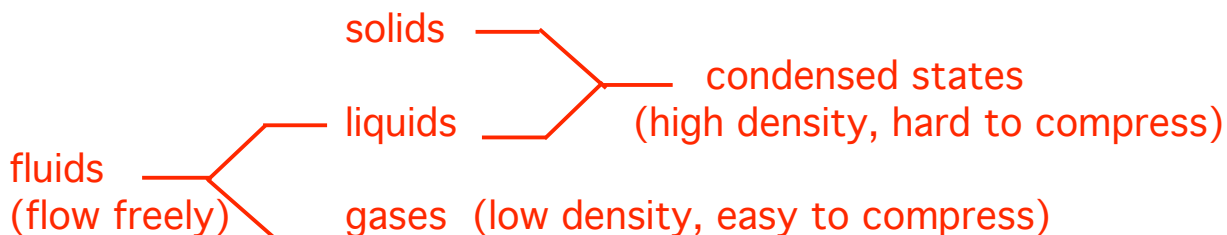


CHAPTER FIVE: THE GASEOUS STATE

Part One: The Gas Laws

A. Introduction.

1. Comparison of three states of matter:



1 mole liquid H₂O occupies 18 mL

1 mole H₂O vapor at 100° C and atmospheric pressure occupies 30,600mL

Thus, gas molecules must be far apart compared to molecular sizes and interact only weakly.

2. Composition of dry air by volume:

78% N₂, 21% O₂, 1% Ar, traces of other.

3. Properties of gases:

- Easily compressed into small volumes by applying pressure.
- Exert a pressure P on their surroundings; an equal pressure must be applied to confine them.
- Expand without limit to uniformly and completely occupy the volume of any container.
- Individual molecules exhibit a chaotic motion called diffusion.
- Properties described by gas laws.

Show them “A Little Box of Air.”

B. Pressure (P). (Section 5.1)

1. $P = \text{force per unit area produced by incessant collisions of particles with container walls.}$
2. Measurement of atmospheric pressure (Torricelli barometer):

$h \propto \text{pressure}$

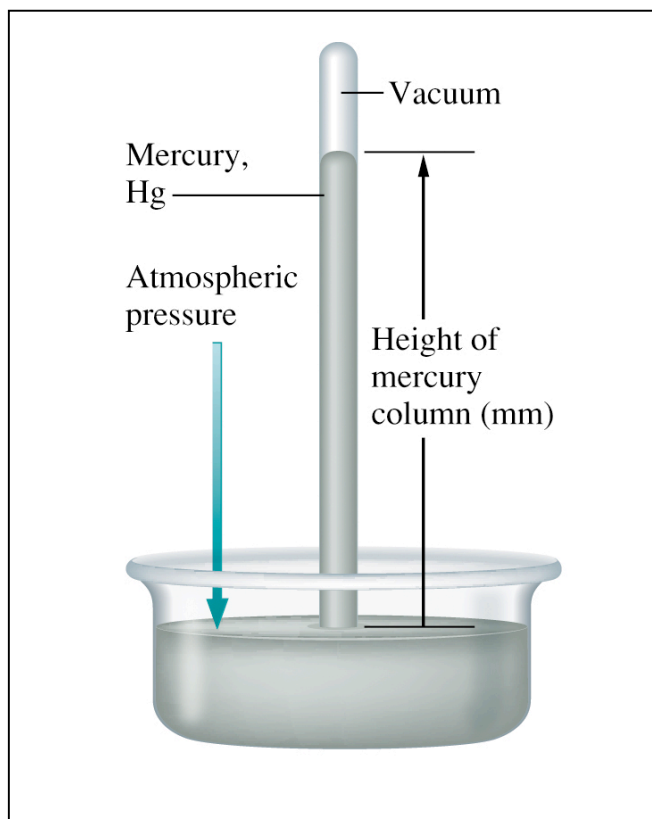
average height h :
 $= 760 \text{ mm Hg at sea level}$

