CHAPTER 5
THE GASEOUS STATE

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5. The Gaseous State

FIGURE 5.1

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

- Cylinder
- Tank
- Pressure
- Gauge
- Temperature
- Volume
- Compressibility

5.1 Gas Pressure and Its Measurement

TABLE 5.1 **Properties of Selected Gases**

Name	Formula	Color	Odor	Toxicity
Ammonia	NH_3	Colorless	Penetrating	Toxic
Carbon dioxide	CO_2	Colorless	Odorless	Nontoxic
Carbon monoxide	CO	Colorless	Odorless	Very toxic
Chlorine	Cl_2	Pale green	Irritating	Very toxic
Hydrogen	H_2	Colorless	Odorless	Nontoxic
Hydrogen sulfide	H_2S	Colorless	Foul	Very toxic
Methane	CH_4	Colorless	Odorless	Nontoxic
Nitrogen dioxide	NO_2	Red-brown	Irritating	Very toxic

5.1 Gas Pressure and Its Measurement

- Pressure: the force exerted per unit area of surface.

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

TABLE 5.2 Important Units of Pressure

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

5.1 Gas Pressure and Its Measurement

- **A mercury barometer**

Atmospheric pressure (atm)

= 760 mmHg

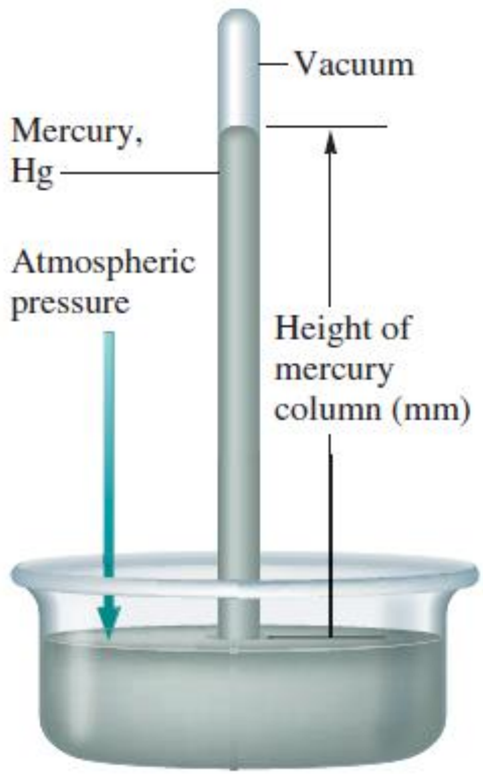
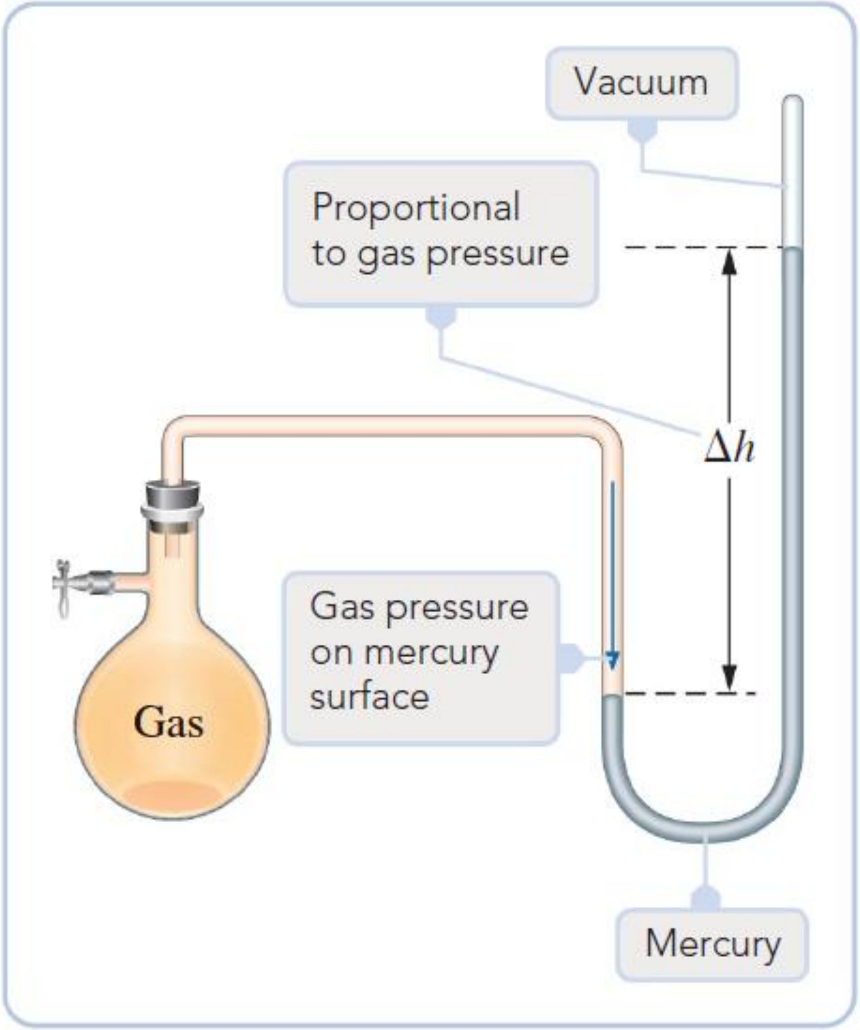


