Chapter 10

Gases & Kinetic Molecular Theory

I) Gases, Liquids, Solids

Gases	Liquids	Solids
Particles far apart	Particles touching	Particles closely packed
very compressible	slightly comp.	Incomp.
D_g	$\ll D_\ell$	$< D_s$
No definite vol.	def. vol.	def. vol.
No def. shape	No def. shape	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

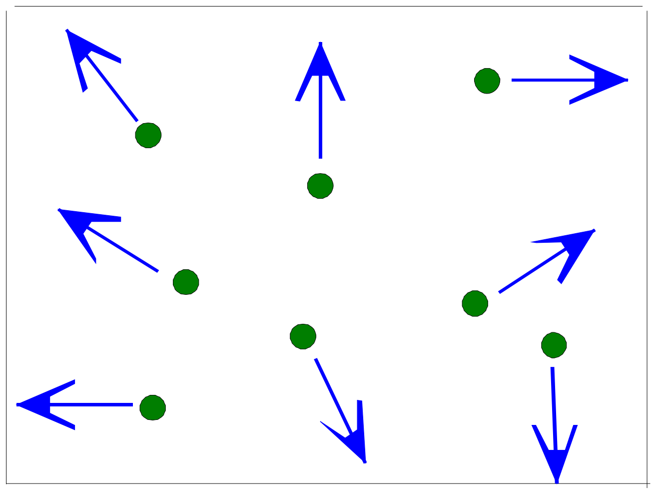
- MUST use Kelvin

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 $\Longrightarrow$ higher pressure

