

Chapter 10

Gases & Kinetic Molecular Theory

I) Gases, Liquids, Solids

Gases

Particles
far apart

very
compressible

D_g

No definite
vol.

No def.
shape

Liquids

Particles
touching

slightly
comp.

\ll

D_l

def.
vol.

No def.
shape

Solids

Particles
closely packed

Incomp.

$<$

D_s

def.
vol.

def.
shape

II) Properties of Gases

A) Amount (mass or moles)

low molar masses

Independent of vol. (V),
pressure (P), temp. (T)

B) Volume

Gas takes shape of its container
& completely fills it.

vol. gas = vol. container

Dependent on P & T

C) Temperature

Both **P** & **V** depend on **T**

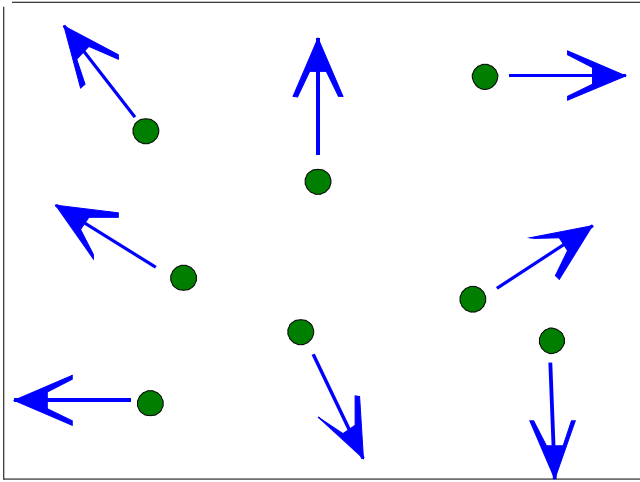
- **MUST** use **Kelvin**

D) **All** gases are **miscible**

- **mix** completely

homogeneous mixture

E) Pressure



$$P = \frac{\text{Force}}{\text{Area}}$$

Gas particles exert **pressure** by **colliding** w. **walls of container**

more
collisions/area \implies **higher**
pressure

Depends on **V** & **T**

SI unit : **Pascal**, $1 \text{ Pa} = 1 \text{ N/m}^2$

1) Pressure Measurement

Barometer: measures pressure of atmosphere

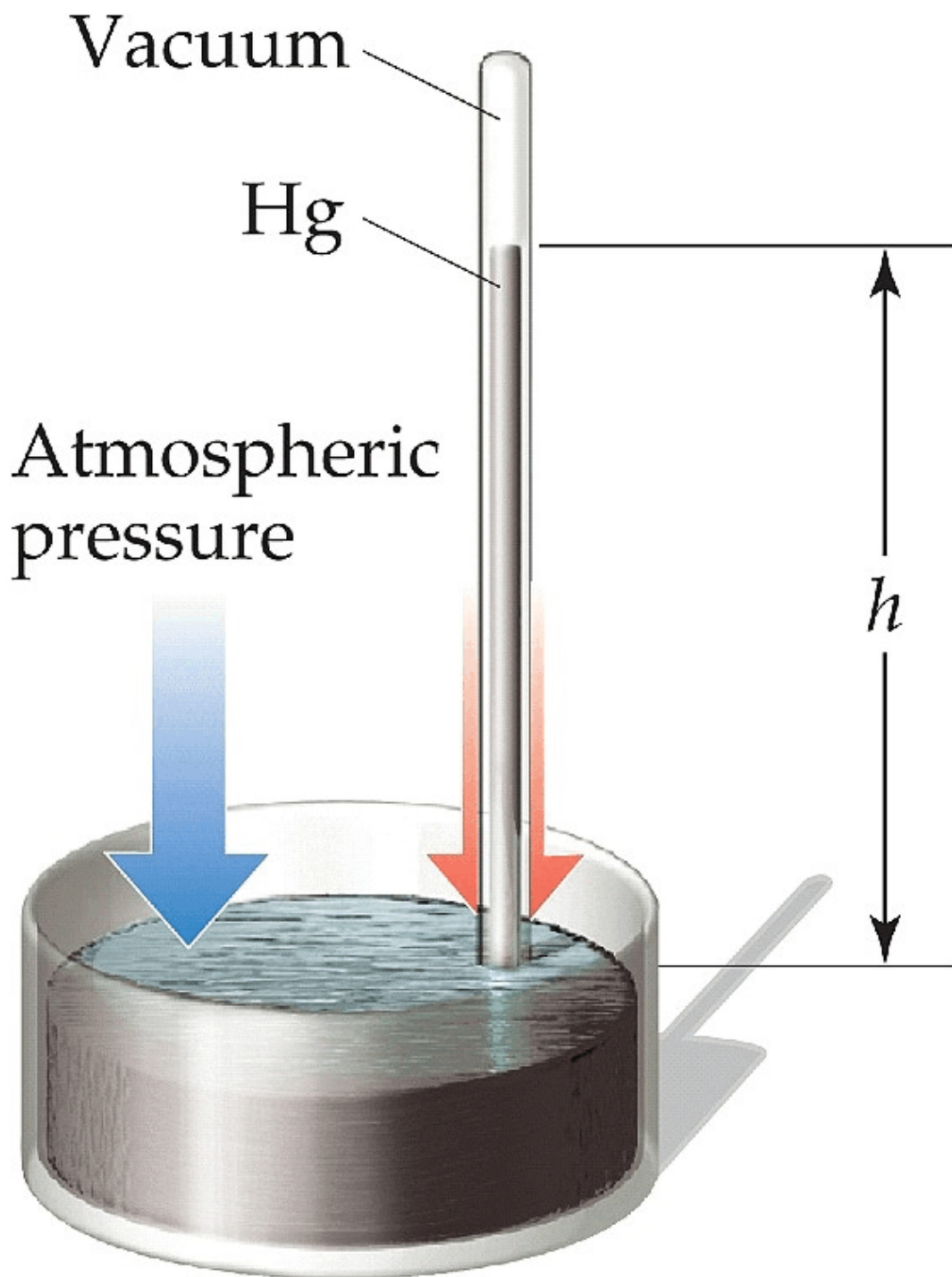
Manometer: measures press. of gas or gas above a liquid in a vessel

