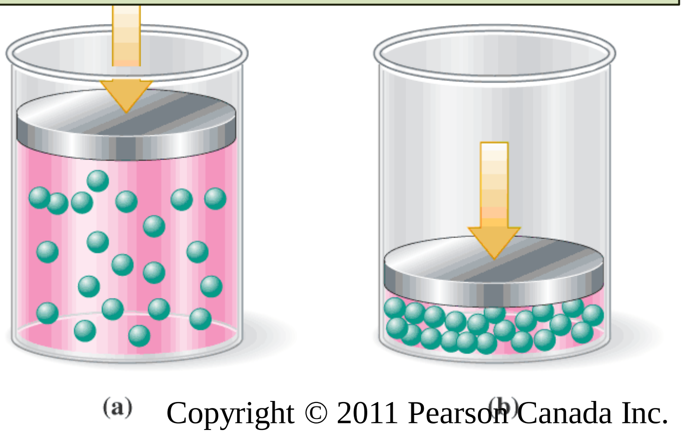
The principal conclusion from this plot is that

-all gases behave ideally at sufficiently low pressures, say, below 1 atm, but that deviations set in at increased pressures.

- At very high pressures, the compressibility factor is always greater than one.

- Boyle' s law predicts that at very high pressures, a gas volume becomes extremely small and approaches zero. However, the molecules themselves occupy space and are practically incompressible. The volume of the system is only slightly greater than the total volume of the molecules.

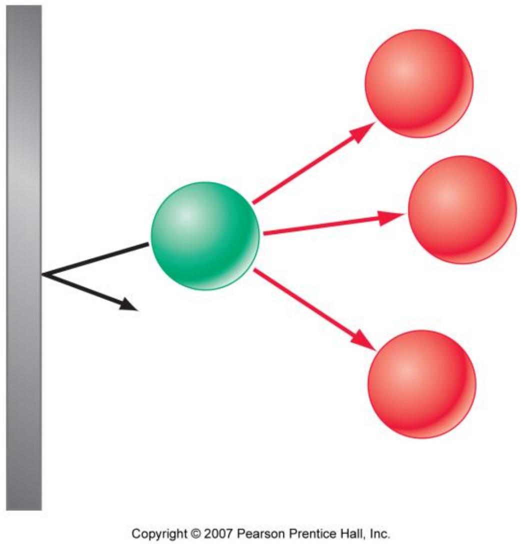
Because of the finite size of the molecules, the *PV product at high pressures is* larger than predicted for an ideal gas, and the compressibility factor is greater than one



▲ FIGURE 6-21

The effect of finite molecular size

Another consideration is that intermolecular forces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Intermolecular forces of attraction
Attractive forces of the red molecules for the green molecule cause the green molecule to exert less force when it collides with the wall than if these attractions did not exist.

Because of attractive forces between the molecules, the gas exerts less force on the container walls.
- Intermolecular forces of attraction account for compressibility factors of less than one.

These forces become increasingly important at low temperatures, where translational molecular motion slows down.

To summarize:

Gases tend to behave *ideally at high temperatures and low pressures.*

Gases tend to behave *nonideally at low temperatures and high pressures.*

The van der Waals Equation

-A number of equations can be used for real gases, equations that apply over a wider range of temperatures and pressures than the ideal gas equation.

-Such equations are not as general as the ideal gas equation. They contain terms that have specific, but different, values for different gases.

-Such equations must correct for the volume associated with the molecules themselves and for intermolecular forces of attraction.

- Of all the equations that chemists use for modeling the behavior of real gases, the *van der Waals equation,* is the simplest to use and interpret.

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

van der Waals equation

The two molecular parameters, *a and b, whose values* vary from molecule to molecule .

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

- The first term in the equation $P + \frac{an^2}{V^2}$ is the modified pressure factor, and takes into account the decrease in pressure caused by intermolecular attractions

-The equation given above for *P predicts that the pressure* exerted by a real gas will be less than that of an ideal gas.

-The proportionality constant, *a, provides a measure of how strongly* the molecules attract each other.