Depends on V & T

SI unit : Pascal, 1 Pa = 1 N/m^2

1) Pressure Measurement

Barometer: measures pressure of atmosphere

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

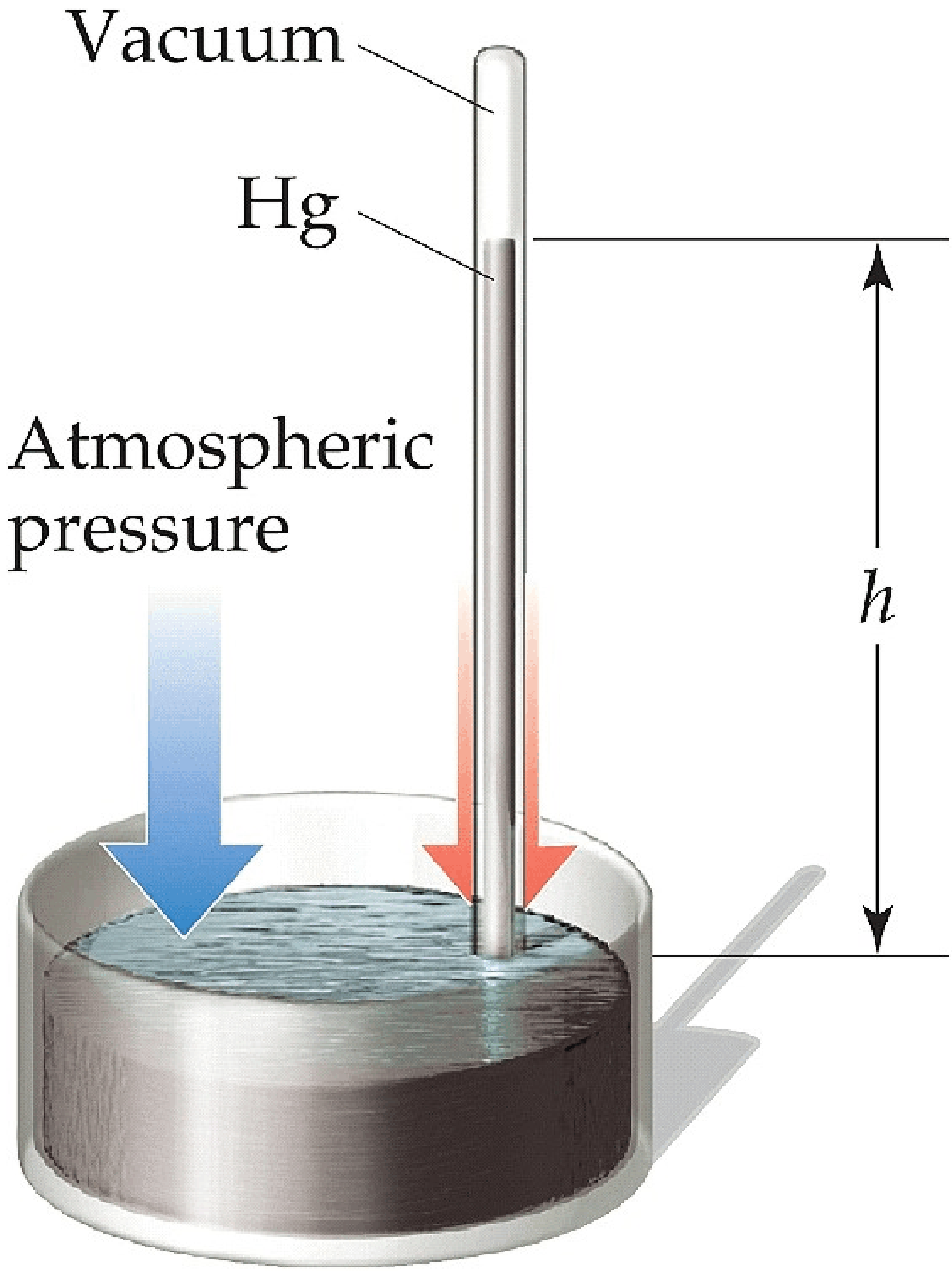
a) Units

Standard Atmospheric Pressure

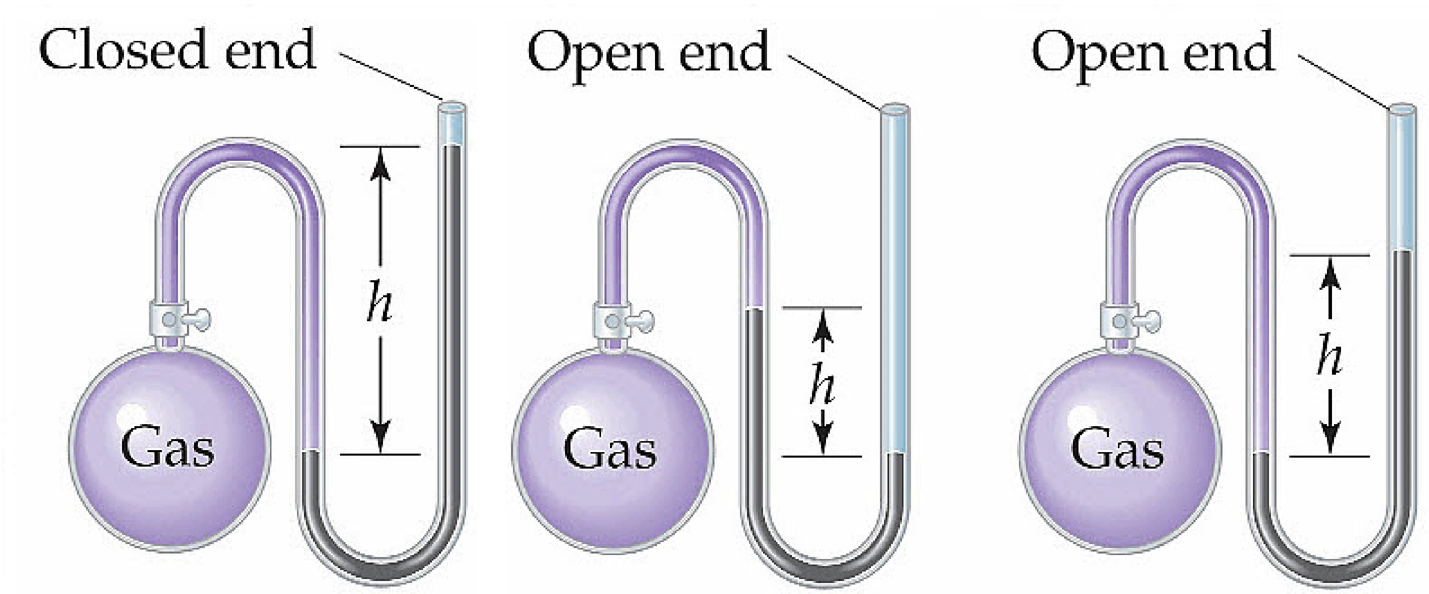
Avg. atmospheric pressure at 0°C at sea level that supports a column of Hg 760 mm high. (1 atm)

1 atm = 760 mm Hg = 760 torr

= 101.325 k Pa = 14.7 lbs/in^2


Vacuum
Hg
Atmospheric pressure
h

b) Ex: What would be the height of H_2O in a barometer if the atmospheric pressure were 760.0 torr? The density of H_2O is 1.00 g/mL and that of Hg is 13.6 g/mL.



