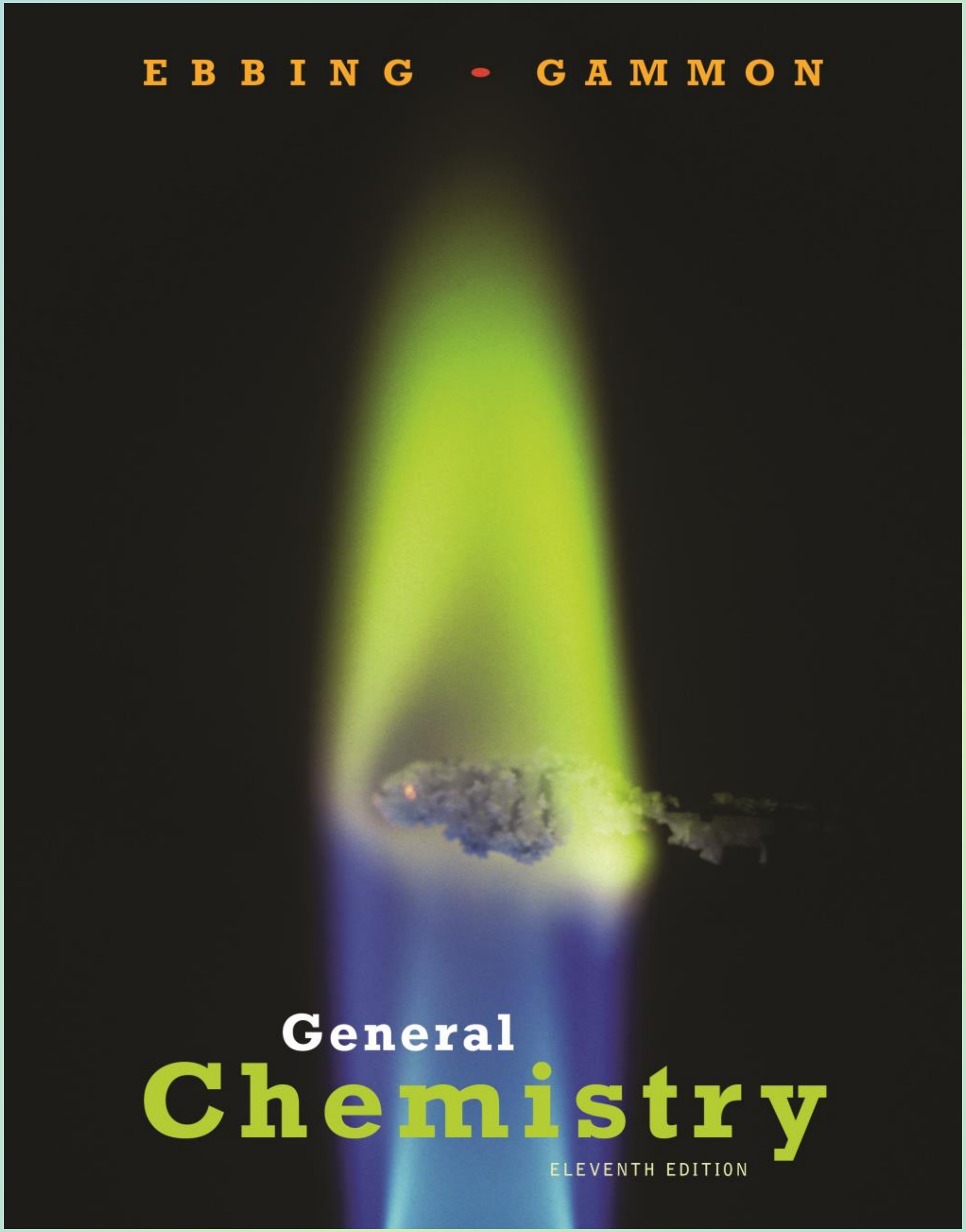


The Gaseous State

➢ Gas Laws

Most substances composed of small molecules are gases under normal conditions or else are easily vaporized liquids

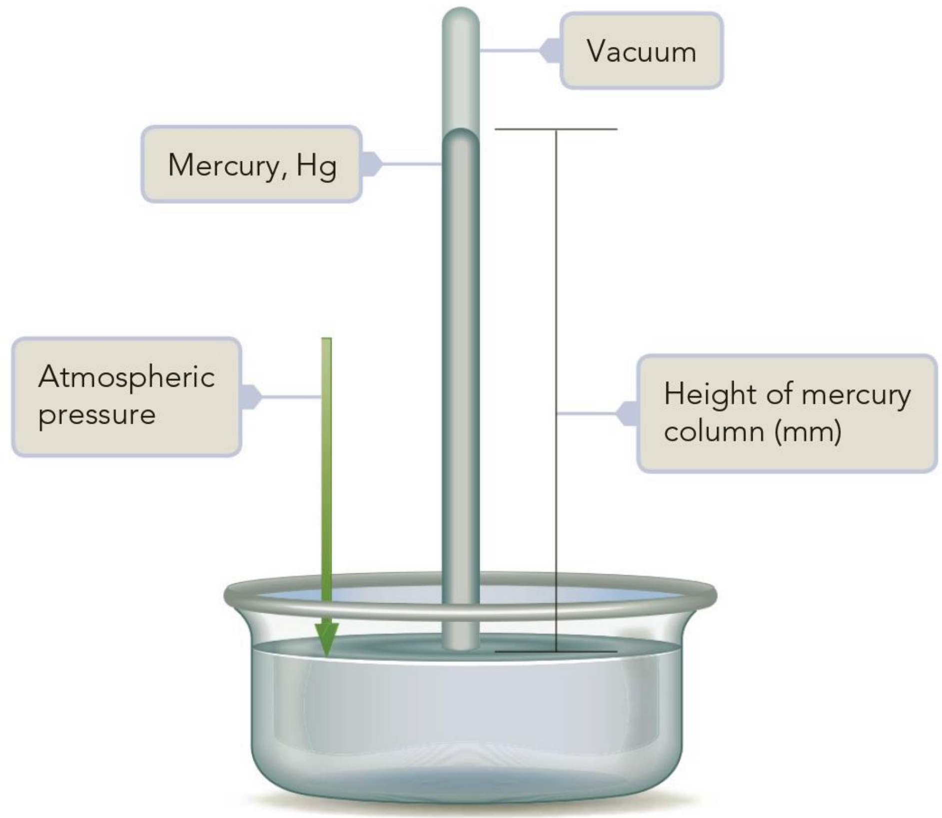
Table 5.1 Properties of Selected Gases

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 is defined as *the force exerted per unit area of surface*