FIGURE 5.2

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

5.1 Gas Pressure and Its Measurement

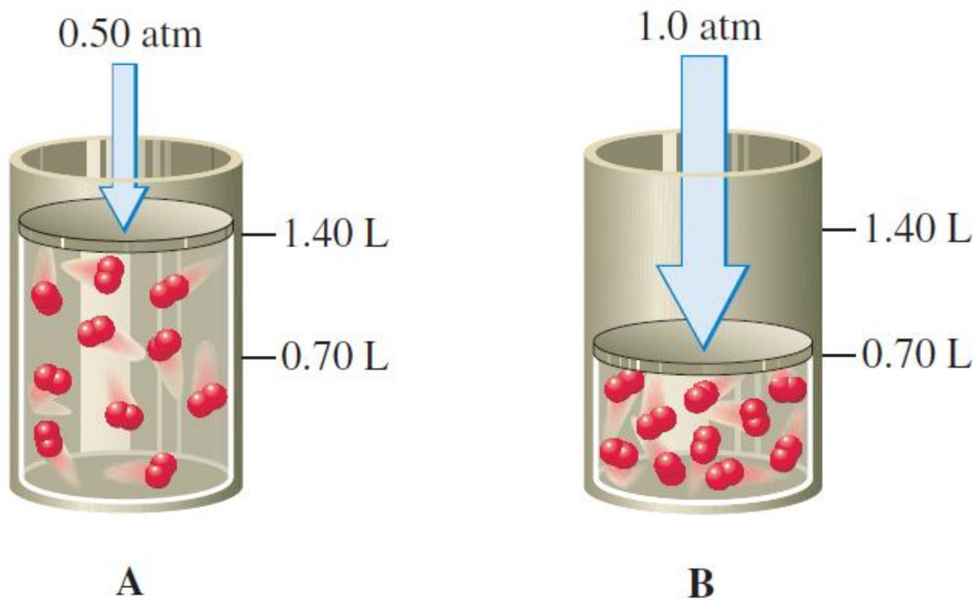
- **A manometer**



5.2 Empirical Gas Laws

- Boyle's Law: the volume of a sample of gas at a given temperature varies inversely with the applied pressure

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



P180 Example 5.2 Using Boyle's Law

A volume of air occupying 12.0 dm^3 at 98.9 kPa is compressed to a pressure of 119.0 kPa. The temperature remains constant. What is the new volume?

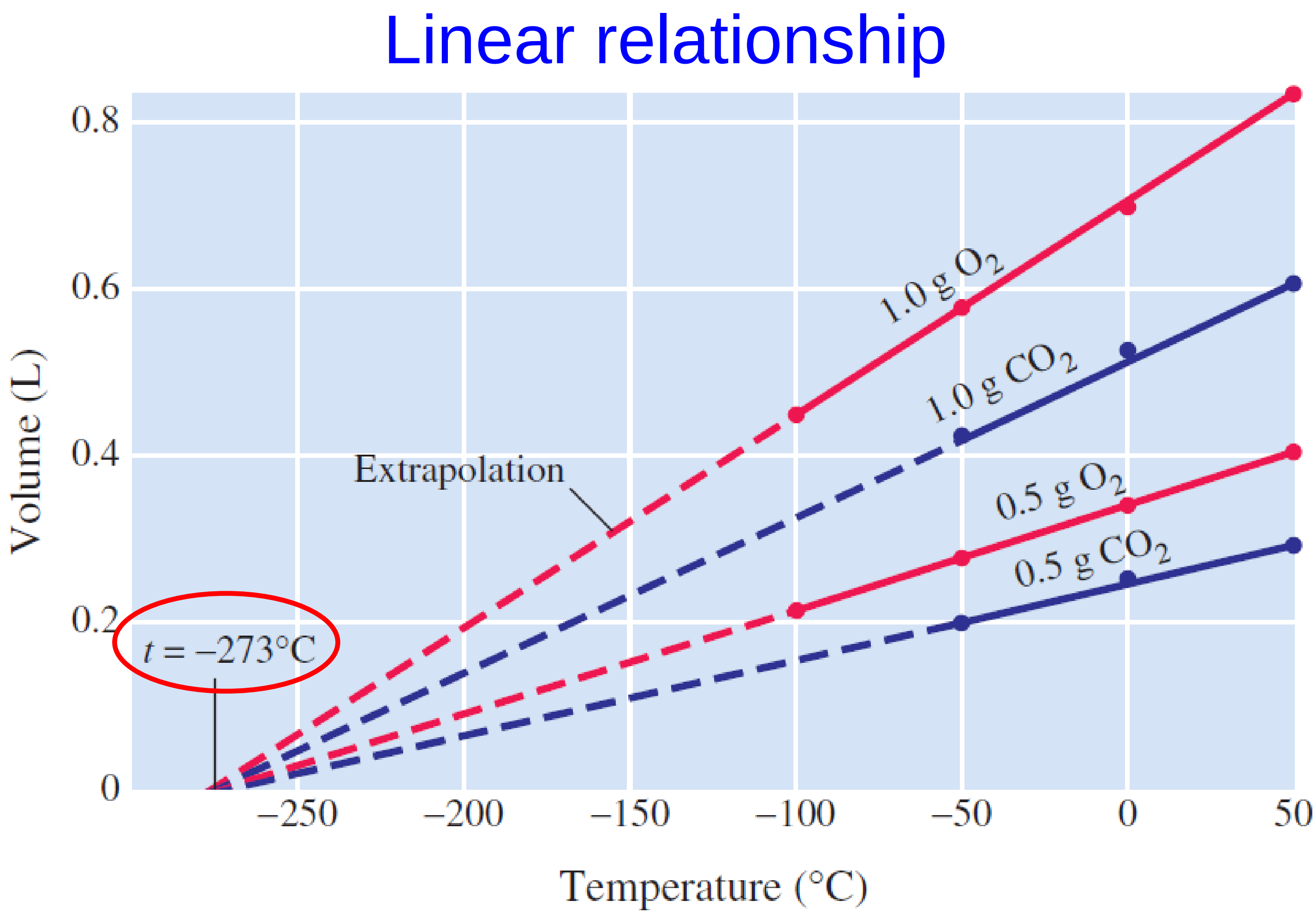
$$V_f = V_i \times \frac{P_i}{P_f} = 12.0\ \mathrm{dm}^3 \times \frac{98.9\ \cancel{\mathrm{kPa}}}{119.0\ \cancel{\mathrm{kPa}}} = \mathbf{9.97\ dm^3}$$