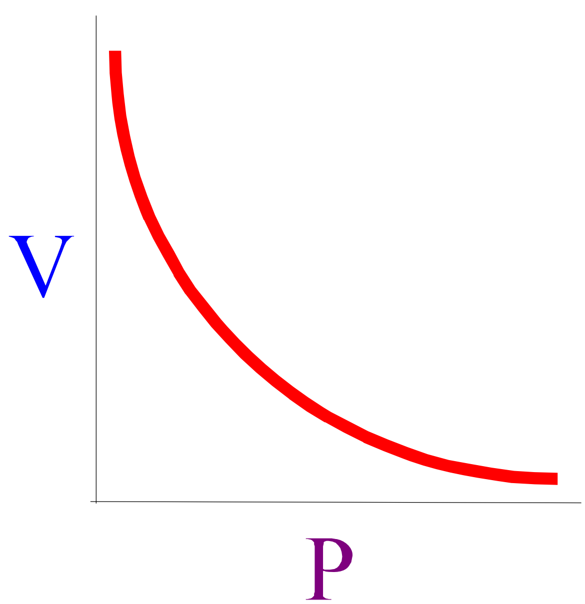
$P_{gas} = P_h$ $\quad$ $P_{gas} = P_{atm} - P_h$ $\quad$ $P_{gas} = P_{atm} + P_h$

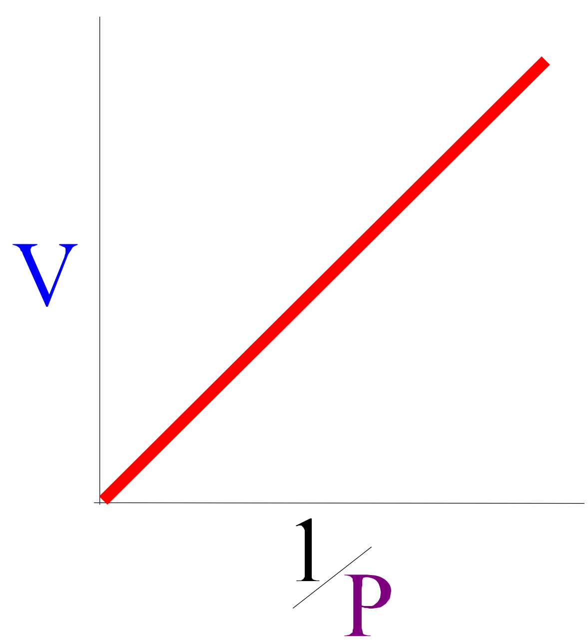
III) Gas Laws

A) Boyle's Law

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

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





$$P_2 V_2 = P_1 V_1$$

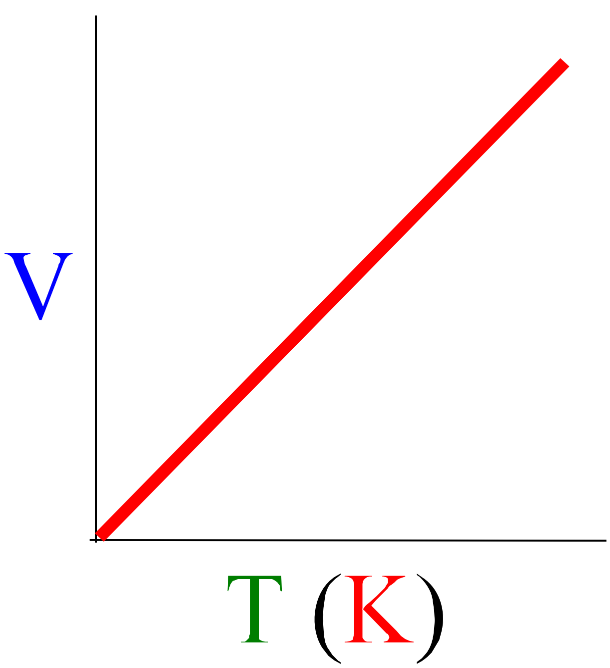
1) Ex: To what pressure must a gas be compressed to get it into a 3.00 ft^3 tank if it occupies 40.0 ft^3 at 1.00 atm?