- ✓ Force = mass × constant acceleration of gravity
- ✓ *SI unit of pressure, $kg/(m \cdot s^2)$,* is given the name **pascal (Pa)**
- ✓ A **barometer** is *a device for measuring the pressure of the atmosphere*
- ✓ A **manometer**, *a device that measures the pressure of a gas or liquid in a vessel*



mercury barometer

✓ Pressure of a coin (9.3 mm in radius and 2.5 g)

Force = mass x g = $(2.5 \times 10^{-3}\ \text{kg}) \times (9.81\ \text{m/s}^2)$

Area = π x $(\text{radius})^2 = 3.14 \times (9.3 \times 10^{-3}\ \text{m})^2$

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

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

$$P = gdh$$

Table 5.2 Important Units of Pressure

Unit	Relationship or Definition
Pascal (Pa)	$\text{kg/(m·s}^2)$
Atmosphere (atm)	$1\ \text{atm} = 1.01325 \times 10^5\ \text{Pa} \simeq 101\ \text{kPa}$
mmHg, or torr	$760\ \text{mmHg} = 1\ \text{atm}$
Bar	$1.01325\ \text{bar} = 1\ \text{atm}$

Example 5.1 Converting Units of Pressure

(Q) The pressure of a gas in a flask is measured to be 797.7 mmHg. What is this pressure in pascals and atmospheres?

Solution Conversion to pascals:

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

Conversion to atmospheres:

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

- **5.2 Empirical Gas Laws**

- Boyle's Law: Relating Volume and Pressure

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

the volume of a sample of gas at a given temperature varies inversely with the applied pressure. That is, $V \propto 1/P$, where V is the volume, P is the pressure,

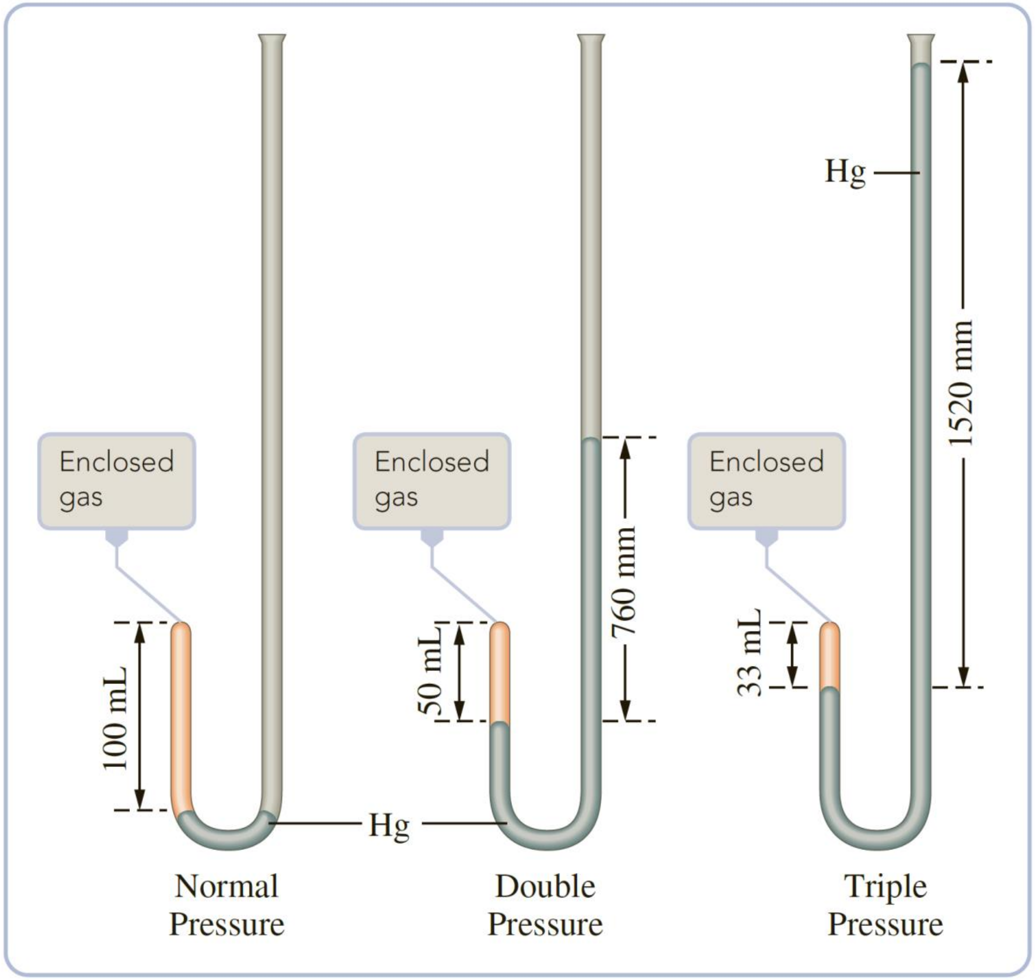


Table 5.3 Pressure–Volume Data for 1.000 g O_2 at 0°C

P (atm)	V (L)	PV
0.2500	2.801	0.7002
0.5000	1.400	0.7000
0.7500	0.9333	0.7000
1.000	0.6998	0.6998
2.000	0.3495	0.6990
3.000	0.2328	0.6984
4.000	0.1744	0.6976
5.000	0.1394	0.6970

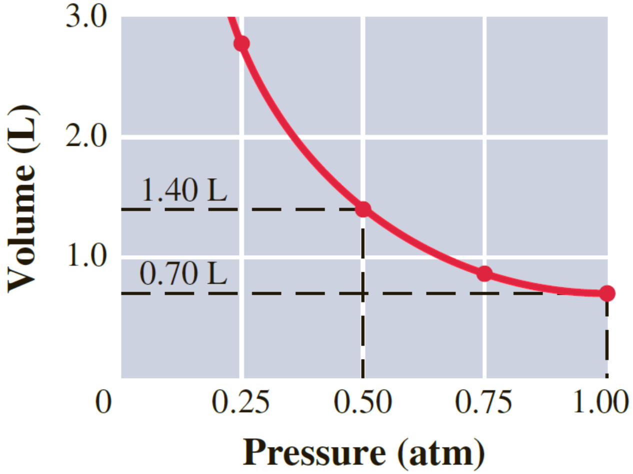
Increasing pressure (↓) — Increasing volume (↑)

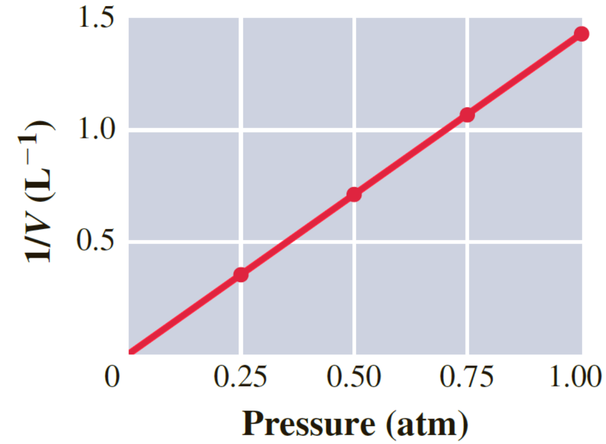
- Boyle's experiment:

The volume of the gas at normal atmospheric pressure (760 mmHg) is 100 mL. When the pressure is doubled by adding 760 mm of mercury, the volume is halved (to 50 mL).