5.2 Empirical Gas Laws

- Charles's Law: the volume occupied by any sample of gas at a constant pressure is directly proportional to the absolute temperature

5.2 Empirical Gas Laws

- Charles's Law



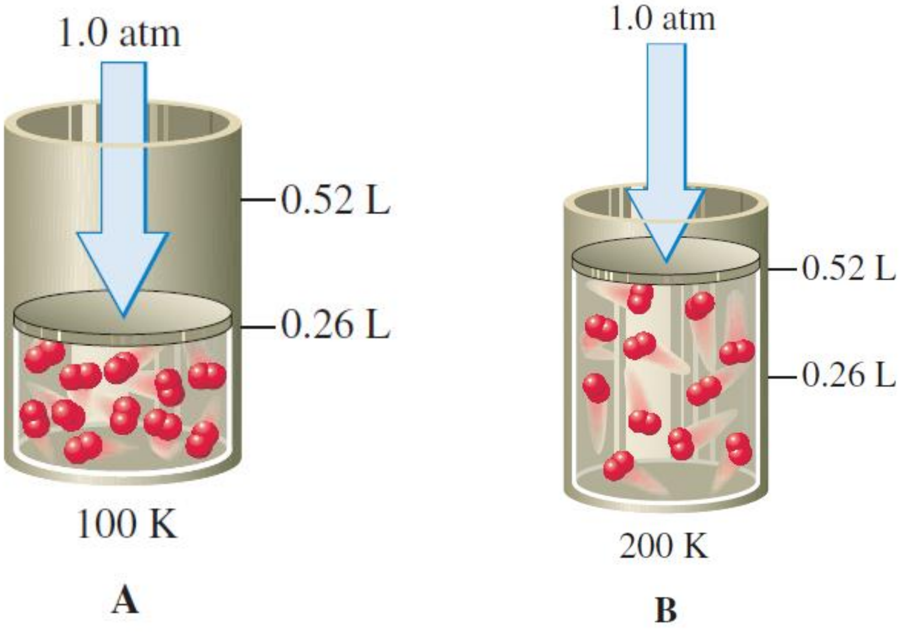
5.2 Empirical Gas Laws

- Charles's Law

Charles's law:

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

absolute temperature (K)



P182 Example 5.3 Using Charles's Law

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

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

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

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

5.2 Empirical Gas Laws

- Combined Gas Law

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

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

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

P184 Example 5.4 Using the Combined Gas Law

Modern determination of %N in an organic compound is an automated version of one developed by the French chemist Jean-Baptiste Dumas in 1830. The Dumas method uses hot copper(II) oxide to oxidize C and H in the compound to CO_2 and H_2O (both are trapped chemically) and to convert N in the compound to N_2 gas. Using the Dumas method, 39.8 mg of caffeine gives 10.1 cm^3 of nitrogen gas at 23 °C and 746 mmHg. What is the volume of nitrogen at 0 °C and 760 mmHg?

P184 Example 5.4 Using the Combined Gas Law

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

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

5.2 Empirical Gas Laws

- Avogadro's Law: equal volumes of any two gases at the same temperature and pressure contain the same number of molecules.
- Molar gas volume (V_m): the volume of one mole of gas
- Standard temperature and pressure (STP): 0 °C, 1 atm
- At STP, the molar gas volume is found to be 22.4 L/mol

5.3 The Ideal Gas Law

TABLE 5.5

Molar Gas Constant in Various Units

Value of *R*
0.082058 L·atm/(K·mol)
8.3145 J/(K·mol)*
8.3145 kg·m²/(s²·K·mol)
8.3145 kPa·dm³/(K·mol)
1.9872 cal/(K·mol)*

Ideal gas law:

$$PV = nRT$$

molar gas constant

= 8.314 J/(mol·K)

= 0.0821 L·atm/(mol·K)

P189 Exercise 5.6 Using the Ideal Gas Law

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

Variable	*Value*
P	15.7 atm
V	50.0 L
T	$(21 + 273)\ \text{K} = 294\ \text{K}$
n	?