$P = 760 \text{ mm Hg}$
 $= 1 \text{ atmosphere (atm)}$
 $\approx 30 \text{ inches}$

$1 \text{ mm Hg} = 1 \text{ "torr"}$

SI unit of P is the pascal (Pa)

760 mm Hg :
 $= 1 \text{ atm}$
 $= 1.01325 \times 10^5 \text{ Pa}$
 $= 101.325 \text{ kPa}$



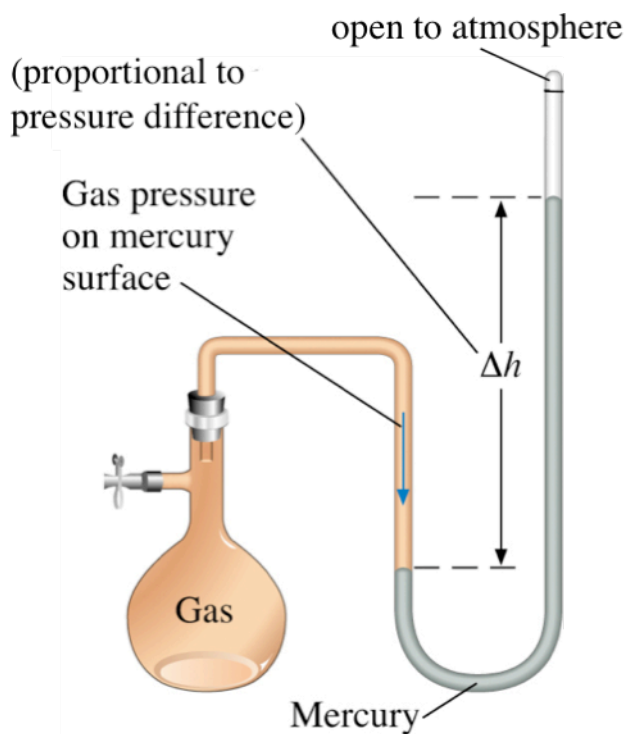
3. Pressure of a column of liquid = hydrostatic pressure:

$P = gdh = \text{accel. of gravity} \times \text{density of liquid} \times \text{height of column}$

$g = 9.81 \text{ m/s}^2$

TABLE 5.2		Important Units of Pressure
Unit	Relationship or Definition	
Pascal (Pa)	$\text{kg}/(\text{m} \cdot \text{s}^2)$	
Atmosphere (atm)	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} \approx 100 \text{ kPa}$	
mmHg, or torr	$760 \text{ mmHg} = 1 \text{ atm}$	
Bar	$1.01325 \text{ bar} = 1 \text{ atm}$	

4. Manometer = device that measures pressure in a vessel relative to atmospheric pressure outside.



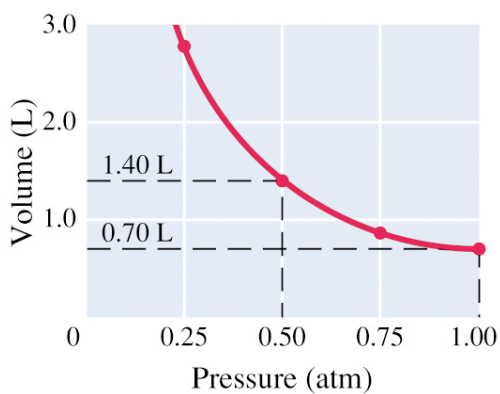
C. Boyle's Law: $P \leftrightarrow V$ Relationship. (Section 5.2)