Tripling the pressure decreases the volume to one-third of the original (to 33 mL).

$$PV = \text{constant} \rightarrow P_1V_1 = P_2V_2$$





(Q) 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?

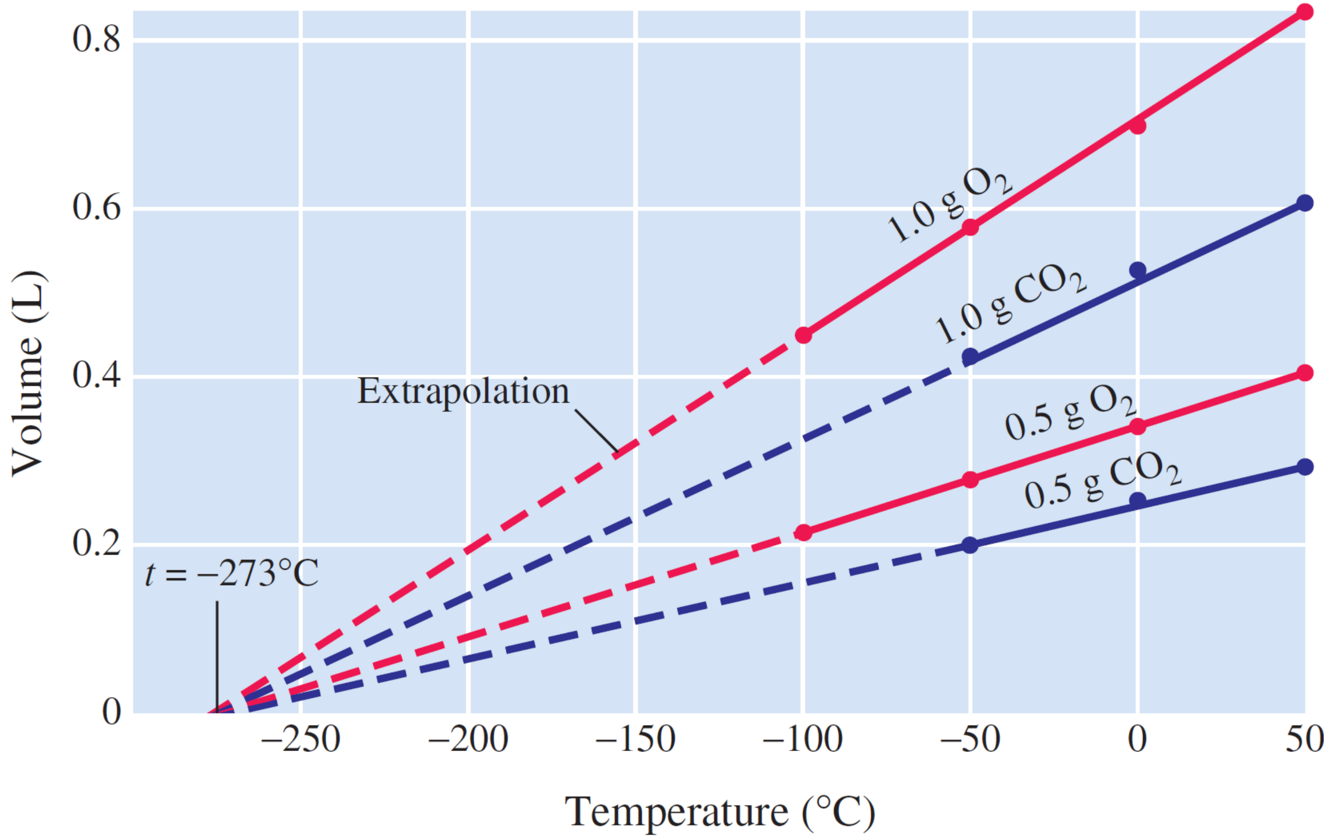
$$P_iV_i = P_fV_f$$

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

➢ Charles's Law: Relating Volume and Temperature

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

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



Exercise 5.3 If you expect a chemical reaction to produce 4.38 dm^3 of oxygen, O_2, at 19°C and 101 kPa, what will be the volume at 25°C and 101 kPa?

First, convert the temperatures to the Kelvin.

T_i = (19 + 273) = 292 K

T_f = (25 + 273) = 298 K

Apply Charles's law

$$V_f = V_i \times \frac{T_f}{T_i} = 4.38\ \text{dm}^3 \times \frac{298\ \text{K}}{292\ \text{K}} = 4.4\underline{7}0 = 4.47\ \text{dm}^3$$

- Combined Gas Law: Relating Volume, Temperature, and Pressure

- ✓ Boyle's law ($V \propto 1/P$) and Charles's law ($V \propto T$) can be combined to:

$$V \propto T/P$$

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

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

(Q) A 39.8 mg sample of caffeine gives 10.1 cm^3 of N_2 gas at 23°C and 746 mmHg. What is the volume of N_2 at 0°C and 760 mmHg?

T_i = (23 + 273) K = 296 K

T_f = (0 + 273) K = 273 K

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

(Q) What will be the final pressure of a sample of nitrogen gas with a volume of 950. m^3 at 745 torr and 25.0 °C if it is heated to 60.0 °C and given a final volume of 1150 m^3?

Exercise 5.4

A balloon contains 5.41 dm^3 of helium, He, at 24°C and 101.5 kPa. Suppose the gas in the balloon is heated to 35°C. If the helium pressure is now 102.8 kPa, what is the volume of the gas?