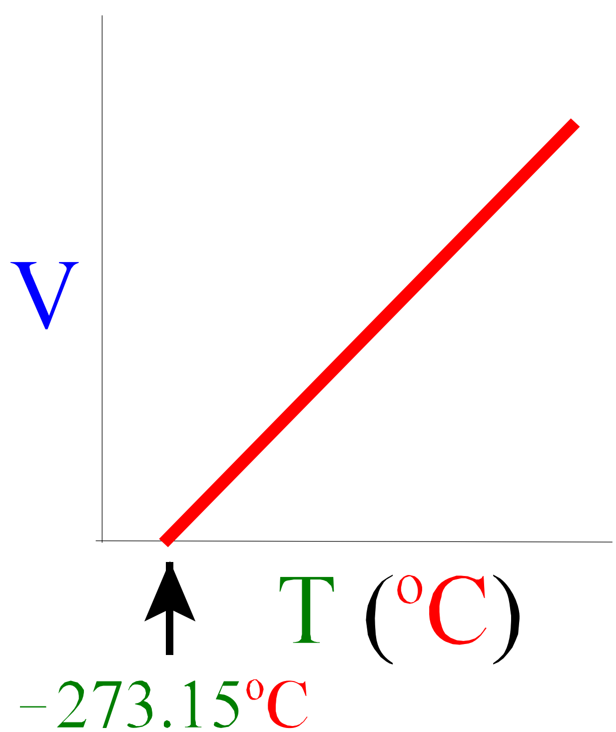
B) Charles's Law

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

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

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





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

$$V = k_3 \cdot n$$

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

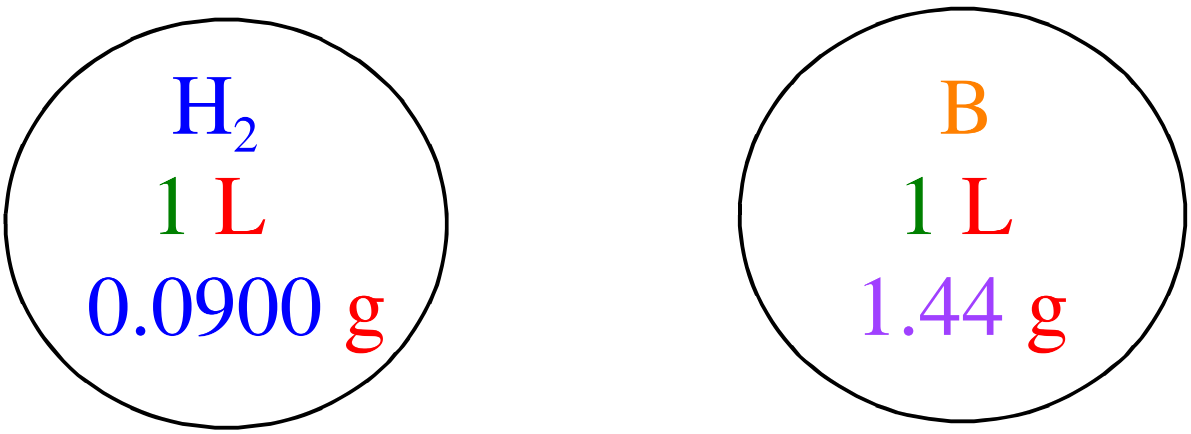
1) Determination of Mol. Wt.

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

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

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

Replace proportionality & rearrange

$$PV = nRT$$

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

Universal Gas Constant

Ideal Gas

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

Real Gas $\longrightarrow$ Ideal Gas

low P, high T

A) Standard Temp. & Pressure

Temp. & Pressure affect Volume

Need a "standard" T & P
as a reference point

STP

T = 0 °C (273.15 K)

P = 1 atm

B) Molar Volume

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

At STP:

Standard Molar Volume

1 mole gas	=	22.41 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.

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V) Further Applications of IGL

A) Determine MW & Molecular Formula

$$MF = (EF)_n$$

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

Determine EF & EFW from % composition data

Determine MW

$PV = nRT$ $\mathcal{M} = m/n$ $D = m/V$

$$D = \frac{P\mathcal{M}}{RT}$$

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 C_2H_5. What is its molecular formula?