P189 Exercise 5.6 Using the Ideal Gas Law

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

$$32.5\ \cancel{\text{mol O}_2} \times \frac{32.0\ \text{g O}_2}{1\ \cancel{\text{mol O}_2}} = \mathbf{1.04 \times 10^3\ g\ O_2}$$

5.3 The Ideal Gas Law

$$PM_M = dRT$$

What is the molecular mass of a substance weighing 0.970 g whose vapor occupies 200.0 mL at 99 °C and 733 mmHg?

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

5.4 Stoichiometry Problems Involving Gas Volumes

$$2KClO_3(s) \xrightarrow[MnO_2]{\Delta} 2KCl(s) + 3O_2(g)$$

0.0100 mol

? L
at 298 K
and 1.02 atm

P193 Example 5.9

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

$$6NaN_3(s) + Fe_2O_3(s) \rightarrow 3Na_2O(s) + 2Fe(s) + 9N_2(g)$$

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

P193 Example 5.9

Variable	*Value*
P	$748\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.984\ \text{atm}$
V	75.0 L
T	$(25 + 273)\ \text{K} = 298\ \text{K}$
n	?

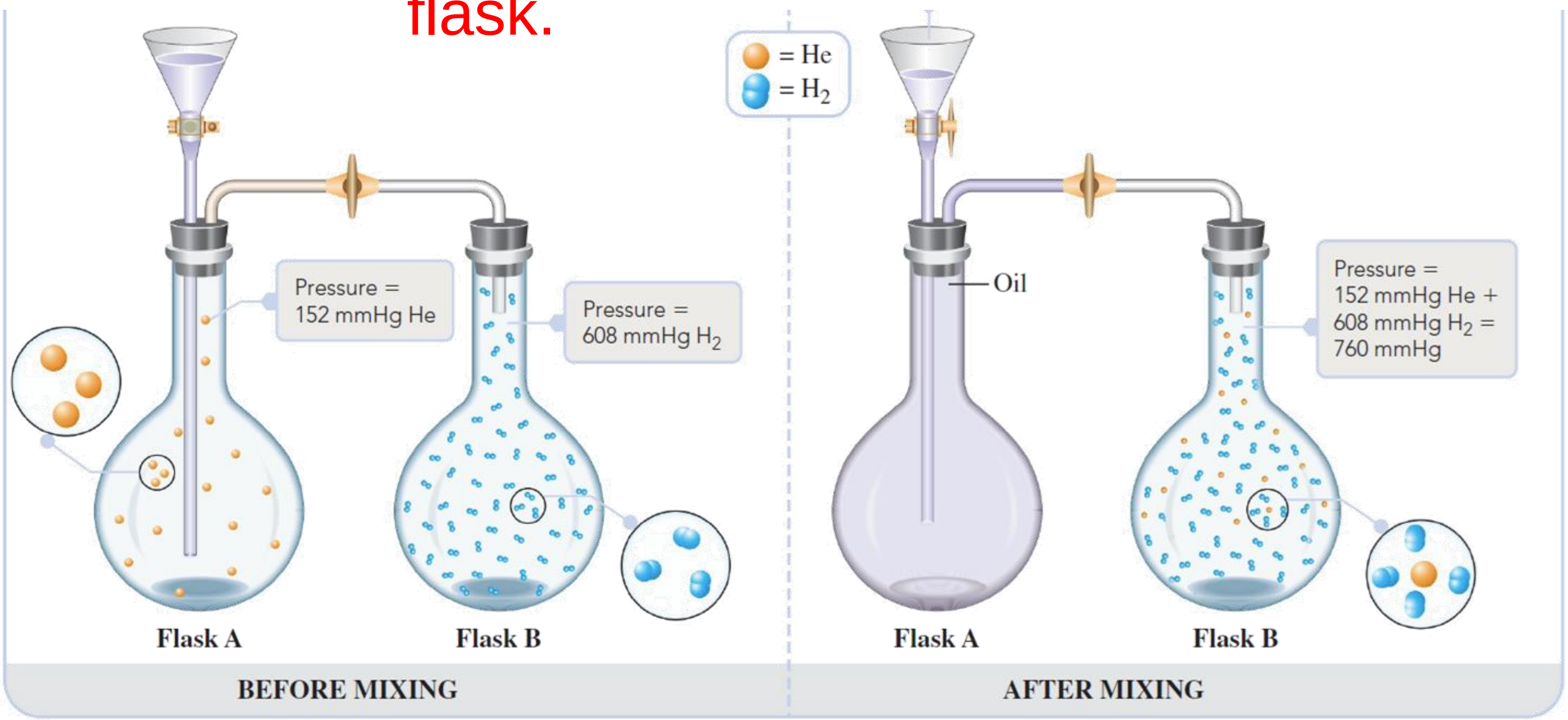
$$n = \frac{0.984\ \cancel{\text{atm}} \times 75.0\ \cancel{\text{L}}}{0.0821\ \cancel{\text{L}}\cdot\cancel{\text{atm}}/(\cancel{\text{K}}\cdot\text{mol}) \times 298\ \cancel{\text{K}}} = 3.02\ \text{mol}$$

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

$$2.01\ \cancel{\text{mol NaN}_3} \times \frac{65.01\ \text{g NaN}_3}{1\ \cancel{\text{mol NaN}_3}} = \mathbf{131\ g\ NaN_3}$$

5.5 Gas Mixtures; Law of Partial Pressures

Each gas exerts the same pressure it would exert if it were the only gas in the flask.