a) Units

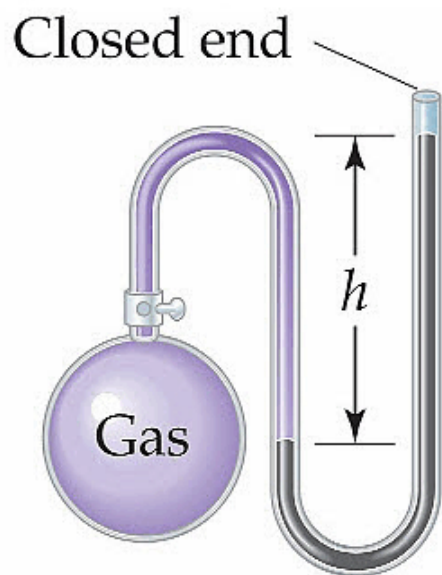
Standard Atmospheric Pressure

Avg. atmospheric pressure at 0°C at sea level that supports a column of Hg 760 mm high. (1 atm)

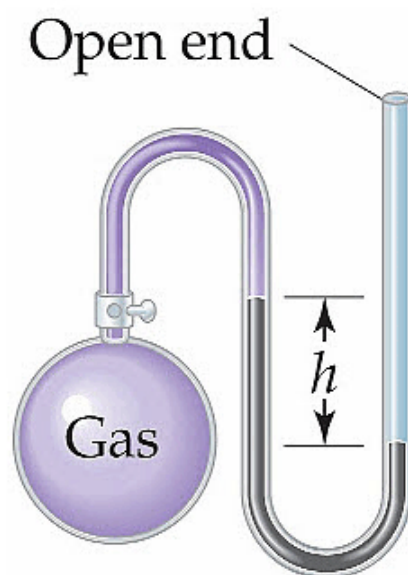
$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mm Hg} = 760 \text{ torr} \\ &= 101.325 \text{ kPa} = 14.7 \text{ lbs/in}^2 \end{aligned}$$



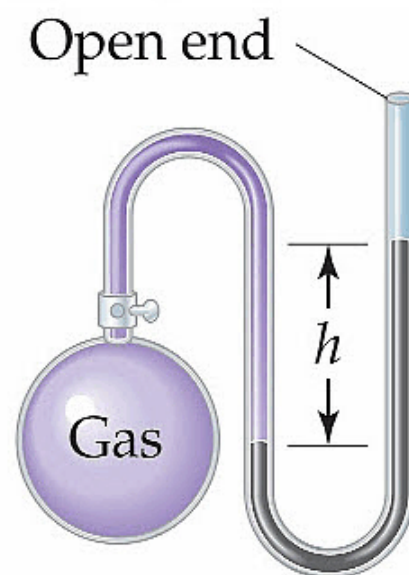
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$$P_{\text{gas}} = P_h$$