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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

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

$$V = k\,n$$

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

1) Ex 1: What volume of oxygen gas would be required to produce 0.50 L of SO_2 by the following rx.?

$$2\ ZnS + 3\ O_2(g) \rightarrow 2\ ZnO + 2\ SO_2(g)$$

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?

$$Sb_4O_6 \ + \ 6\,C \ \rightarrow \ 4\,Sb \ + \ 6\,CO(g)$$

3) Ex 3: What vol. of $N_2(g)$ at STP would be produced by the rxn. of 0.86 g of NO(g)?

$$2\,NO(g) \;+\; 2\,H_2(g) \rightarrow 2\,H_2O(g) \;+\; N_2(g)$$

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

$$P_{tot} = P_1 + P_2 + P_3 + \cdots$$

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

Assume each gas behaves ideally

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

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

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?

B) Collecting Gases over Water

Gaseous product is collected in an inverted tube full of H_2O

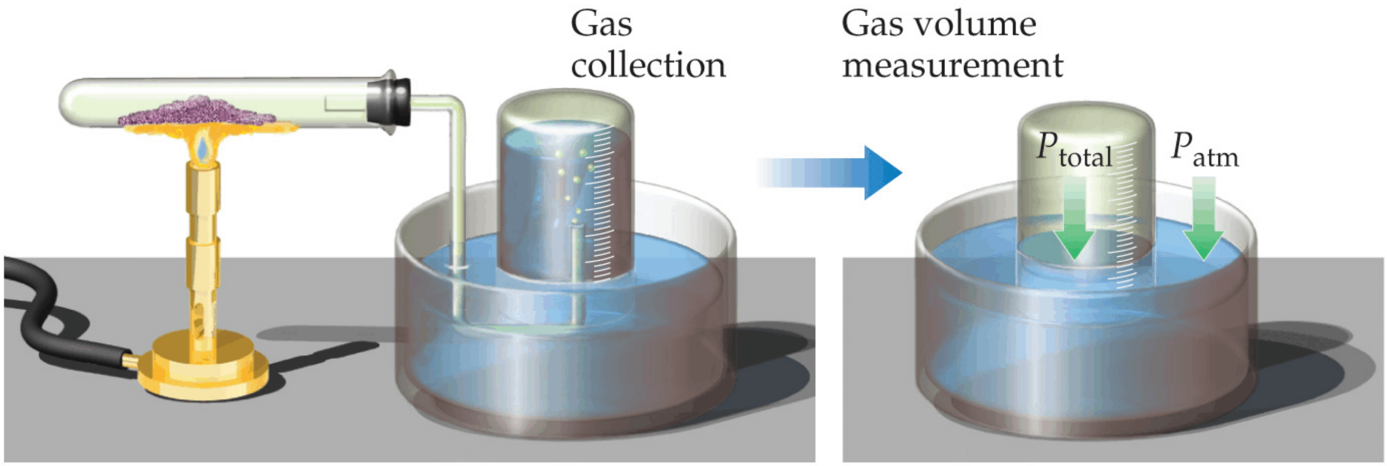
Gas displaces the H_2O

Gas collected is "wet"

- has water vapor

$$P_{\mathbf{Tot}} = P_{\mathbf{gas}} + P_{\mathbf{H2O}}$$

$$P_{\mathbf{gas}} = P_{\mathbf{Tot}} - P_{\mathbf{H2O}}$$



Gas
collection
Gas volume
measurement
P_{total}
P_{atm}

1) Ex:

$CaH_2(s) + 2\ H_2O \rightarrow Ca(OH)_2 + 2\ H_2(g)$

A student collected 90.0 mL of H_2 over water at 25°C & a total pressure of 755.0 mm Hg. How many grams of CaH_2 decomposed? (The vapor pressure of H_2O at 25°C is 23.8 mm Hg.)