1. $PV = \text{fixed for a confined gas at constant temperature.}$

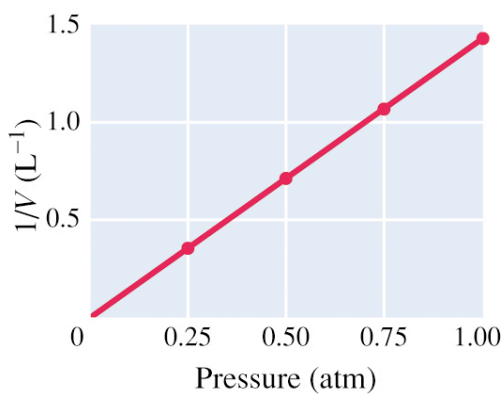
$$P \uparrow \quad V \downarrow \quad P \propto \frac{1}{V}$$

$$P \downarrow \quad V \uparrow$$

2. $P_1V_1 = P_2V_2$ fixed amount and T



A



B

3. Example: All the air in a 20 x 20 x 20 meter room is compressed into a 2.0 Liter container. What is its final pressure in atm if its initial pressure was 0.98 atm?

$$P_1V_1 = P_2V_2$$

$$(0.98 \text{ atm}) \times (8000 \text{ m}^3) = P_2 \times (2.0 \text{ L})$$

-first convert 8000 m³ to Liters:

$$8000 \text{ m}^3 \times \left(100 \frac{\text{cm}}{\text{m}}\right)^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 8000000 \text{ L}$$

$$(0.98 \text{ atm} \times 8 \times 10^6 \text{ L}) = P_2 \times 2.0 \text{ L}$$

$$P_2 = (0.98 \times 8 \times 10^6) / 2.0 \text{ atm} = 3.9 \times 10^6 \text{ atm}$$

D. Charles' Law; V ↔ T Relationship. (Section 5.2)

1. **V/T = fixed for confined gas at constant Pressure.**

$$T \uparrow \quad V \uparrow \quad V \propto T$$

$$T \downarrow \quad V \downarrow$$

- 2.

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}} \quad \text{fixed amt and P}$$

3. T must be in Kelvin temperature.

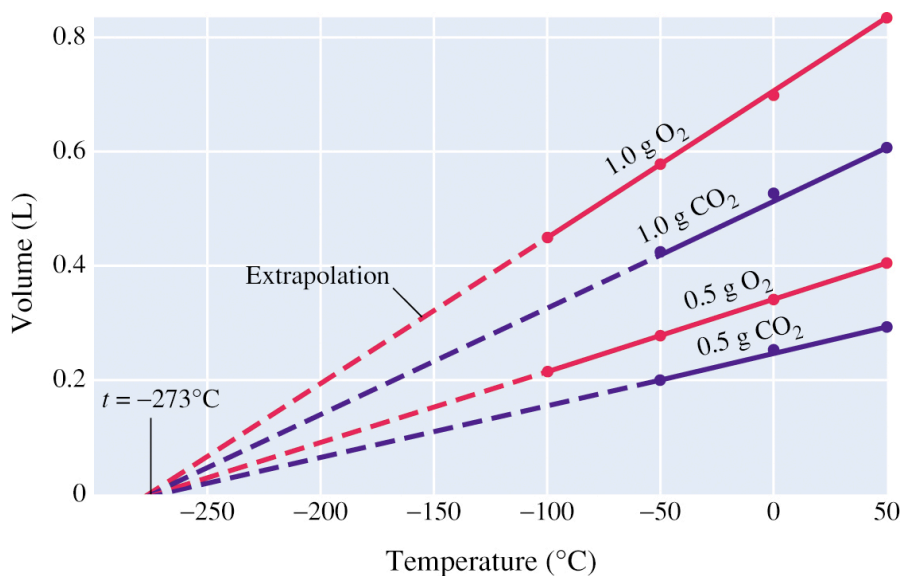
$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15^{\circ}$$

4. Example: A sample of gas occupies 2.0 Liters at 0°C. What volume does it occupy after heated to 100°C?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \frac{2.0 \text{ L}}{(0^{\circ} + 273.15)} = \frac{V_2}{(100^{\circ} + 273.15)}$$

$$\frac{2.0 \text{ L}}{273.15^{\circ}} = \frac{V_2}{373.15} \quad V_2 = 2.73 \text{ L}$$

5. All V versus T plots extrapolate to V=0 at T = 0 K = -273.15°C. (See Fig. 5.9)



Thus we find an absolute zero for Temperature.