5.5 Gas Mixtures; Law of Partial Pressures

- Partial Pressures
  - The pressure exerted by a particular gas in a mixture is the partial pressure of that gas.
  - According to Dalton's law of partial pressures, the sum of the partial pressures of all the different gases in a mixture is equal to the total pressure of the mixture.

Dalton's law of partial pressures:

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

5.5 Gas Mixtures; Law of Partial Pressures

- Mole Fractions
  - The fraction of moles of that component in the total moles of gas mixture.

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

P196 Example 5.10

A 1.00-L sample of dry air at 25 °C and 786 mmHg contains 0.925 g N_2, plus other gases including oxygen, argon, and carbon dioxide. a. What is the partial pressure (in mmHg) of N_2 in the air sample? b. What is the mole fraction and mole percent of N_2 in the mixture?

a.

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

$$P_{N_2} = \frac{n_{N_2}RT}{V}$$

$$= \frac{0.0330\ \cancel{\text{mol}} \times 0.0821\ \cancel{\text{L}}\cdot\text{atm}/(\cancel{\text{K}}\cdot\cancel{\text{mol}}) \times 298\ \cancel{\text{K}}}{1.00\ \cancel{\text{L}}}$$

$$= 0.807\ \text{atm}\ (\mathbf{= 613\ mmHg})$$

P196 Example 5.10

b.

$$\text{Mole fraction of } N_2 = \frac{P_{N_2}}{P} = \frac{613\ \cancel{\text{mmHg}}}{786\ \cancel{\text{mmHg}}} = \mathbf{0.780}$$

5.6 Kinetic Theory of an Ideal Gas

- Gas pressure results from the continual bombardment of the container walls by constantly moving molecules.

5.6 Kinetic Theory of an Ideal Gas

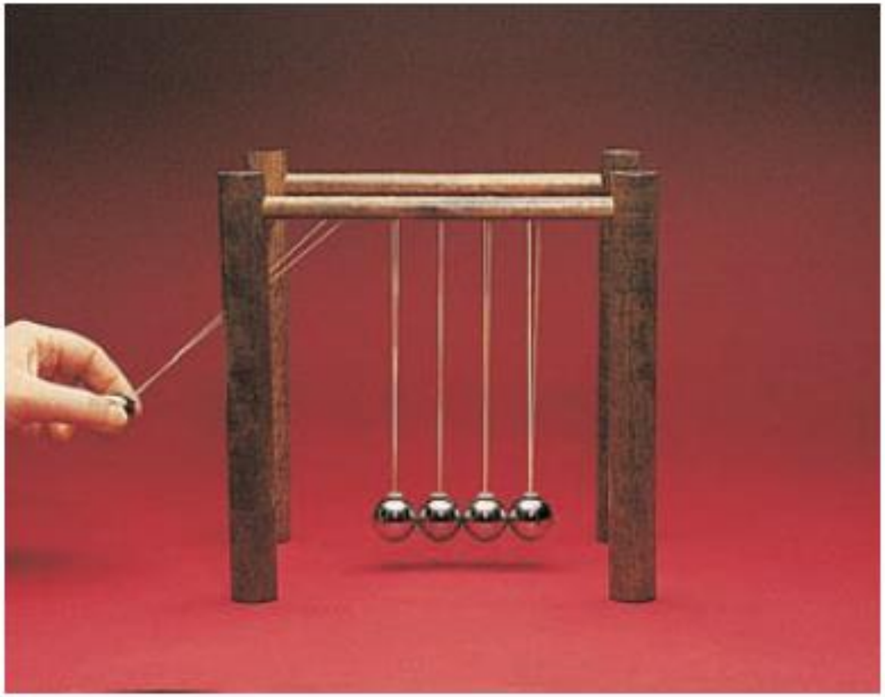
- Postulates of Kinetic Theory
- **Postulate 1:** Gases are composed of molecules whose size is negligible compared with the average distance between them.
- **Postulate 2:** Molecules move randomly in straight lines in all directions and at various speeds.