$$P_{\text{gas}} = P_{\text{atm}} - P_h$$



$$P_{\text{gas}} = P_{\text{atm}} + P_h$$

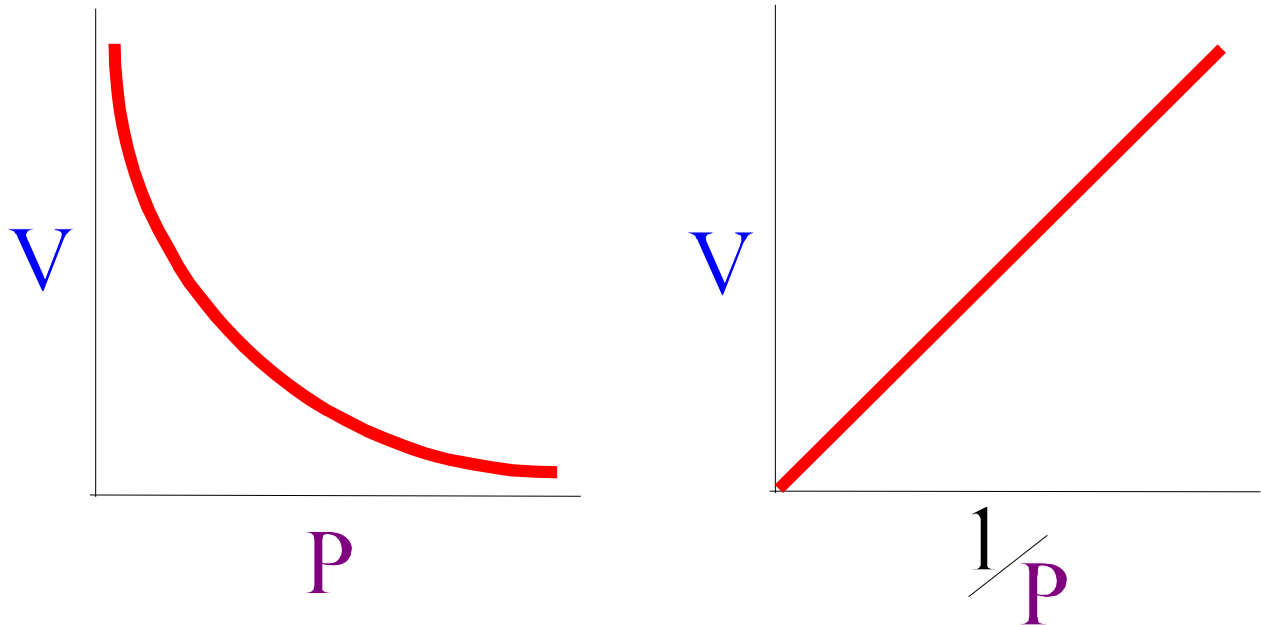
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III) Gas Laws

A) Boyle's Law

Volume is **inversely**
proportional to **Pressure**
(**constant T** & **fixed amt. gas**)

$$V = k_1 \frac{1}{P} \quad \text{or} \quad P V = k_1$$



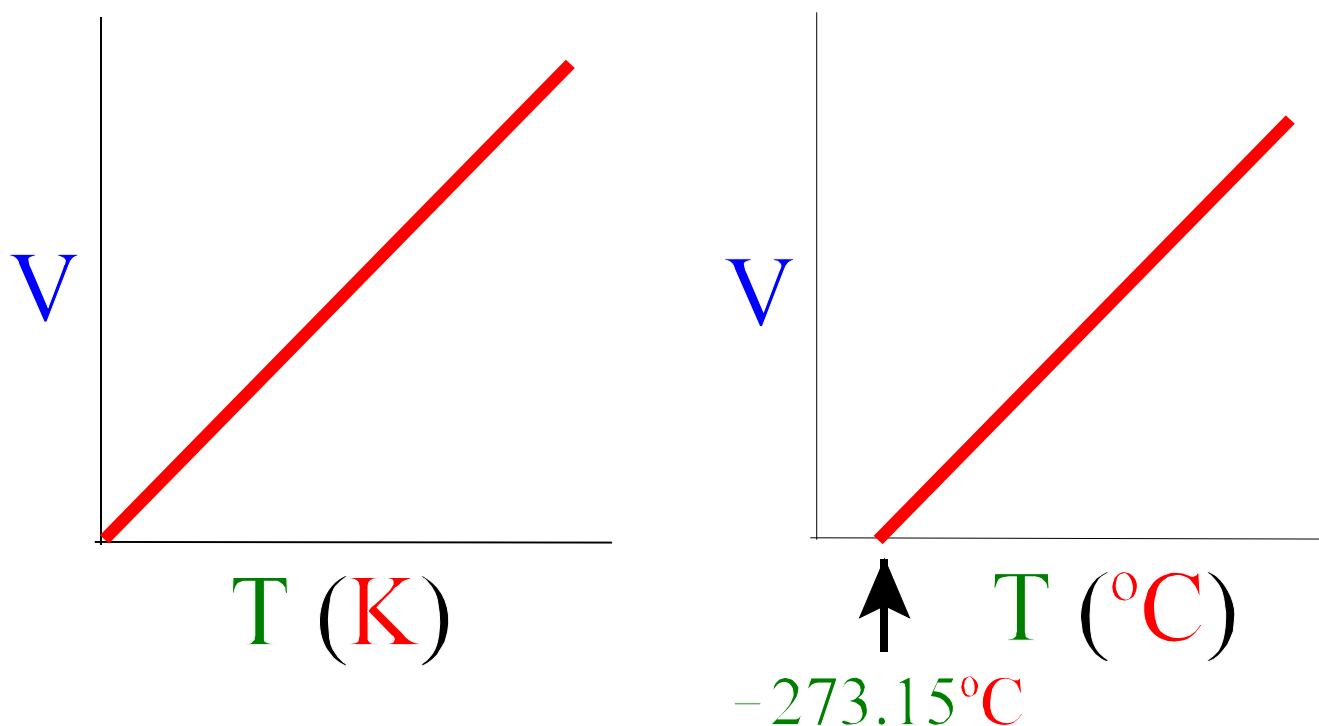
$$P_2 V_2 = P_1 V_1$$

B) Charles's Law

Volume is directly proportional to Absolute Temp.
(constant P & fixed amt. gas)

$$V = k_2 T \quad \text{or} \quad \frac{V}{T} = k_2$$

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



1) Ex: A gas occupies a vol. of 12.3 L at 177°C . What is its vol. when the temp. is 27°C ?