T = -273.15°C is lowest temp \equiv 0 K

E. Combined Gas Law: (Section 5.2)

1.

$$\boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}} \quad \text{fixed amount of gas}$$

2. Example: The volume inside a cold tire is 4.3 L at 20°C and the pressure is 1.7 atm. On the highway the temperature inside the tire reaches 50°C and the volume expands to 4.5 L. What is the tire's pressure then?

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{1.7 \text{ atm} \times 4.3 \text{ L}}{293.15 \text{ K}} = \frac{P_2 \times 4.5 \text{ L}}{323.15 \text{ K}}$$

$$P_2 = 1.7 \text{ atm} \times \left(\frac{4.3 \text{ L}}{4.5 \text{ L}}\right) \times \left(\frac{323.15 \text{ K}}{293.15 \text{ K}}\right)$$

$$P_2 = 1.79 \text{ atm}$$

3. How much would the pressure have increased if the tire was perfectly rigid (no expansion)?

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{since } V_1 = V_2$$

$$\frac{1.7 \text{ atm}}{293.15\text{K}} = \frac{P_2}{323.15\text{K}}$$

$$P_2 = 1.7 \text{ atm} \times \left(\frac{323.15}{293.15} \right)$$

$$P_2 = 1.87 \text{ atm}$$

4. Standard Temperature and Pressure (an old definition):

a. "STP" = 0°C (273.15 K) and 1.0 atm (760 torr).

F. Avogadro's Law ($V \leftrightarrow$ amount). (Section 5.2)

1. States that **at the same T and P, equal volumes of all gases contain the same number of particles.**
2. **$V \propto n$ volume of a gas proportional to number of moles n of gas regardless of kind of gas**
3. **Molar volume = 22.414 L/mol at STP.**
4. Slight deviations from this reflect that there are slight interactions between the particles different for every gas. (Deviations from ideal gas behavior.) See Table 5.4.

TABLE 5.4	
Molar Volumes of Several Gases at 0.0°C and 1.00 atm	
Gas	Molar Volume (L)
He	22.40
H ₂	22.43
O ₂	22.39
CO ₂	22.29
NH ₃	22.09
Ideal gas*	22.41

*An ideal gas follows the empirical gas laws.

- One mole He occupies same volume as 1 mole O₂, everything else being the same.
- Therefore all gases have same number density:

$$6.02 \times 10^{23} \text{ gas particles occupy } 22.414 \text{ L at STP}$$

- However, since the “particles” don’t have the same mass:

$$4.0 \text{ gram He occupy same } V \text{ as } 28.0 \text{ grams } N_2.$$

- Thus, gases have different mass densities.

$$\text{mass density of } N_2 \text{ at STP} = \frac{28.0 \text{ g}}{22.414 \text{ L}} = 1.25 \text{ g/L}$$

$$\text{mass density of He at STP} = \frac{4.0 \text{ g}}{22.414 \text{ L}} = 0.178 \text{ g/L}$$

- Mass density of a gas \propto molar mass.
- Suppose a propane (C₃H₈) gas leak develops in my camper van. Which bunk would you rather be sleeping in, the lower or higher bunk?

G. The Ideal Gas Law. (Section 5.3)

1. $PV = nRT$

Pressure x Volume = moles x gas constant x Kelvin temperature.

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

$$R = 8.3145 \text{ Joules/mol K}$$

2. Mathematically describes how all 4 variables depend on each other: P, V, T, n.
3. All the other gas laws can be derived from this one law.

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

Rearrange to:

so :

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

etc

4. Problem: A 2.0 L bottle is filled with N_2 gas at 25°C and 5.0 atm pressure. How many grams of nitrogen are in the bottle.