T_i = (24 + 273) = 297 K

T_f = (35 + 273) = 308 K

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i} = 5.41\ \text{dm}^3 \times \frac{101.5\ \text{kPa}}{102.8\ \text{kPa}} \times \frac{308\ \text{K}}{297\ \text{K}} = 5.5\underline{3}9 = 5.54\ \text{dm}^3$$

➢ Avogadro's Law: Relating Volume and Amount

- ✓ French chemist Joseph Louis Gay-Lussac concluded from experiments on gas reactions that:

the volumes of reactant gases at the same pressure and temperature are in ratios of small whole numbers (*the law of combining volumes*).

$$\underset{\text{2 volumes}}{2H_2(g)} + \underset{\text{1 volume}}{O_2(g)} \longrightarrow 2H_2O(g)$$

- ✓ **Avogadro's law**:

equal volumes of any two gases at the same temperature and pressure contain the same number of molecules.

- ✓ *volume of **one mole** of gas* is called the molar gas volume, V_m.

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

STP = Standard Temperature and Pressure (*0°C and 1 atm*)

➢ **5.3** The Ideal Gas Law

$$PV = nRT$$

(Q) How many grams of oxygen are there in a 50.0-L gas cylinder at 21°C when the oxygen pressure is 15.7 atm?

Exercise 5.6

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

(Q) Calculate the volume (in L) occupied by 7.40 g of NH_3 at STP

$$V = 7.40\ \cancel{\text{g NH}_3} \times \frac{1\ \cancel{\text{mol NH}_3}}{17.03\ \cancel{\text{g NH}_3}} \times \frac{22.41\ \text{L}}{1\ \cancel{\text{mol NH}_3}}$$

$$= 9.74\ \text{L}$$

➢ Gas Density; Molecular-Weight Determination

$$PM_m = dRT$$

d is the density of the gas in g/L

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

$d = PM_m/RT = (0.85 \text{ X } 32)/ (0.082 \text{ X } 298) = 1.11$ g/L

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

$M_m = dRT/P = (2.26 \times 0.082 \times 298) / 0.862 = 64.1$ g/mol

5.4 Stoichiometry Problems Involving Gas Volumes

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

Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3

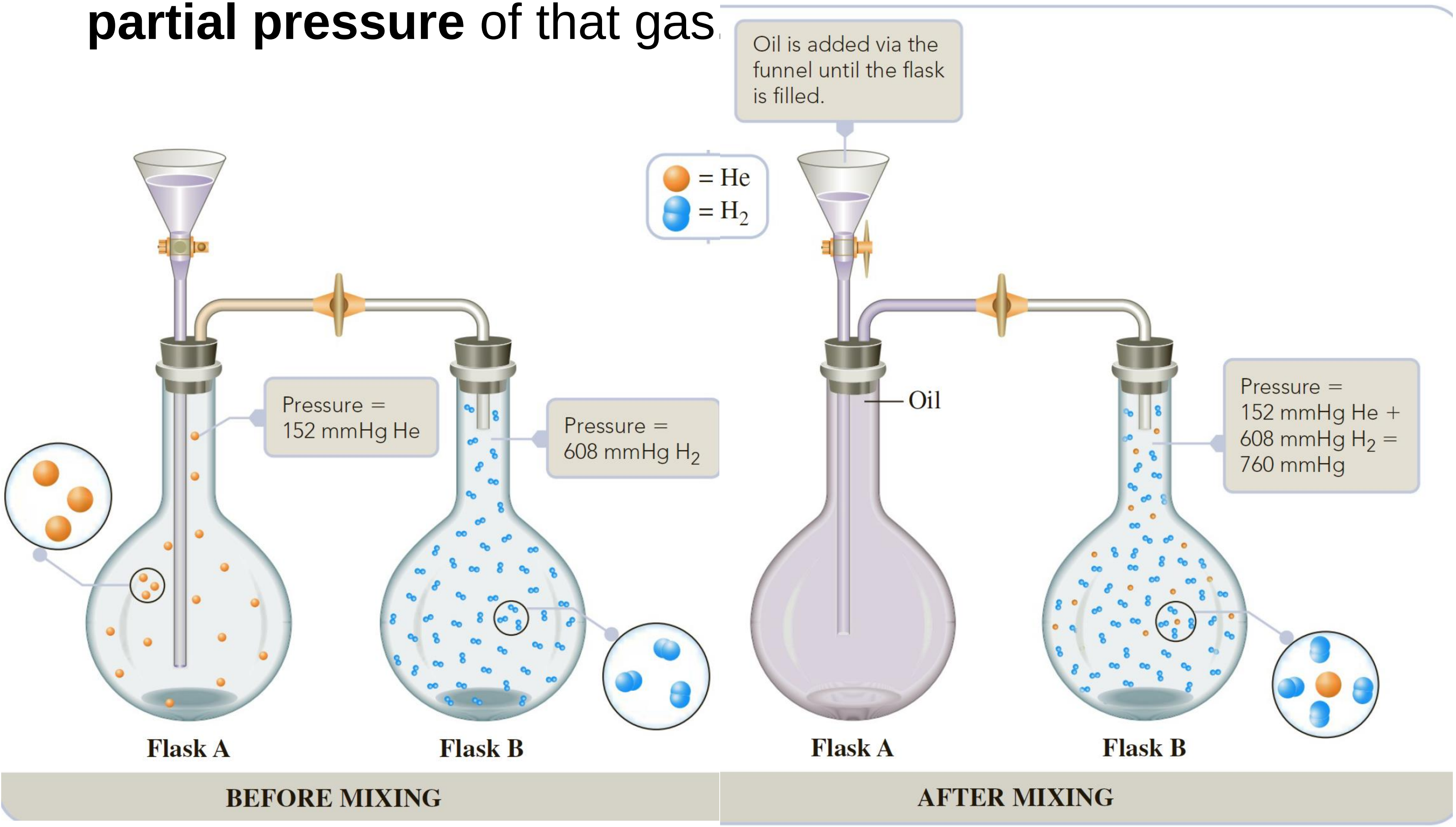
Exercise 5.9 How many liters of chlorine gas, Cl_2, can be obtained at 40°C and 787 mmHg from 9.41 g of hydrogen chloride, HCl, according to the following equation?

$$2KMnO_4(s) + 16HCl(aq) \rightarrow 8H_2O(l) + 2KCl(aq) + 2MnCl_2(aq) + 5Cl_2(g)$$

5.5 Gas Mixtures; Law of Partial Pressures

- Partial Pressures and Mole Fractions

✓ **Dalton's law of partial pressures:**
The pressure exerted by a particular gas in a mixture is the **partial pressure** of that gas.



Dalton's law of partial pressures:
$P = P_A + P_B + P_C + \cdots$

✓ The individual partial pressures follow the ideal gas law. For component *A*, $P_A V = n_A RT$

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

(Q) 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?