C) Avogadro's Law

Avogadro's Hypothesis:

Equal volumes of gases, at same T & P, contain equal numbers of particles.

Avogadro's Law

Volume of a gas is directly proportional to the number of moles of gas

$$V = k_3 \cdot n$$

$$\frac{V_2}{n_2} = \frac{V_1}{n_1}$$

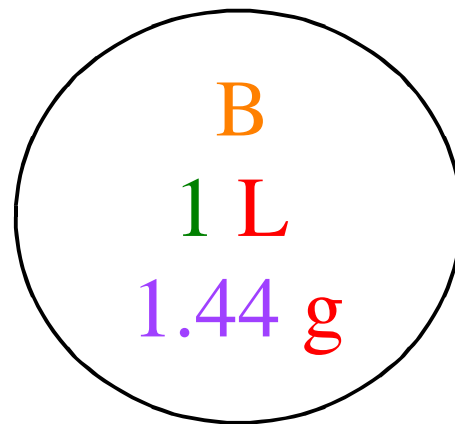
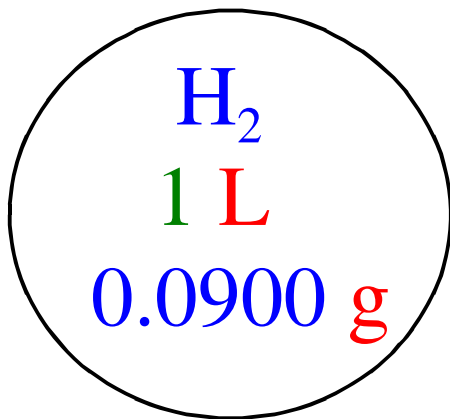
1) Determination of Mol. Wt.

If 2 gases have **equal vol.** then there are **equal numbers** of particles &


$$\frac{\text{mass 1 molecule B (amu)}}{\text{mass 1 molecule A (amu)}} = \frac{\text{mass B (g)}}{\text{mass A (g)}}$$

Proof

2) Ex: There are 2 balloons at same P & T. One balloon contains H_2 & the other contains an unknown gas, B, each w. a vol. of 1 L and masses as shown below. What is the MW of B?



IV) Ideal Gas Law

$$V \propto \frac{1}{P} \quad V \propto T \quad V \propto n$$

$$V \propto \frac{nT}{P}$$

Replace proportionality & rearrange

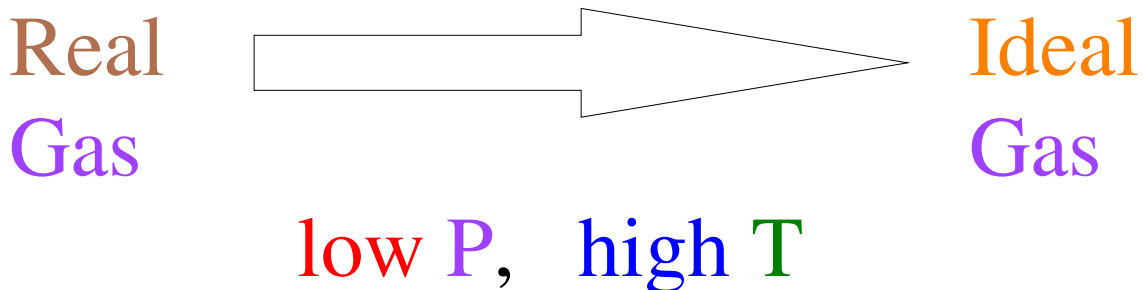
$$PV = nRT$$

$$R = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

Universal Gas Constant

Ideal Gas

Hypothetical gas that behaves according to the **Ideal Gas Law** under **all conditions**



A) Standard Temp. & Pressure

Temp. & Pressure affect Volume

Need a “standard” T & P
as a reference point

STP

$$T = 0\text{ }^{\circ}\text{C} \quad (273.15\text{ K})$$

$$P = 1\text{ atm}$$

B) Molar Volume

Volume of 1 mole of an ideal gas, V_m , at a given T & P

At **STP**:

Standard Molar Volume

$$\begin{array}{l} 1 \text{ mole} \\ \text{gas} \end{array} = 22.41 \text{ L}$$

1) Ex: What volume does 3.0 mol of gas occupy at **STP**?

C) Super Combined Gas Law

Alternate writing of IGL:

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

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

D) Calc. Using Ideal Gas Law

Given any three of **P**, **V**, **n** & **T**
calc. the unknown quantity

- 1) **Ex**: What is the pressure in a container that holds 0.452 g of NH_3 , in a vol. of 400.0 mL & a temp. of 25°C ?

2) **Ex:** A sample of gas occupies a vol. of 5.0 L at a pressure of 650.0 torr & a temp. of 24°C. We want to put the gas in a 100.0 mL container which can only withstand a pressure of 3.0 atm. What temp. must be maintained so that the container doesn't explode.

V) Further Applications of IGL

A) Determine MW & Molecular Formula

$$\text{MF} = (\text{EF})_n$$

$$n = \frac{\text{MF}}{\text{EFW}}$$

Determine EF & EFW from
% composition data

Determine MW

$$PV = nRT \quad m = m/n \quad D = m/V$$

$$D = \frac{P m}{R T}$$

1) Ex: An unknown gas has a mass of 0.50 g. It occupies 1.1 L at a pressure of 252 torr & a temp. of 243 °C. Its emp. formula is C₂H₅. What is its molecular formula?