H. Determination of Molar Mass. (Section 5.3)

1. Ideal gas law provides a basis for determining molar mass (M) of a gaseous substance.
2. Derive relationship of gas properties with molar mass:

Start with: $PV = nRT$

Remember that $n = m/M = \text{mass in grams/molar mass}$

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

rearrange to give

$$M = \frac{mRT}{PV}$$

- Thus, if we know, P, V, T and grams of gas m, we can solve for M.
- Problem: A gaseous hydrocarbon was found to contain 85.6% C and 14.4% H. A mass of 5.61 g of it is found to occupy 4.89 L at 25°C and a pressure of 1.00 atm. What is the molecular formula of this gas?

I. Mass Density of Various Gases.

Start with: $PV = nRT$

Remember that $n = m/M = \text{mass in grams/molar mass}$

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

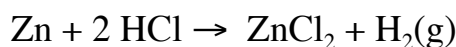
rearrange this time to give

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

$$\text{Density} = \frac{m}{V} \propto \text{MolarMass}$$

J. Stoichiometry Involving Gases. (Section 5.4)

- Example: 10.0 g of Zn metal are added to concentrated HCl and H₂(g) is liberated. What volume of H₂ is liberated if T = 25°C and P = 0.95 atm?



$$10.0 \text{ g Zn} \times \frac{1 \text{ mole Zn}}{65.37 \text{ g}} \times \frac{1 \text{ mol H}_2}{1 \text{ mole Zn}} = 0.153 \text{ mol H}_2 \text{ gas lib.}$$

$$V = \frac{nRT}{P} = \frac{0.153 \text{ mol} \times 0.08206 \text{ L-atm/mol K} \times 298.15\text{K}}{0.95 \text{ atm}}$$

$$V = 3.94 \text{ Liters}$$

K. Dalton's Law of Gas Mixtures. (Section 5.5)

- Treats partial pressures in mixture of gases. Each type of gas in the mixture exerts a pressure as if it were all by itself in the vessel.

2. Based on fact the properties of gases behaving ideally depends on number of moles and not on their identity.

i.e. for mixture, still have: $PV = nRT$

but now $n = \text{total moles} = n_A + n_B + \dots$

3. Could then write:

$$P_{\text{total}} = \frac{nRT}{V} = n_A \frac{RT}{V} + n_B \frac{RT}{V} + \dots$$

$$P_{\text{Total}} = P_A + P_B + \dots$$

4. $P_A, P_B \dots$ are called the partial pressures.

$$P_A = \frac{n_A RT}{V}$$

5. In other words, gas pressures are additive.

6. Problem: A 2.0 liter flask contains 0.20 mol of methane, and 0.40 mol of ammonia. The temperature is 20°C. What is the total pressure inside the flask, in atm, and the partial pressures?

$$P_{\text{CH}_4} = \frac{n_{\text{CH}_4} RT}{V} = 0.20 \text{ mol} \times \frac{0.08206 \frac{\text{L-atm}}{\text{mol K}} \times 293.15\text{K}}{2.0 \text{ L}}$$

$$= 0.20 \text{ mol} \times 12.0 \text{ atm/mol}$$

$$P_{\text{CH}_4} = 2.4 \text{ atm}$$

$$P_{\text{NH}_3} = 0.40 \text{ mol} \times 12.0 \text{ atm/mol} = 4.8 \text{ atm}$$

$$P_{\text{Total}} = 2.4 + 4.8 = 7.2 \text{ atm}$$

7. Mole fractions in mixtures:

$$X_{\text{CH}_4} = \frac{n_{\text{CH}_4}}{n_{\text{Total}}}$$

In previous problem:

$$X_{\text{CH}_4} = (0.20 \text{ mol}) / (0.60 \text{ mol}) = 0.333$$

$$X_{\text{NH}_3} = 0.666$$

8. Also, $X_{\text{CH}_4} = \frac{P_{\text{CH}_4}}{P_{\text{Total}}}$, etc. and so we could write:

$$P_{\text{CH}_4} = X_{\text{CH}_4} P_{\text{Total}}$$

9. Need Dalton's Law to treat gases collected over water, as in lab experiment:

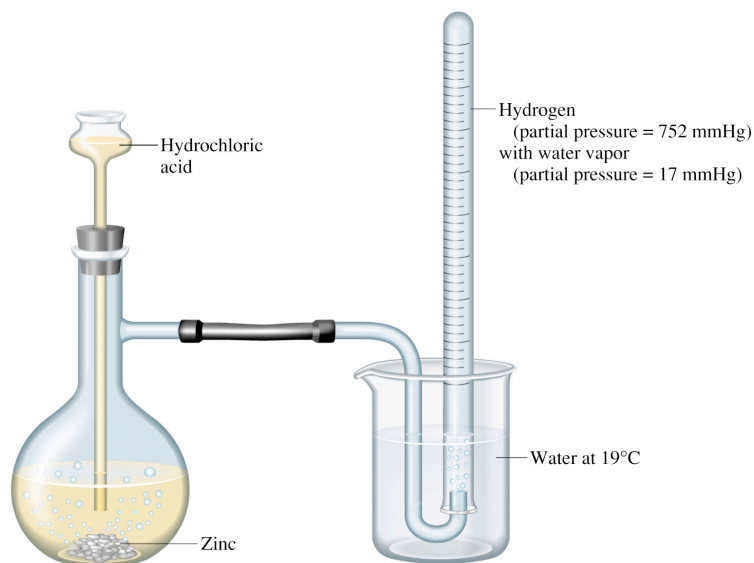


Figure 5.20

$$P_{\text{Total}} = P_{\text{H}_2} + P_{\text{H}_2\text{O}}$$

$P_{\text{H}_2\text{O}}$ depends on water temperature (see Table 5.6)

$$P_{\text{H}_2} = P_{\text{Total}} - P_{\text{H}_2\text{O}}$$

Part Two: Kinetic-Molecular Theory

A. The Kinetic-Molecular Theory. (Section 5.6)

1. Theory that explains Boyle's, Dalton's, Charles', and Avogadro's laws on the molecular level.
2. Basic assumptions:
 - a. Gases consist of particles (molecules), whose sizes are very small compared to the average distance between them.
 - b. Molecules move in continuous, random, straight-line motion with varying velocities.
 - c. Between collisions, molecules exert negligible attractive or repulsive forces on one another.
 - d. Collisions between gas molecules and with the walls are elastic. (no net energy gain or loss)
 - e. The average kinetic energy of a molecule is proportional to the absolute temperature.

HyperChem simulation

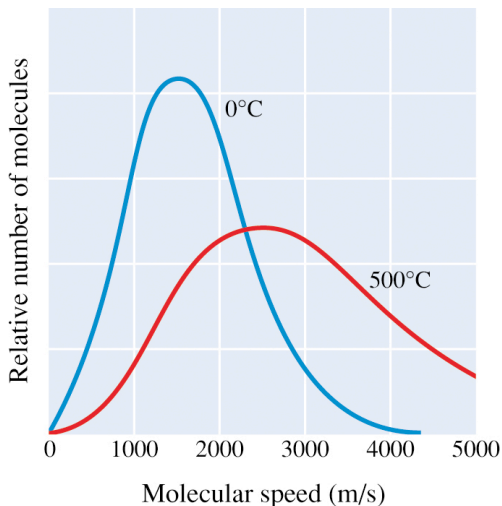
3. Kinetic energy (KE) of molecules and molecular speeds.
 - a. $KE = 1/2 mu^2$, where m (mass) and u (speed).
 - b. Average KE of gaseous molecules is directly proportional to temperature of the sample.
 - c. Average KE of molecules of different gases are equal at a given temperature.
 - d. $\overline{KE} = \frac{3}{2} k_B T$, $k_B = 1.38 \times 10^{-23}$ J/K (Boltzmann's constant)
 - e. Derive the root-mean-square molecular speed = u (rms speed)

$$\left(\frac{mu^2}{2}\right) = \frac{3k_B T}{2}; \quad \overline{u^2} = \frac{3k_B T}{m}; \quad u = \sqrt{u^2}$$

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

- e. Thus, in sample of H_2 , He, and CO_2 at the same temperature, all the molecules have the same average KE. But the lighter molecules, H_2 and He, have much higher average **speeds** than do the heavier molecules, CO_2 .