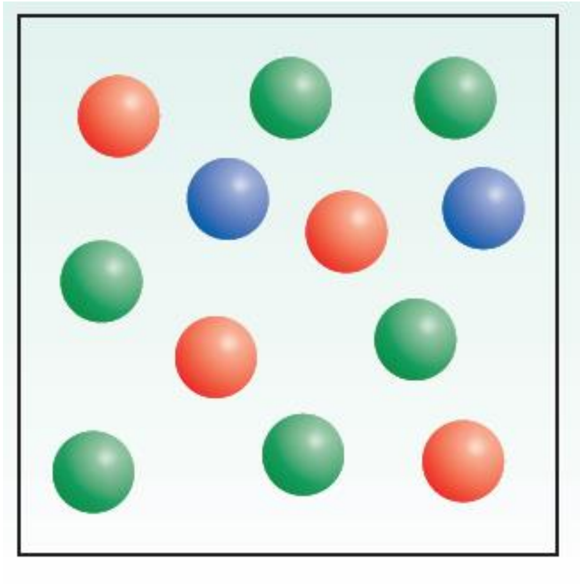
$$0.925\ \cancel{\text{g N}_2} \times \frac{1\ \text{mol N}_2}{28.0\ \cancel{\text{g N}_2}} = 0.0330\ \text{mol N}_2$$

$$P_{N_2} = \frac{n_{N_2}RT}{V} = \frac{0.0330\ \cancel{\text{mol}} \times 0.0821\ \cancel{\text{L}}\cdot\text{atm}/(\cancel{\text{K}}\cdot\cancel{\text{mol}}) \times 298\ \cancel{\text{K}}}{1.00\ \cancel{\text{L}}} = 0.807\ \text{atm}\ (\mathbf{= 613\ mmHg})$$

$$\text{Mole fraction of N}_2 = \frac{P_{N_2}}{P} = \frac{613\ \cancel{\text{mmHg}}}{786\ \cancel{\text{mmHg}}} = \mathbf{0.780}$$

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

(Q) Each of the color spheres represents a different gas molecule. Calculate the partial pressures of the gases if the total pressure is 2.6 atm.



(Q) A mixture consists of 122 moles of N_2, 137 moles of C_3H_8, and 212 moles of CO_2 at 200 K in a 75.0 L container. What is the total pressure of the gas and the partial pressure of CO_2?

A. 46.4 atm, 20.9 atm

B. 103 atm, 26.7 atm

C. 103 atm, 46.4 atm

D. 103 atm, 29.9 atm

E. 46.4 atm, 46.4 atm

$$P_{total} = \frac{(471\ \text{moles})(0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1})(200\ \text{K})}{75.0\ \text{L}} \qquad P_{total} = 103\ \text{atm}$$

$$\text{mole fraction } CO_2 : \frac{212\ \text{moles } CO_2}{122 + 137 + 212\ \text{total}} = 0.450$$

$$P_{CO_2} = (\chi_{CO_2})(P_{total}) = (0.450)(103\ \text{atm}) \qquad P_{CO_2} = 46.4\ \text{atm}$$

(Q) A mixture of 250 mL of methane, CH_4, at 35˚ C and 0.55 atm and 750 mL of propane, C_3H_8, at 35˚ C and 1.5 atm was introduced into a 10.0 L container. What is the mole fraction of methane in the mixture?

A. 0.50

B. 0.11

C. 0.89

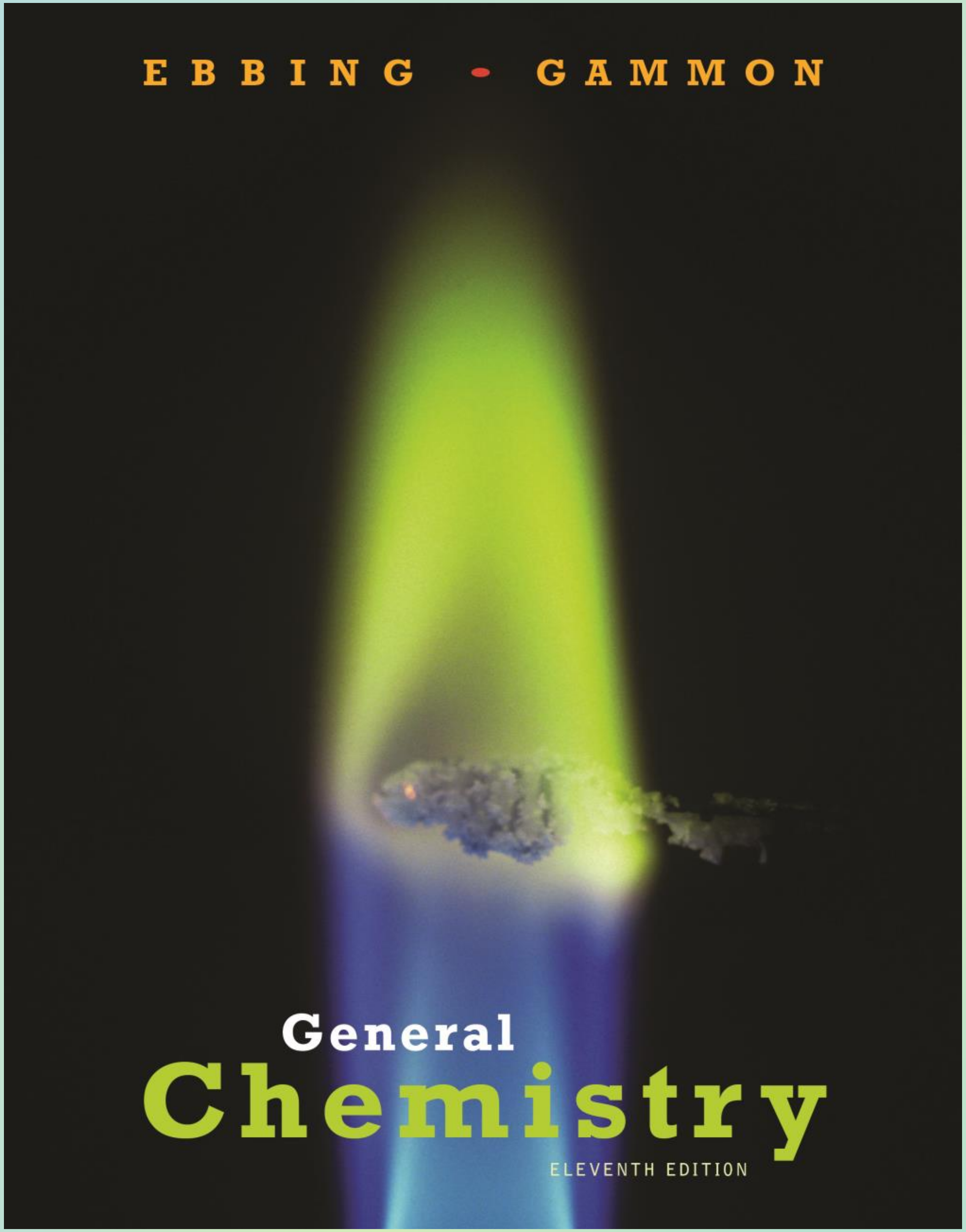
D. 0.25

E. 0.33

$$P_{CH_4} = \frac{0.55 \text{ atm} \times 0.250 \text{ L}}{10.0 \text{ L}} = 0.0138 \text{ atm}$$