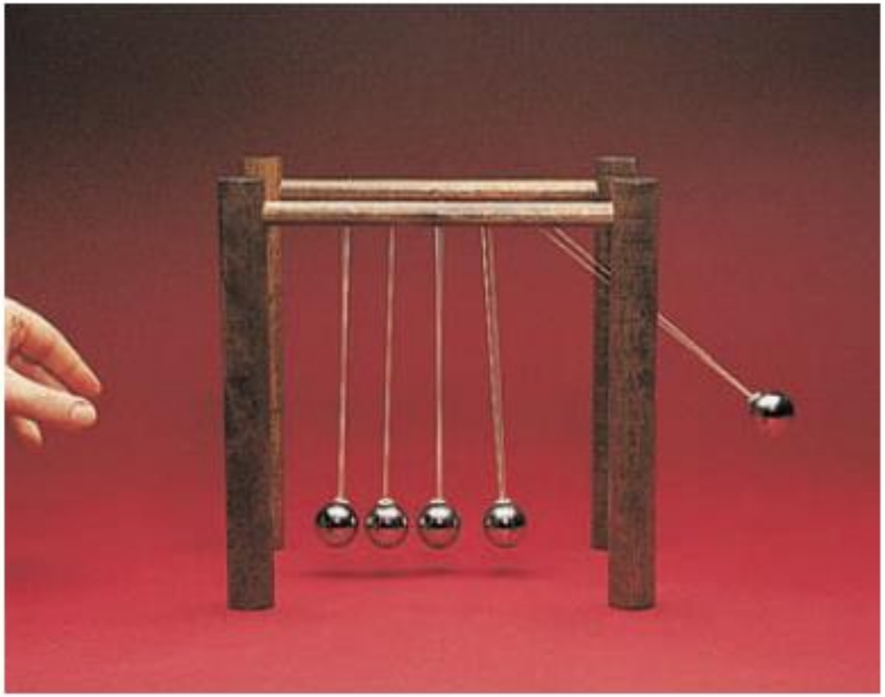
5.6 Kinetic Theory of an Ideal Gas

- Postulates of Kinetic Theory
- **Postulate 3:** The forces of attraction or repulsion between two molecules (intermolecular forces) in a gas are very weak or negligible, except when they collide.

5.6 Kinetic Theory of an Ideal Gas

- Postulates of Kinetic Theory
- **Postulate 4:** When molecules collide with one another, the collisions are elastic.





5.6 Kinetic Theory of an Ideal Gas

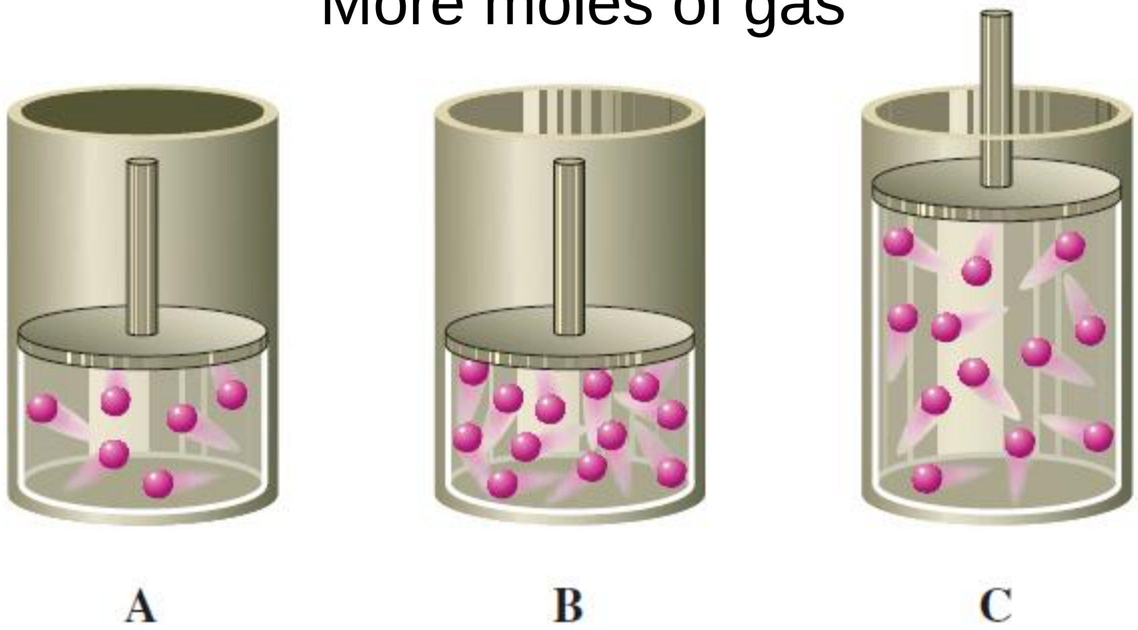
- Postulates of Kinetic Theory
- **Postulate 5:** The average kinetic energy of a molecule is proportional to the absolute temperature.