4. Maxwell's distribution of molecular speeds (here of H_2 molecules):



The Maxwellian distribution function for molecular speeds.

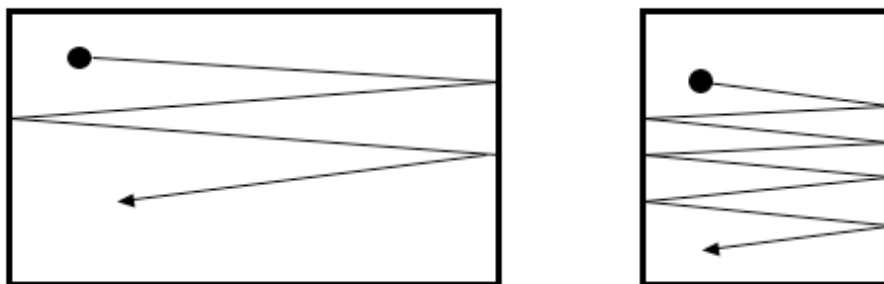
5. Boyle's Law Explained.

a. $P \propto \frac{1}{V}$; at fixed T and n.

b. Pressure depends upon two factors:

- 1.) Number of molecules striking the walls per unit time.
- 2.) How vigorously the molecules strike (mean speed).

c. Example: Halving the volume doubles the pressure because twice as many molecules strike a given area on the walls per unit time.



6. Charles' Law Explained.

a. $\overline{KE} \propto T$

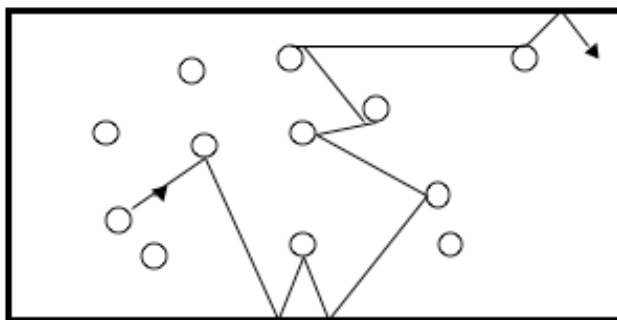
b. Doubling T doubles average KE.

c. Increased force of the collisions of molecules with the walls doubles the volume at constant pressure.

B. Diffusion and Effusion of Gases. (Section 5.7)

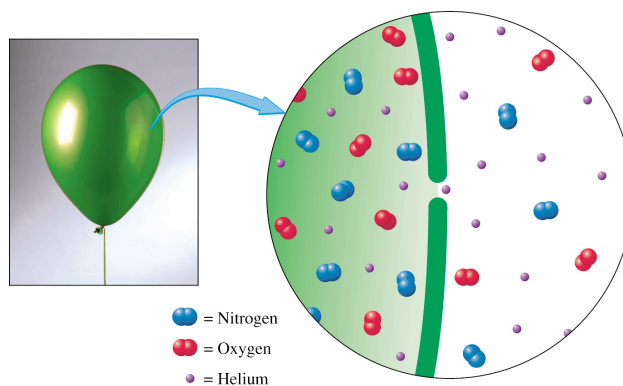
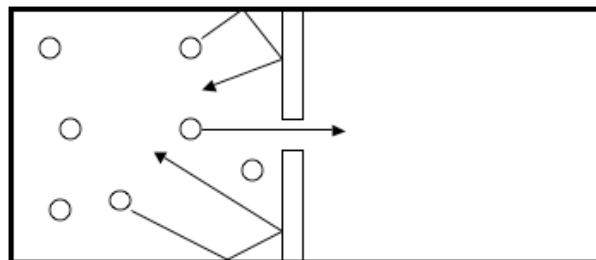
1. Gas molecules are in constant, rapid, random motion, diffuse quickly throughout any container.