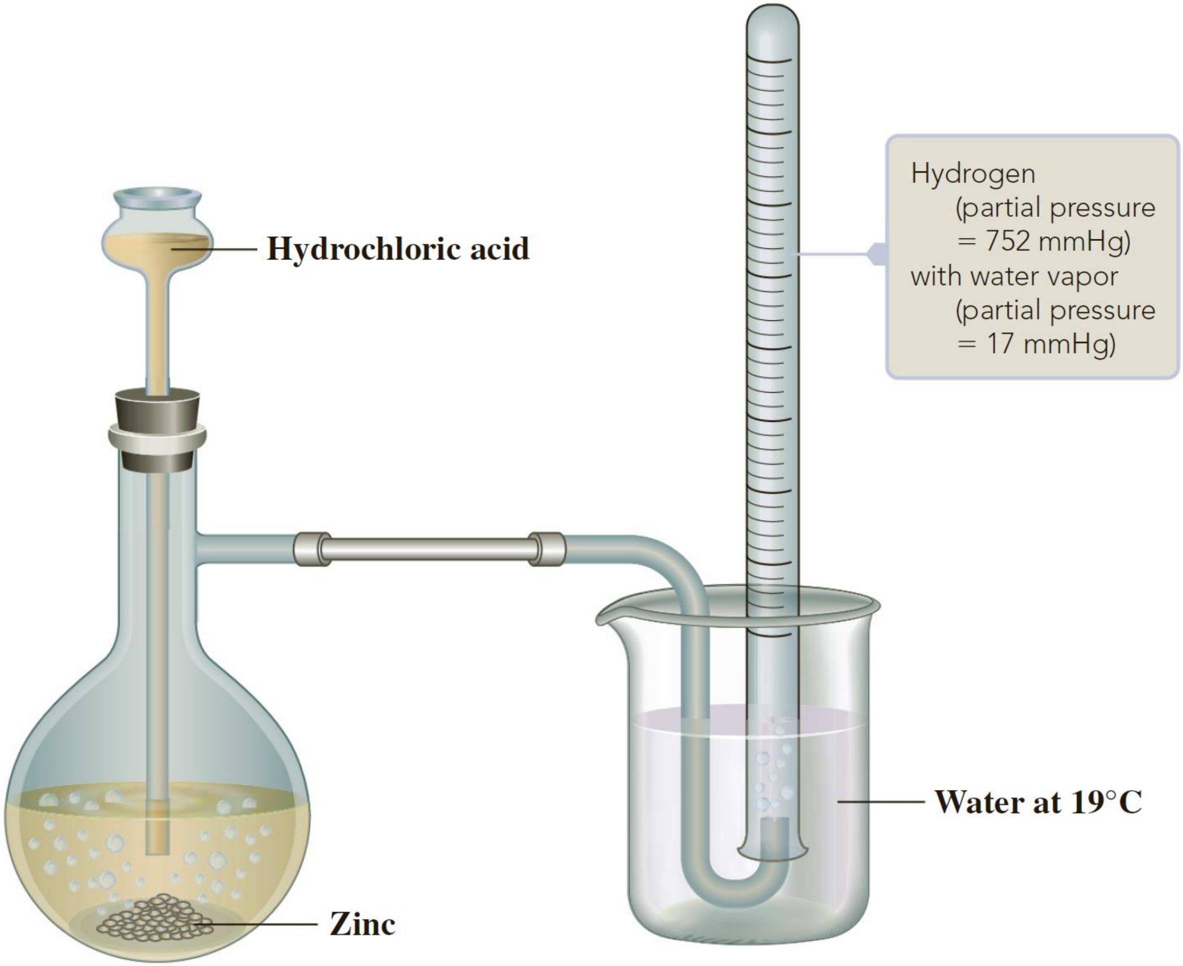
$$P_{C_3H_8} = \frac{1.5 \text{ atm} \times 0.750 \text{ L}}{10.0 \text{ L}} = 0.112 \text{ atm}$$

$$\chi_{CH_4} = \frac{0.0138 \text{ atm}}{0.0138 \text{ atm} + 0.112 \text{ atm}} = 0.110$$



The Gaseous State

➢ Collecting Gases over Water



Vapor Pressure of Water at Various Temperatures*

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

Example 5.11

Hydrogen gas is produced according to the following reaction:

$$2HCl(aq) + Zn(s) \longrightarrow ZnCl_2(aq) + H_2(g)$$

The gas is collected over water. If 156 mL of gas is collected at 19°C and 769 mmHg total pressure, what is the mass of hydrogen collected? The vapor pressure of water at 19°C is 16.5 mmHg

(Q)An unknown gas was collected by water displacement. The following data was recorded: T = 27.0 °C; P = 750 torr;
V = 37.5 mL; Gas mass = 0.0873 g;
$P_{H_2O(vap)}$ = 26.98 torr
Determine the molecular weight of the gas.

A. 5.42 g/mol

B. 30.2 g/mol

C. 60.3 g/mol

D. 58.1 g/mol

E. 5.81 g/mol

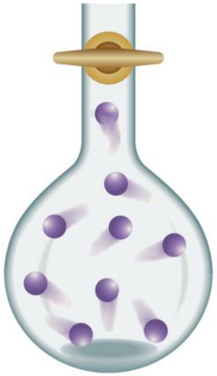
➢ Kinetic-Molecular Theory

According to this theory, *a gas consists of molecules in constant random motion.*

Kinetic energy, E_k, is the energy associated with the motion of an object of mass *m.*

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

5.6 Kinetic Theory of an Ideal Gas



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

➢ Postulates of Kinetic Theory

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

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

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

Postulate 4: *When molecules collide with one another, the collisions are elastic.* In an elastic collision, the total kinetic energy remains constant; no kinetic energy is lost.