5.6 Kinetic Theory of an Ideal Gas

- Qualitative Interpretation of the Gas Laws

Avogadro's Law

More moles of gas



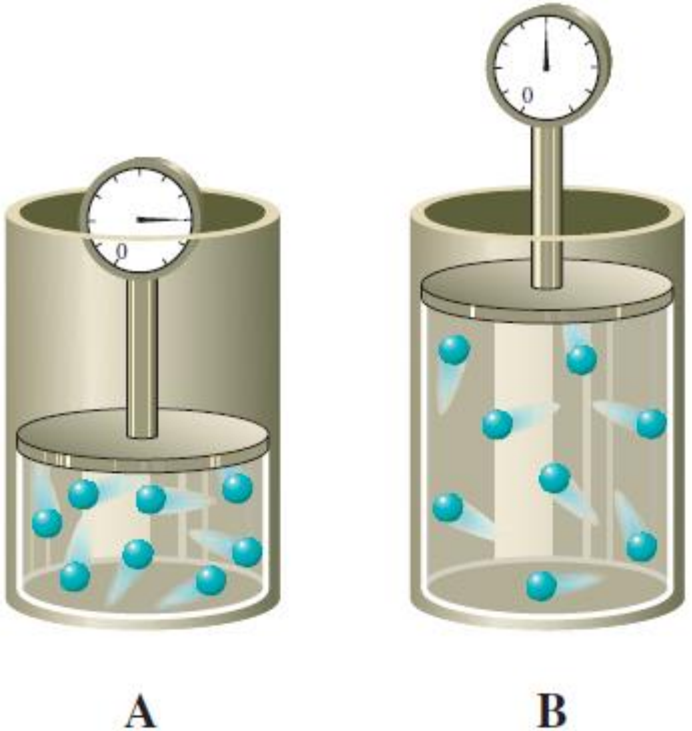
Volume increases

Pressure remains constant

5.6 Kinetic Theory of an Ideal Gas

- Qualitative Interpretation of the Gas Laws

Boyle's Law



Volume increases

Temperature constant

Pressure decreases

5.6 Kinetic Theory of an Ideal Gas

- Qualitative Interpretation of the Gas Laws

Charles's Law

Temperature increases

pressure constant

⇩

volume increases

- The Ideal Gas Law from Kinetic Theory

$$PV = nRT$$

5.7 Molecular Speeds; Diffusion and Effusion

- Molecular Speeds

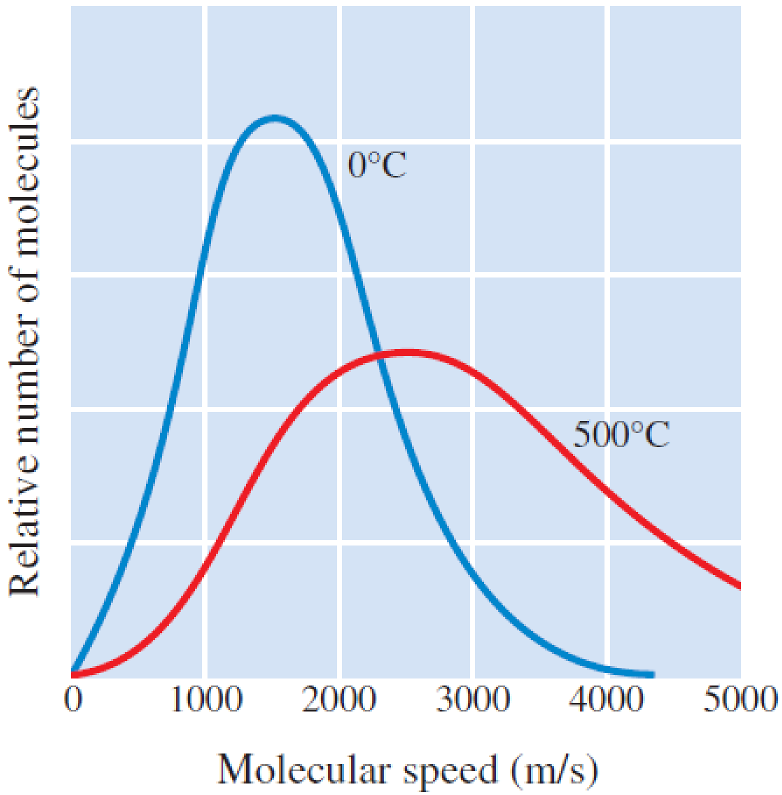


FIGURE 5.25

Maxwell's distribution of molecular speeds

root-mean-square (rms) molecular speed

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

R is the molar gas constant,

T is the absolute temperature,

M_m is the molar mass for the gas

5.7 Molecular Speeds; Diffusion and Effusion

- Molecular Speeds

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

R = 8.31 kg·m^2/(s^2·K·mol))