B) Stoichiometry Problems Involving Gases

Moles of reactants & products are related by **balanced eqn.**

Moles of gases related to **P, V & T**

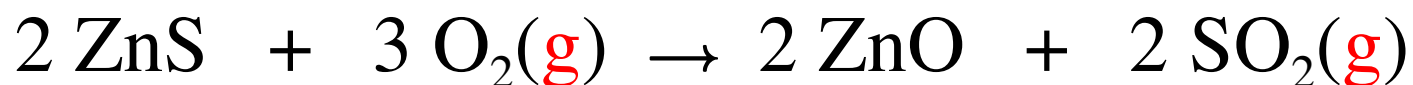
Use **Avogadro's Law** to express quantities of gas in **volumes**

$$V \propto n \quad (\text{constant } T \text{ \& } P)$$

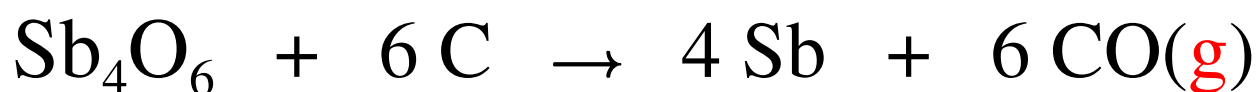
$$V = k n$$

$$\frac{V_2}{n_2} = \frac{V_1}{n_1}$$

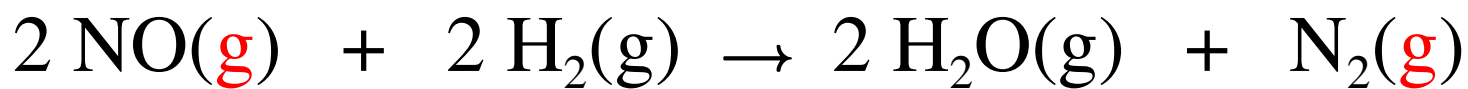
1) Ex 1: What volume of oxygen gas would be required to produce 0.50 L of SO₂ by the following rx.?



2) Ex 2: When the following rxn. was carried to completion at 27°C & 0.987 atm 3.20 L of CO was produced. How many moles of Sb_4O_6 were initially present?



3) Ex 3: What vol. of $\text{N}_2(\text{g})$ at **STP** would be produced by the rxn. of 0.86 g of $\text{NO}(\text{g})$?



Remember: **1 mol** gas = **22.41 L** at **STP**

VI) Gas Mixtures & Partial Pressures

Each gas acts independently.

Total pressure depends only on the total # particles & not kind.

A) Partial Pressures

Pressure each gas would exert if it were the only gas present at same T & V as for mixture.

Dalton's Law of Partial Pressures

$$P_{\text{tot}} = P_1 + P_2 + P_3 + \dots$$

$$P_{\text{tot}} = \sum_{j=1}^N P_j$$

Assume **each** gas behaves **ideally**

$$P_j = n_j \left(\frac{RT}{V} \right)$$

$$P_{\text{tot}} = \sum_{j=1}^N P_j = (RT/V) \sum_{j=1}^N n_j = (RT/V) n_{\text{tot}}$$

1) Mole Fraction

$$\chi_j = \frac{n_j}{n_T}$$

Related to partial pressures

$$\frac{P_j}{P_T} = \frac{n_j (RT/V)}{n_T (RT/V)} = \chi_j$$

$$P_j = \chi_j P_T$$

2) Ex: A mixture of 40.0 g of O_2 & 40.0 g of He has a total pressure of 0.900 atm. What is the partial pressure of O_2 ?