Postulate 5: *The average kinetic energy of a molecule is proportional to the absolute temperature*

➢ The Ideal Gas Law from Kinetic Theory

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

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

$$PV \propto Nmu^2$$

$$PV \propto nT$$

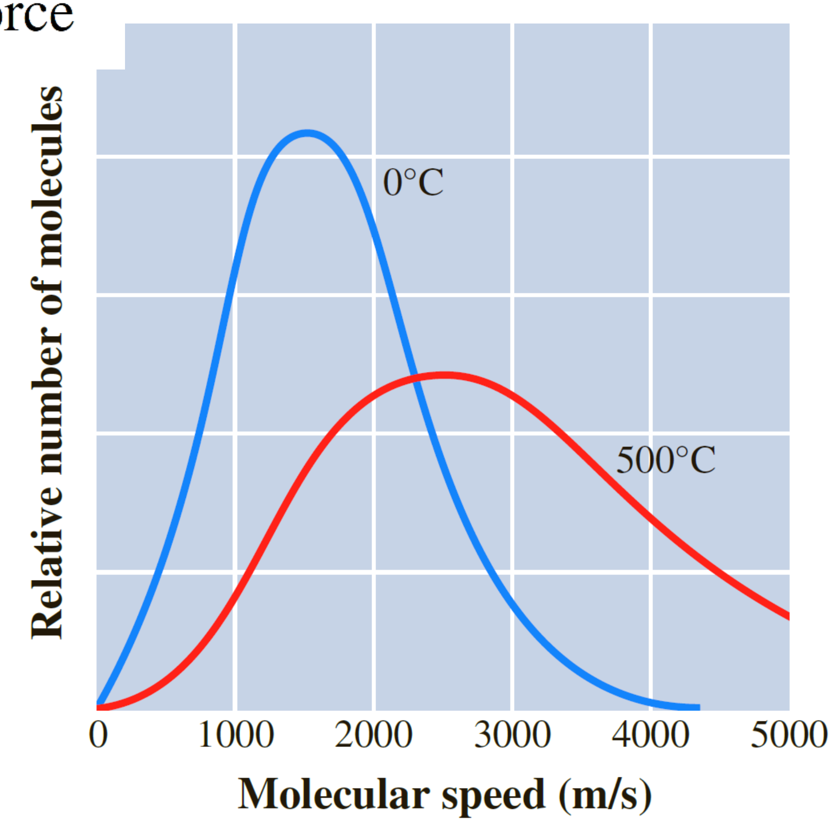
$$PV = nRT$$

5.7 Molecular Speeds; Diffusion and Effusion

➢ Molecular Speeds

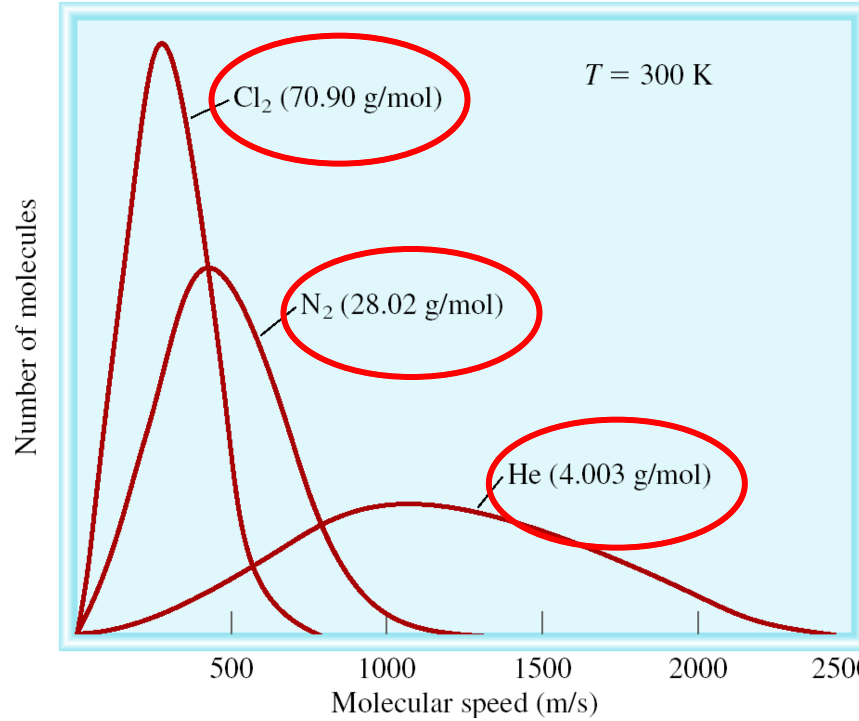
root-mean-square (rms) molecular speed (*u*)

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



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

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



R (= 8.314 kg·m^2/(s^2·K·mol)), T (K), and M_m (kg/mol),

(Q) Calculate the rms speed of O_2 molecules in a cylinder at 21°C and 15.7 atm

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

Exercise 5.13 At what temperature do hydrogen molecules, H_2, have the same rms speed as nitrogen molecules, N_2, at 455°C? At what temperature do hydrogen molecules have the same average kinetic energy?

Determine the rms molecular speed for N_2 at 455°C (728 K):

$$u = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3 \times 8.31\ \text{kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \times 728\ \text{K}}{28.02 \times 10^{-3}\ \text{kg/mol}}\right)^{\frac{1}{2}} = 80\underline{4}.81\ \text{m/s}$$

$$T = \frac{u^2 M}{3R} = \frac{(804.81\ \text{m/s})^2 (2.016 \times 10^{-3}\ \text{kg/mol})}{(3)(8.31\ \text{kg} \bullet \text{m}^2/\text{s}^2 \bullet \text{K} \bullet \text{mol})} = 52.4\ \text{K}$$

Any two gases at the same temperature will have the same average kinetic energy

Because the average kinetic energy of a molecule is proportional to only *T*

➢ Diffusion and Effusion

✓ **Diffusion** is *the process whereby a gas spreads out through another gas to occupy the space uniformly.*

✓ **Effusion** is *the process in which a gas flows through a small hole in a container*

✓ **Graham's law of effusion**

$$u = \sqrt{\frac{3RT}{M_m}}$$

Graham's law of effusion:

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

(for the same container at constant T and P)

(Q) 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.

$$\frac{\text{Rate of effusion of } CO_2}{\text{Rate of effusion of } SO_2} = \frac{\dfrac{1}{\sqrt{M_m(CO_2)}}}{\dfrac{1}{\sqrt{M_m(SO_2)}}} \rightarrow$$

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

carbon dioxide effuses 1.21 times faster than sulfur dioxide

Exercise 5.14 If it takes 3.52 s for 10.0 mL of He to effuse through a hole in a container at a particular temperature and pressure, how long would it take for 10.0 mL of O_2 to effuse from the same container at the same temperature and pressure? (Note that the rate of effusion can be given in terms of volume of gas effused per second.)