T in K,

M_m in kg/mol

u in m/s

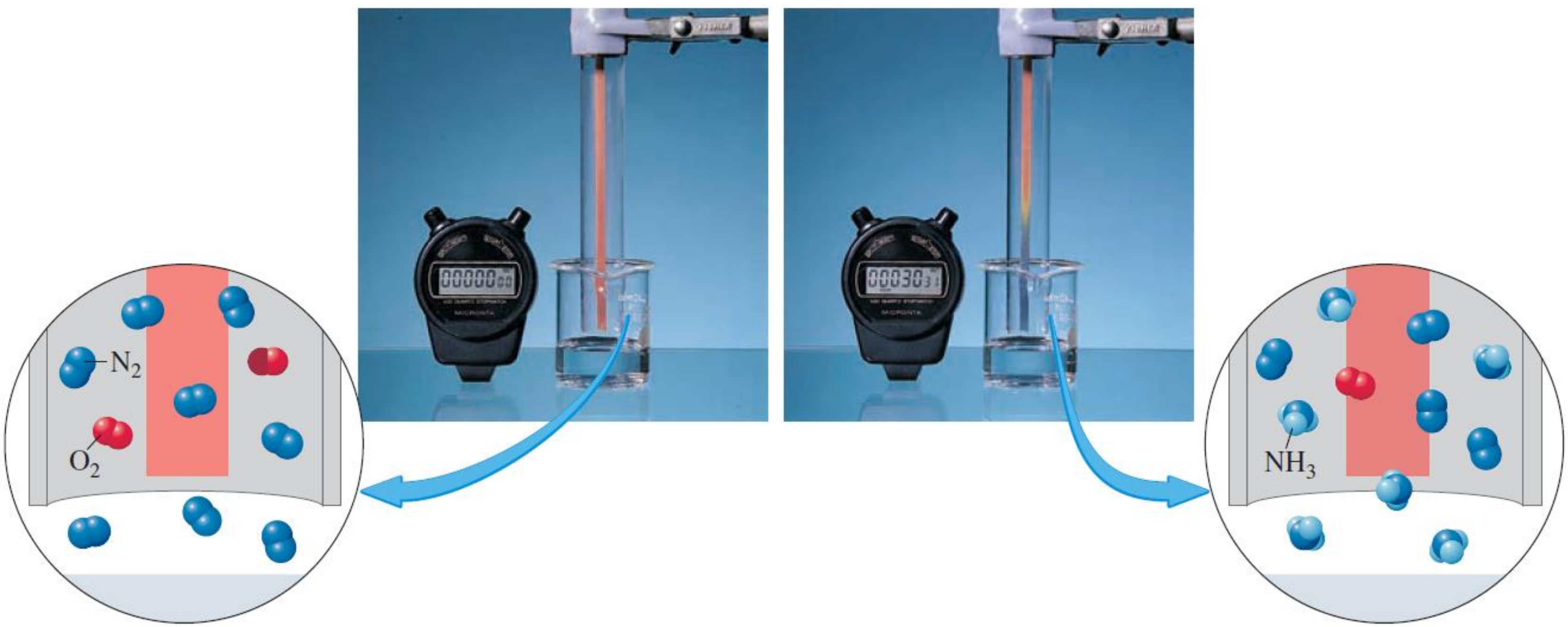
P202 Example 5.12

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

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

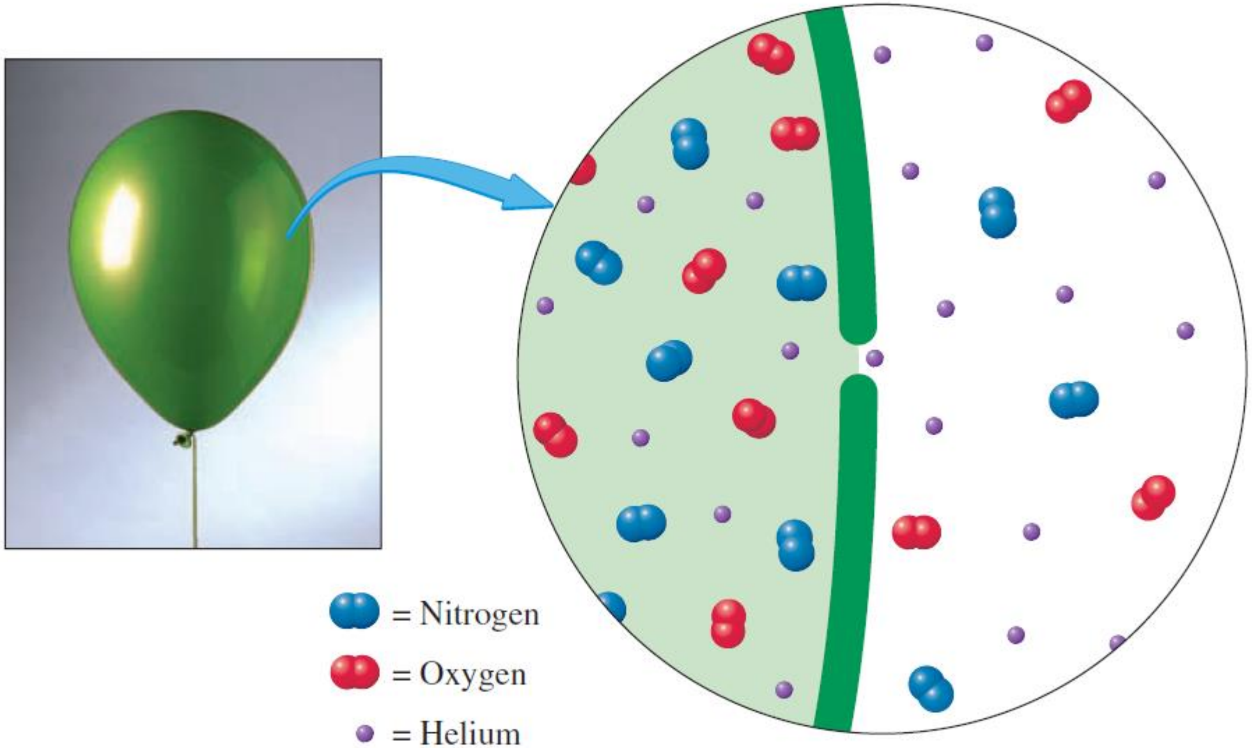
5.7 Molecular Speeds; Diffusion and Effusion

- Diffusion and Effusion
- Gaseous **diffusion** is the process whereby a gas spreads out through another gas to occupy the space uniformly



5.7 Molecular Speeds; Diffusion and Effusion

- Diffusion and Effusion
- The process in which a gas flows through a small hole in a container is called effusion.



5.7 Molecular Speeds; Diffusion and Effusion

- Effusion: Graham's law of effusion
- The rate of effusion of gas molecules from a particular hole is inversely proportional to the square root of the molecular mass of the gas at constant temperature and pressure.

Graham's law of effusion:

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

P205 Example 5.13

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

$$\frac{\text{Rate of effusion of } CO_2}{\text{Rate of effusion of } SO_2} = \sqrt{\frac{64.1 \text{ g/mol}}{44.0 \text{ g/mol}}} = \mathbf{1.21}$$

5.8 Real Gases

- The ideal gas law describes the behavior of real gases quite well at low pressures and moderate temperatures,
- but not at high pressures and low temperatures

van der Waals equation

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