VII) Kinetic-Molecular Theory

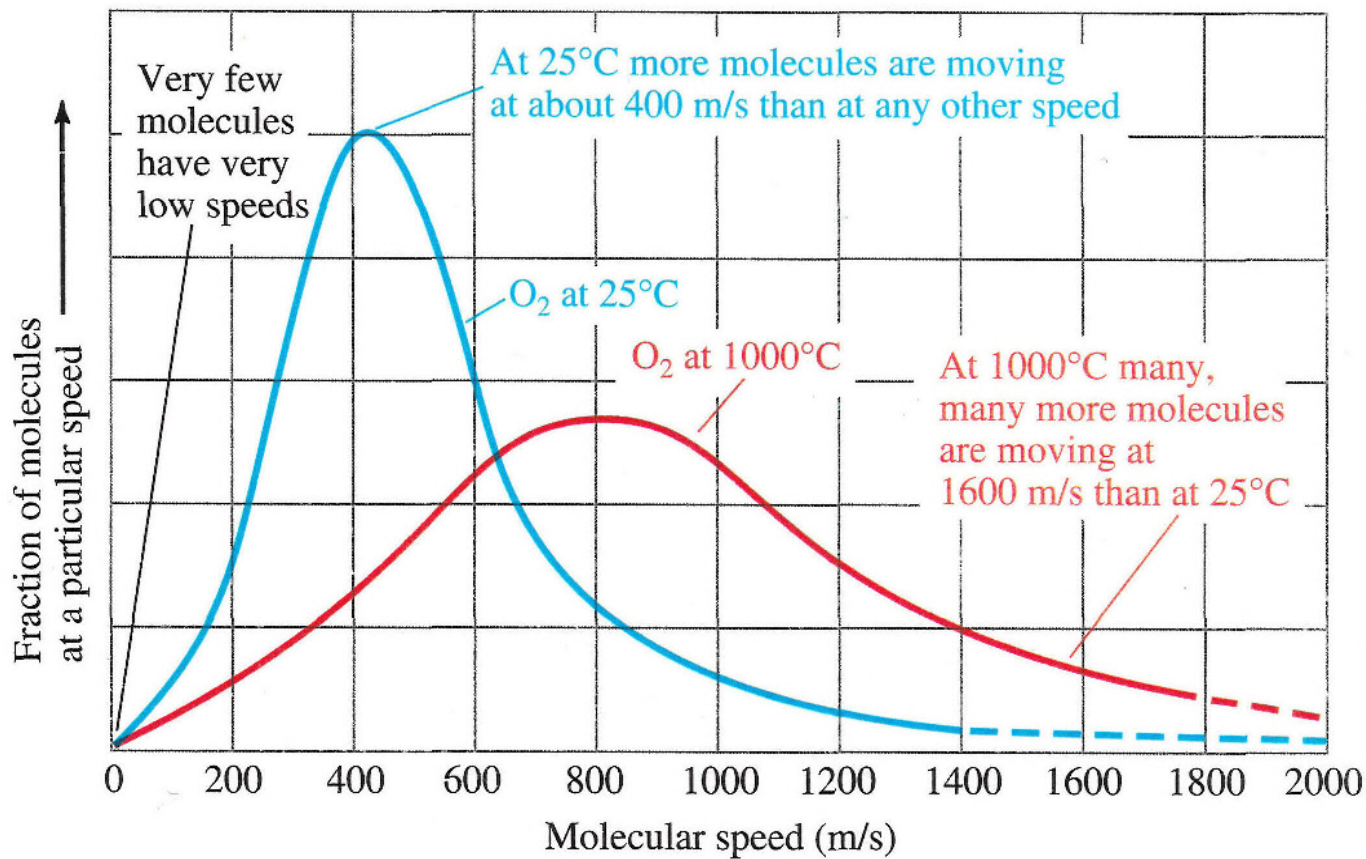
Explains behavior of **ideal** gases

A **gas** consists of molecules
in **constant random motion**

$$\text{K.E.} = \frac{1}{2} m (\mathbf{u}_{\text{rms}})^2$$

\mathbf{u}_{rms} = **root-mean-square (rms) speed**

$$\mathbf{u}_{\text{rms}} = \left(\frac{1}{N} \sum_i^N s_i^2 \right)^{1/2}$$



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5 Postulates of Kinetic Theory

- (1) Molecules move continuously and randomly in straight lines in all directions and various speeds.
 - Properties of a gas that depend on motion of molecules, such as pressure, will be the same in all directions.
- (2) Gases are composed of molecules whose size is negligible compared to the average distance between them.
 - Most of the volume occupied by a gas is empty space.
 - Ignore the volume occupied by the molecules.
- (3) Intermolecular forces (attractive and repulsive forces between molecules) are negligible, except when the molecules collide with each other.
 - A molecule continues moving in a straight line with undiminished speed until it collides with another gas molecule or with the walls of the container.
- (4) Molecular collisions are elastic.
 - Energy can be transferred between molecules but the total average kinetic energy remains constant.
- (5) The average kinetic energy of the molecules is proportional to the absolute temperature, K (kelvin).
 - At any given temperature, the molecules of ALL gases have the SAME average kinetic energy.
 - The higher the temperature, the greater the average kinetic energy.

A) Ideal Gas

Hypothetical gas which conforms to all the assumptions of the K.M.T.

B) Real Gases

Obey K.M.T. (behave ideally) at high temp. & low pressure

High Temp: K.E. great enough to overcome I.A.F.

Low Pressure: few particles in a large volume

C) Molecular Speeds

Distribution of KE & u is dependent on Temperature

$$\text{Total KE of 1 mole of gas} = \frac{3}{2} (RT)$$

$$\text{Avg. KE of 1 molecule} = \frac{1}{2} m u^2$$

$$\frac{1}{2} m u^2 = \frac{1}{N_A} \cdot \frac{3}{2} RT$$

$$u^2 = \frac{3 RT}{N_A m} = \frac{3 RT}{m}$$

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

1) Ex: Calc. the speed of a molecule of O₂ that has the **avg. KE** at room temp, 20°C.

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

D) Qualitative Interpretation of Gas Laws

Pressure caused by collisions of molecules w. container's walls

- frequency of collisions/unit area
- force/collision

Molecular conc. & avg. speed determines the freq. of coll.

Avg. molecular speed determines avg. force/coll.

1) Boyle's Law

T constant \Rightarrow KE constant \Rightarrow u constant

\therefore avg. molecular force/coll.
remains constant

Inc. Volume

Molecular conc. dec.

- freq. of coll./unit area dec.

\therefore P dec.

2) Charles's Law

T inc. \Rightarrow KE inc. \Rightarrow u inc.

- inc. force/coll.