$$\frac{\text{Rate of effusion of O}_2}{\text{Rate of effusion of He}} = \sqrt{\frac{M_m(\text{He})}{M_m(\text{O}_2)}} = \sqrt{\frac{4.00\text{ g/mol}}{32.00\text{ g/mol}}} = 0.35$$

→ Rate of effusion of O_2 = 0.35 × rate of effusion of He.

$$\frac{\text{Volume of O}_2}{\text{Time for O}_2} = 0.35 \times \frac{\text{Volume of He}}{\text{Time for He}}$$

$$\frac{10.0\text{ mL}}{\text{Time for O}_2} = 0.35 \times \frac{10.0\text{ mL}}{3.52\text{ s}}$$

$$\text{Time for O}_2 = \frac{3.52\text{ s}}{0.35\underline{3}55} = 9.96\text{ s}$$

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

$$\frac{\text{Rate of effusion of H}_2}{\text{Rate of effusion of gas}} = \frac{\text{time for gas}}{\text{time for H}_2} = \sqrt{\frac{M_m(\text{gas})}{M_m(\text{H}_2)}} = 4.67$$

$$M_m(\text{gas}) = (4.67)^2 \times M_m(\text{H}_2) = (4.67)^2 \times 2.016 \text{ g/mol} = 43.96\text{g/mol}$$

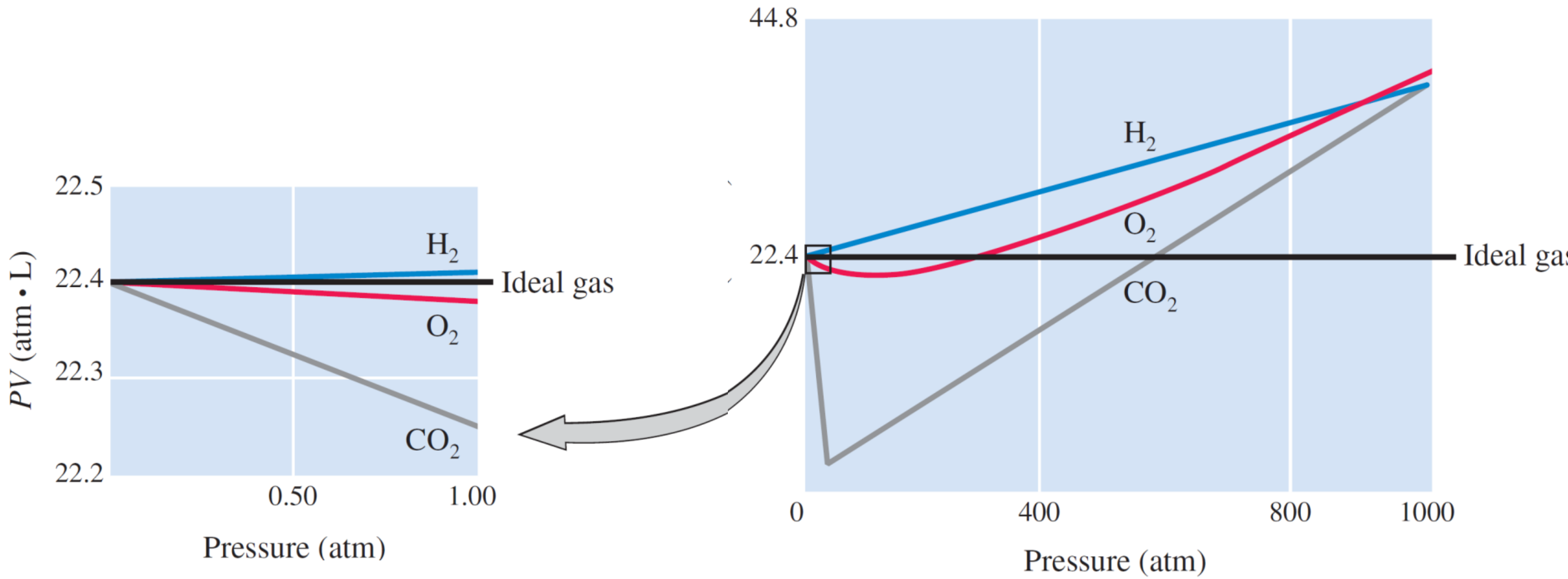
(Q) For the series of gases He, Ne, Ar, H_2, and O_2 what is the order of increasing rate of effusion?

Substance	He	Ne	Ar	H_2	O_2
MM	4	20	40	2	32

Lightest are fastest: H_2 > He > Ne > O_2 >Ar

5.8 Real Gases

Boyle's law (ideal gas) : PV = constant



Pressure–volume product of gases at different pressures

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

Left: Values at low pressure

The **van der Waals equation**
is *an equation similar to the ideal gas law, but includes two constants, a and b, to account for deviations from ideal behavior.*

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

Ideal Gas Equation		***van der Waals Equation***
V	becomes	$V - nb$
P	becomes	$P + n^2a/V^2$

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

(Q)If sulfur dioxide were an ideal gas, the pressure at 0.0°C exerted by 1.000 mole occupying 22.41 L would be 1.000 atm (22.41 L is the molar volume of an ideal gas at STP). Use the van der Waals equation to estimate the pressure of this volume of 1.000 mol SO_2 at 0.0°C. See Table 5.7 for values of *a* and *b*.

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

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

Table 5.7 van der Waals Constants for Some Gases

Gas	*a* L²·atm/mol²	*b* L/mol
CO_2	3.658	0.04286
C_2H_6	5.570	0.06499
C_2H_5OH	12.56	0.08710
He	0.0346	0.0238
H_2	0.2453	0.02651
O_2	1.382	0.03186
SO_2	6.865	0.05679
H_2O	5.537	0.03049

$$P = \frac{1.000\ \cancel{\text{mol}} \times 0.08206\ \cancel{\text{L}}\cdot\text{atm}/(\cancel{\text{K}}\cdot\cancel{\text{mol}}) \times 273.2\ \cancel{\text{K}}}{22.41\ \cancel{\text{L}} - (1.000\ \cancel{\text{mol}} \times 0.05679\ \cancel{\text{L}}/\cancel{\text{mol}})}$$

$$- \frac{(1.000\ \cancel{\text{mol}})^2 \times 6.865\ \cancel{\text{L}^2}\cdot\text{atm}/\cancel{\text{mol}^2}}{(22.41\ \cancel{\text{L}})^2}$$

$$= 1.003\ \text{atm} - 0.014\ \text{atm} = \mathbf{0.989\ atm}$$