The van der Waals Equation

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

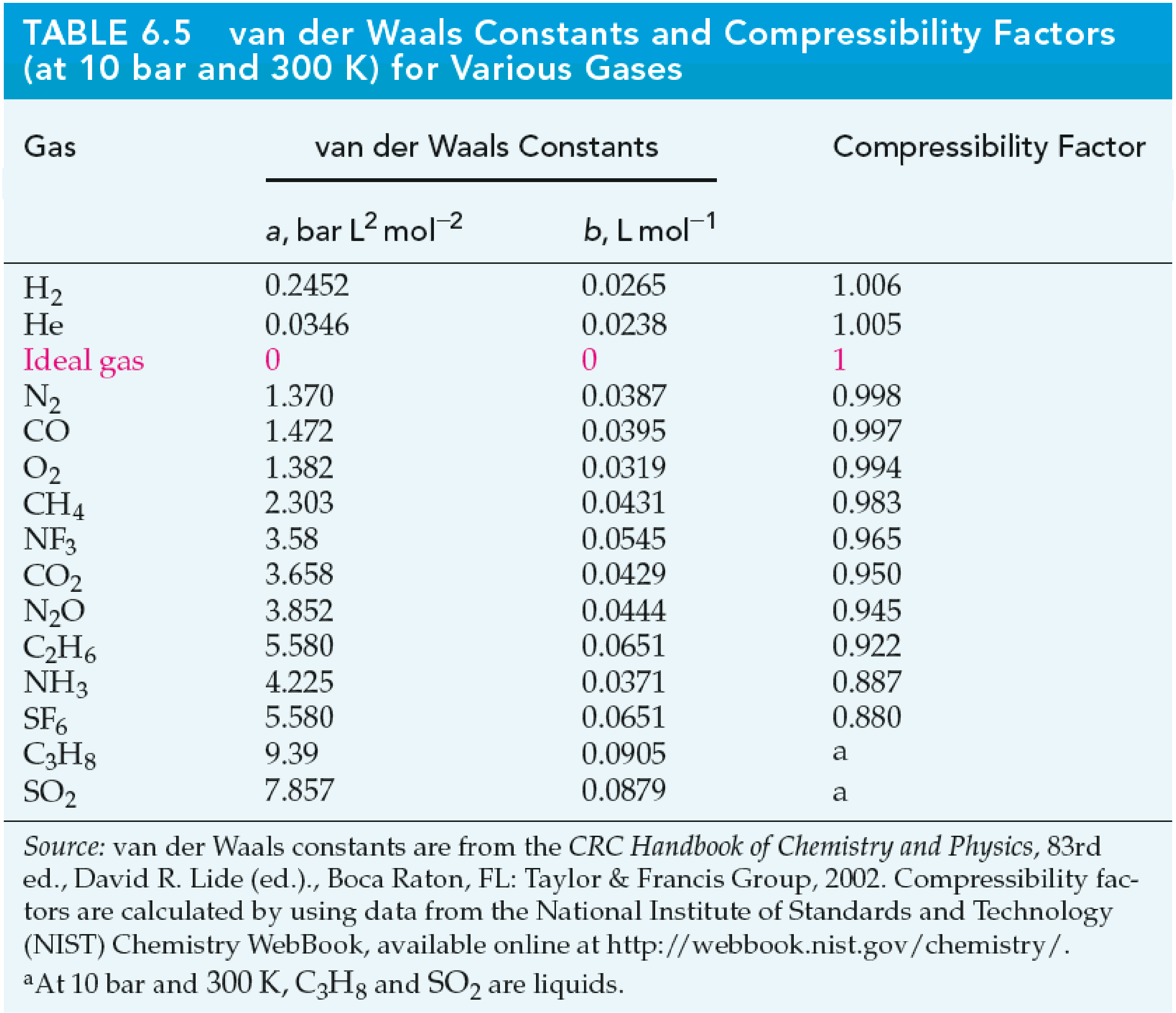
- The second part in the equation is the modified volume factor, $V-nb$ *and* the term 'nb' accounts for the volume of the molecules themselves.

- The parameter *b is* called the *excluded volume per mole, and, to a rough approximation, it is the volume* that one mole of gas occupies when it condenses to a liquid.