$$P_{H2} = P_{Tot} - P_{H2O}$$

VII) Kinetic-Molecular Theory

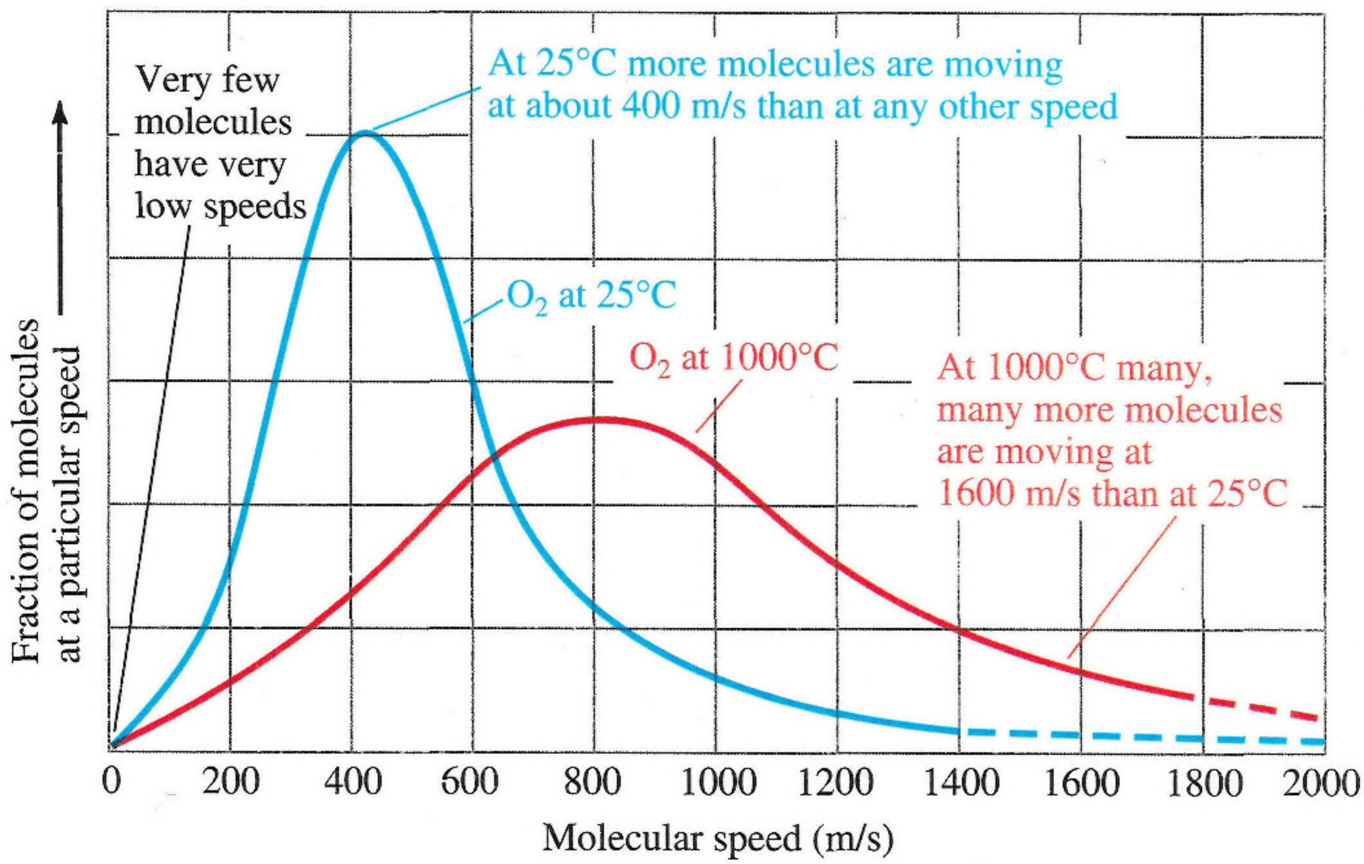
Explains behavior of ideal gases

A gas consists of molecules
in constant random motion

$$K.E. = \tfrac{1}{2} m (u_{rms})^2$$

u_{rms} = root-mean-square (rms) speed

$$u_{rms} = \left(\frac{1}{N} \sum_{i}^{N} s_i^{2}\right)^{1/2}$$



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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

Total KE of 1 mole of gas = 3/2 (RT)

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

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

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

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

1) Ex: Calc. the speed of a molecule of O_2 that has the avg. KE at room temp, 20°C.

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

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 ⇒ KE constant ⇒ u constant

∴ avg. molecular force/coll.
remains constant

Inc. Volume

Molecular conc. dec.

- freq. of coll./unit area dec.

∴ P dec.

1) Charles's Law

T inc. ⇒ KE inc. ⇒ 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.

∴ 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 $\Rightarrow$ Smaller m.f.p.