- inc. freq. of coll.

Keep P constant

Volume must inc. so the
molecules/unit vol. &
freq. of coll. will dec.

\therefore T inc., V inc.

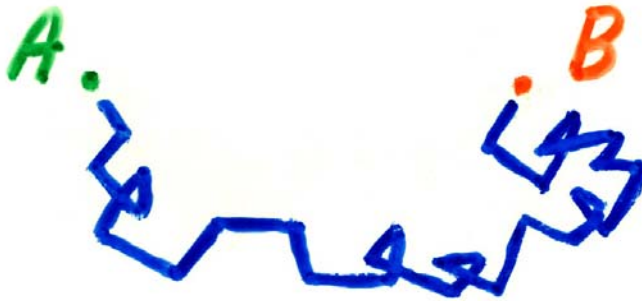
VIII) Diffusion & Effusion

A) Diffusion

Dispersion of a gas throughout a vessel

Why does it take so long for a gas to diffuse?

- have molecular collisions



Avg. distance traveled between collisions is called the mean free path

Higher density
of gas



Smaller
m.f.p.

B) Effusion

Gas escapes through a
small hole in a container

rate of effusion $\propto u$

$$r \propto u$$

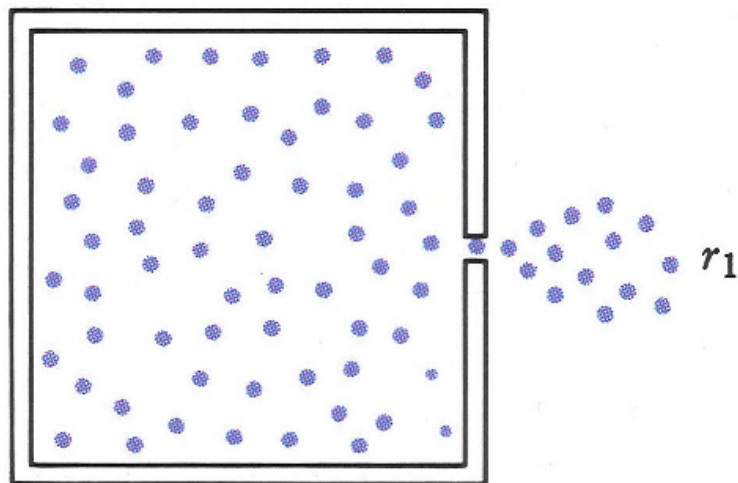
$$\therefore r \propto \left(\frac{3RT}{M}\right)^{1/2}$$

Graham's Law of Effusion

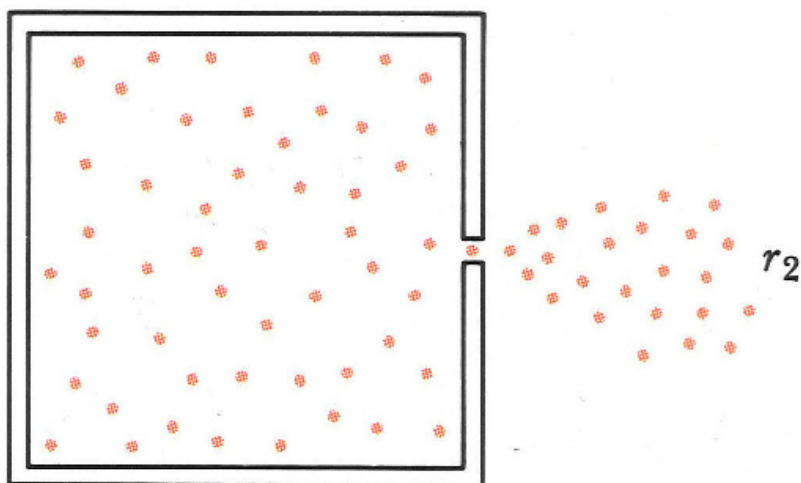
$$r \propto \frac{1}{M^{1/2}}$$

(at constant T & P)

Figure 10.14 Effusion of gases



(a)



(b)

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1) Compare rates of effusion of 2 diff. gases

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \frac{\left(\frac{3RT_1}{M_1}\right)^{1/2}}{\left(\frac{3RT_2}{M_2}\right)^{1/2}}$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{T_1 M_2}{T_2 M_1}}$$

At constant T ,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

2) Ex: The rate of effusion of an unknown gas is 2.91 times faster than that of NH_3 . What is the molecular wt. of the gas?