2. Picture of diffusion:



3. "Effusion" = escape of a gas through a tiny hole.

4. Picture of effusion:



5. Diffusion and Effusion Rates: Graham's Law.

a. $\text{Rate} \propto \sqrt{\frac{T}{M}}$

b. Compare rates of two different gases:

$$\frac{\text{Rate}(\text{O}_2)}{\text{Rate}(\text{N}_2)} \propto \sqrt{\frac{M_{\text{N}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{28}{32}}$$

C. Real Gases - Deviations from Ideality. (Section 5.8)

- Under ordinary conditions most *real* gases do behave ideally.
- Nonideal gas behavior (deviation from the predictions of the ideal gas laws) most significant at *high pressures* and/or *low temperatures*, i.e., near the conditions under which the gas liquefies.

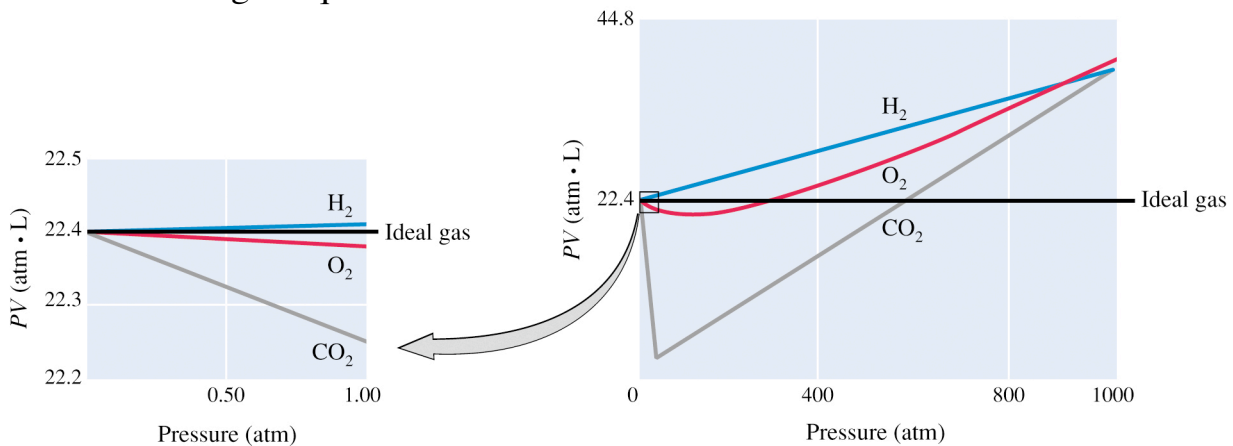


Figure 5.30

3. van der Waals theory of deviations of real gases from ideal behavior. (1867)

a. Ideal gas:

$$PV = nRT$$

b. Under high pressures, a gas is compressed so that the volume of the molecules themselves becomes a significant fraction of the total volume occupied by the gas; *available volume* is less than the *measured volume*.

$$P(V - nb) = nRT$$

- c. When the temperature is quite low even small attractive forces become important. Molecules deviate from their straight-line paths, take longer to reach the walls, fewer collisions in a given time interval.

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

vdW equation

TABLE 5.7		van der Waals Constants for Some Gases	
Gas	<i>a</i>	<i>b</i>	
	L ² ·atm/mol ²	L/mol	
CO ₂	3.658	0.04286	
C ₂ H ₆	5.570	0.06499	
C ₂ H ₅ OH	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 ₂ O	5.537	0.03049	