B) Effusion

Gas escapes through a small hole in a container

rate of effusion $\propto$ u

$$r \propto u$$

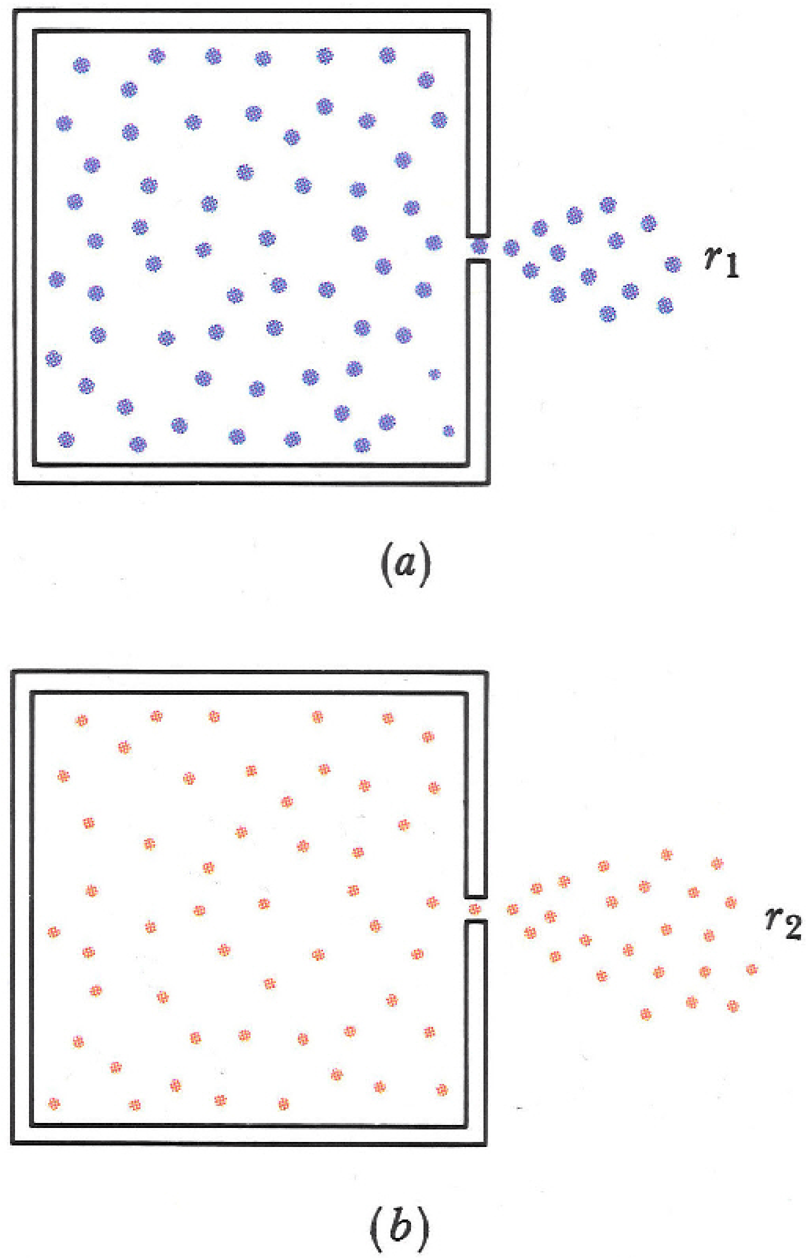
$$\therefore \quad r \propto \left(\frac{3RT}{\mathcal{M}}\right)^{1/2}$$

Graham's Law of Effusion

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

(at constant T & P)

Figure 10.14 Effusion of gases



1) Compare rates of effusion of 2 diff. gases

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \frac{\left(\frac{3RT_1}{\mathcal{M}_1}\right)^{1/2}}{\left(\frac{3RT_2}{\mathcal{M}_2}\right)^{1/2}}$$

$$\therefore \quad \frac{r_1}{r_2} = \sqrt{\frac{T_1 \mathcal{M}_2}{T_2 \mathcal{M}_1}}$$