XIV) Real Gases

Real gases deviate from ideality at,
High P, Low T

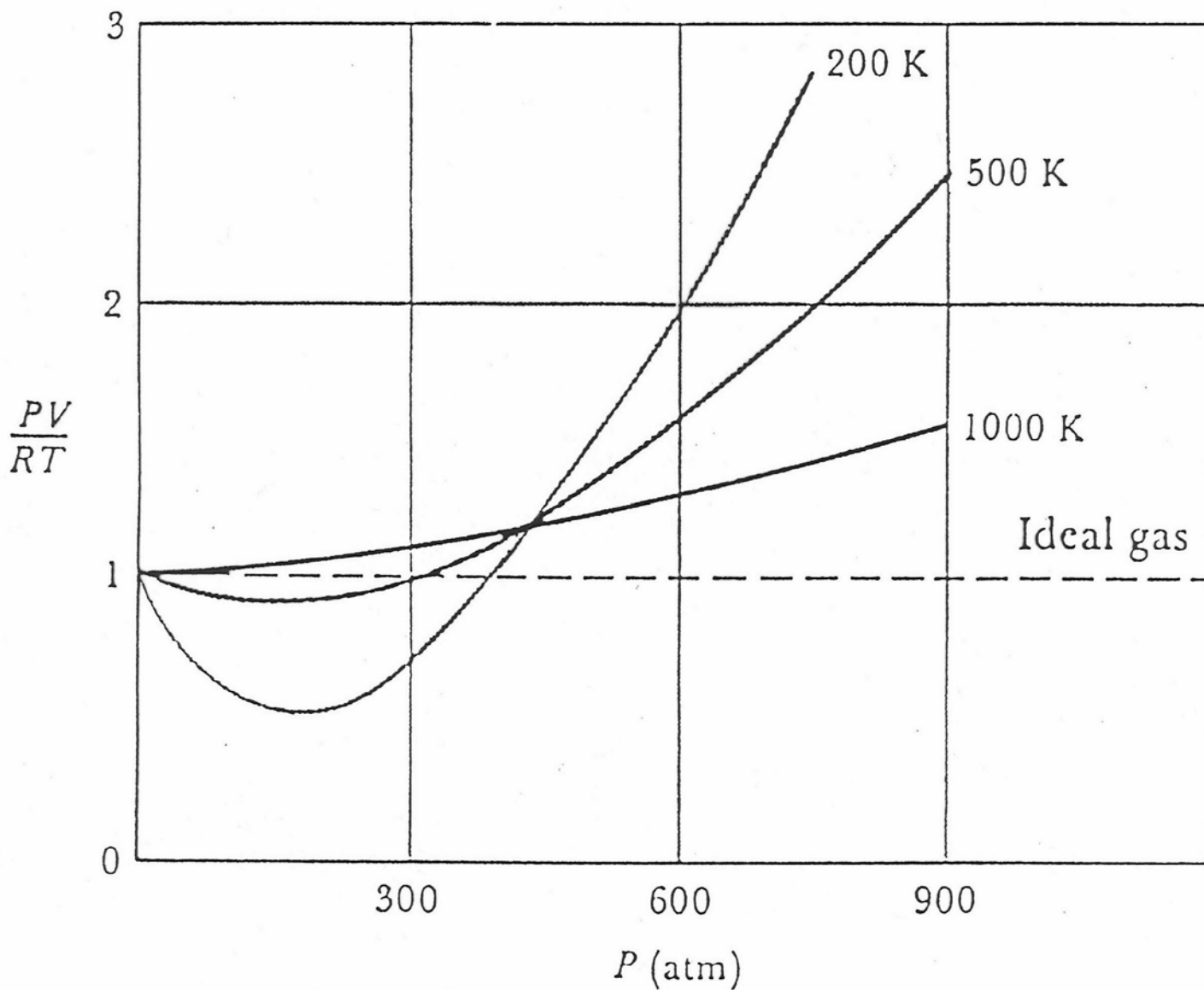
Some assumptions made in
KMT are FALSE

- Molecular volumes are negligible
- Molecules do not interact

Remember, for an ideal gas

$$\frac{PV}{nRT} = 1, \text{ at all } P$$

$\frac{PV}{RT}$ vs. P for 1 mol $N_2(g)$



A) van der Waals Equation

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

ideal gas Law : $P_i = \frac{nRT}{V}$

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



$$P_m > P_i$$



$$P_m < P_i$$

1) nb term

correction for finite
molecular volume

$$V_{\text{available}} = V_m - nb$$

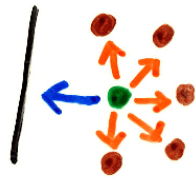
units for b : $\frac{\text{L}}{\text{mol}}$

b inc. w. MW or
complexity of structure

Can be estimated from liquid
density & MW

2) $\frac{n^2 a}{V^2}$ term

corrects for inter molec. attractions



other molec. "pull back"
molec. about to strike wall

- reduces force of impact

$$P_m = P_i - \frac{n^2 a}{V^2}$$

$\frac{n}{V}$: concentration term

units for a : $\frac{L^2 \text{ atm}}{\text{mol}^2}$

a reflects strength of attractions

- inc. w. MW or
complexity of structure

P_{ideal} & P_{vw} as a function of $V_{container}$
 For 1.0 mol $N_2(g)$ at 298 K (25°C). (in atm)

$V(L)$	P_{ideal}	$\frac{nRT}{V-nb}$	$(\frac{n}{V})^2 a$	P_{vw}
10	2.446	2.456	0.0139	2.442
1.0	24.5	25.5	1.39	24.1
0.50	48.9	53.08	5.56	47.5
0.10	245	402	139	263
0.050	489	2245	556	1689

$$a = 1.39 \frac{L^2 \cdot atm}{mol^2}$$

$$b = 0.0391 \frac{L}{mol}$$

B) Calculations

- 1) Ex: The pressure of 2.50 mol of Xe in a 2.000 L flask is 31.6 atm at 75°C. Is the gas behaving ideally?