- Because the molecules are not point masses, the volume of the container must be no smaller than *nb, and the volume available for molecular motion is* , $V-nb$

- As suggested in Figure 6-21(b), the volume available for molecular motion is quite small at high pressures.

A close examination of Table 6.5



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N_2O	3.852	0.0444	0.945
C_2H_6	5.580	0.0651	0.922
NH_3	4.225	0.0371	0.887
SF_6	5.580	0.0651	0.880
C_3H_8	9.39	0.0905	[a]
SO_2	7.857	0.0879	[a]

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[a] At 10 bar and 300 K, C_3H_8 and SO_2 are liquids.

- the values of both *a and b* increase as the sizes of the molecules increase.

-The smaller the values of *a and b, the more closely the gas resembles an ideal gas.*

- *Deviations from ideality, as* measured by the compressibility factor, become more pronounced as the values of *a and b increase.*

EXAMPLE 6-17 Using the van der Waals Equation to Calculate the Pressure of a Gas

Use the van der Waals equation to calculate the pressure exerted by 1.00 mol $Cl_2(g)$ confined to a volume of 2.00 L at 273 K. The value of $a = 6.49\ L^2\ atm\ mol^{-2}$, and that of $b = 0.0562\ L\ mol^{-1}$.

Analyze

This is a straightforward application of equation (6.26). It is important to include units to make sure the units cancel out properly.

Solve

Solve equation (6.26) for P.

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

Then substitute the following values into the equation.

$$n = 1.00\ \text{mol};\ V = 2.00\ \text{L};\ T = 273\ \text{K};\ R = 0.08206\ \text{atm L mol}^{-1}\ \text{K}^{-1}$$

$$n^2a = (1.00)^2\ \text{mol}^2 \times 6.49\frac{\text{L}^2\ \text{atm}}{\text{mol}^2} = 6.49\ \text{L}^2\ \text{atm}$$

$$nb = 1.00\ \text{mol} \times 0.0562\ \text{L mol}^{-1} = 0.0562\ \text{L}$$

$$P = \frac{1.00\ \text{mol} \times 0.08206\ \text{atm L mol}^{-1}\ \text{K}^{-1} \times 273\ \text{K}}{(2.00 - 0.0562)\text{L}} - \frac{6.49\ \text{L}^2\ \text{atm}}{(2.00)^2\ \text{L}^2}$$

$$P = 11.5\ \text{atm} - 1.62\ \text{atm} = 9.9\ \text{atm}$$

Assess

The pressure calculated with the ideal gas equation is 11.2 atm. By including only the b term in the van der Waals equation, we get a value of 11.5 atm. Including the a term reduces the calculated pressure by 1.62 atm. Under the conditions of this problem, intermolecular forces of attraction are the main cause of the departure from ideal behavior. Although the deviation from ideality here is rather large, in problem-solving situations, you can generally assume that the ideal gas equation will give satisfactory results.

PRACTICE EXAMPLE A: Substitute $CO_2(g)$ for $Cl_2(g)$ in Example 6-17, given the values $a = 3.66\ L^2\ bar\ mol^{-2}$ and $b = 0.0427\ L\ mol^{-1}$. Which gas, CO_2 or Cl_2, shows the greater departure from ideal gas behavior? [*Hint:* For which gas do you find the greater difference in calculated pressures, first using the ideal gas equation and then the van der Waals equation?]

PRACTICE EXAMPLE B: Substitute CO(g) for $Cl_2(g)$ in Example 6-17, given the values $a = 1.47\ L^2\ bar\ mol^{-2}$ and $b = 0.0395\ L\ mol^{-1}$. Including CO_2 from Practice Example 6-17A, which of the three gases—Cl_2, CO_2, or CO—shows the greatest departure from ideal gas behavior?

End of Chapter Questions

A problem is like a knot in a ball of wool:

- If you pull hard on any loop:
  - The knot will only tighten.
  - The solution (undoing the knot) will not be achieved.
- If you pull lightly on one loop and then another:
  - You gradually loosen the knot.
  - As more loops are loosened it becomes easier to undo the subsequent ones.

Don’t pull too hard on any one piece of information in your problem, it tightens.