At constant T,

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

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

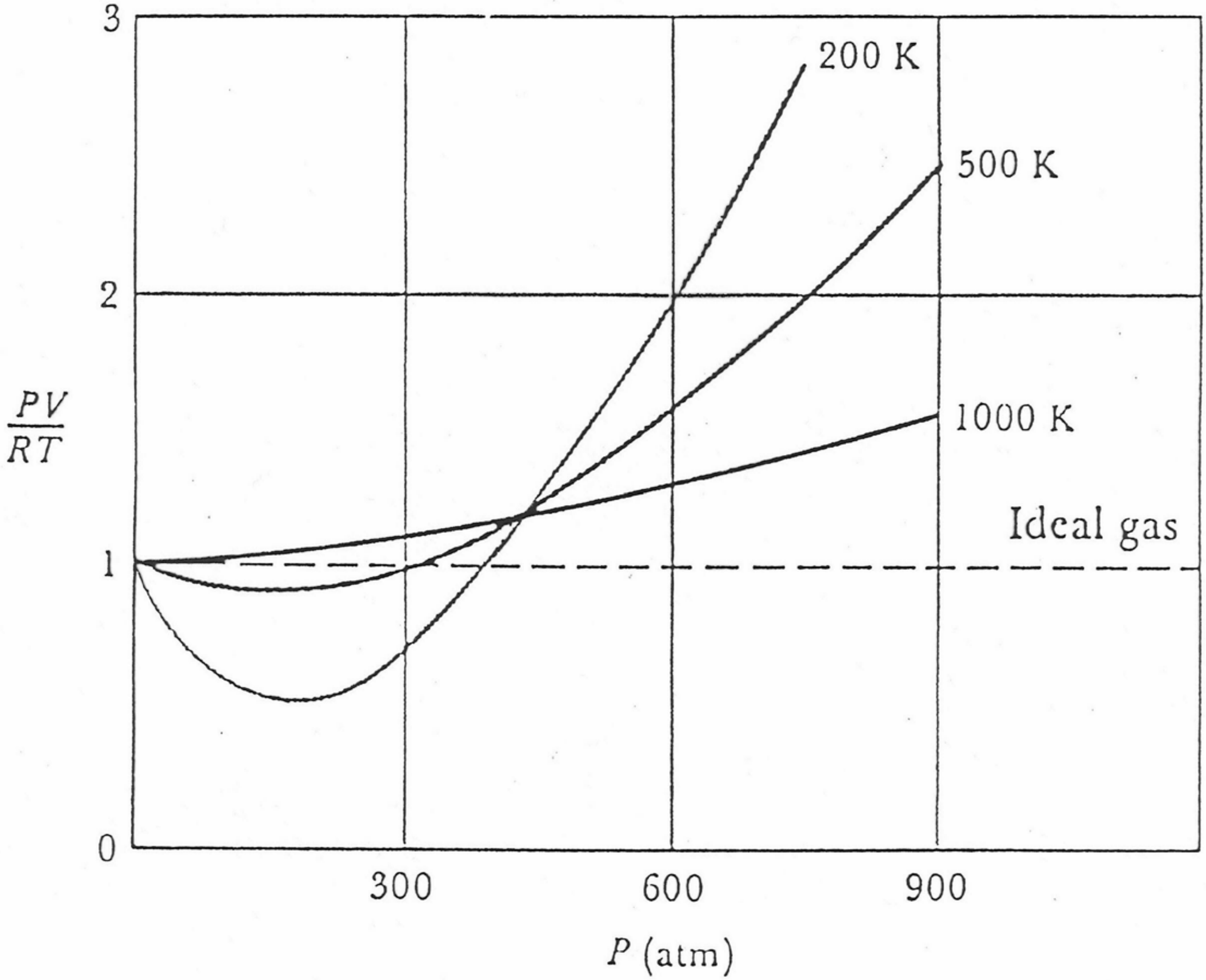
Some assumptions made in KMT are FALSE

- 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

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

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

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

$\Uparrow$ $\qquad\qquad$ $\Downarrow$

$P_m > P_i$ $\qquad\qquad$ $P_m < P_i$

1) nb term

correction for finite molecular volume

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

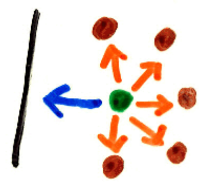
units for b : $\frac{L}{mol}$

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 intermolec. 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}	$\frac{nRT}{V-nb}$	$\left(\frac{n}{V}\right)^2 a$	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

$a = 1.39 \ \frac{L^2 \cdot atm}{mol^2}$ $\quad$ $b = 0.0391$ 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?