

B.Sc. Part-I (Chemistry)

Paper-I

Gaseous State: Part-1

General characteristics of Gases

- (a) Expansibility Expansion
- (b) Compressibility Compression
- (c) Diffusibility Diffusion ^{rapidly} as form homogeneous mixture
- (d) Pressure: exerts pressure on walls of container
- (e) Effect of heat ;
 $P \propto T$
 $V \propto T$

Parameters of a Gas

- (a) volume V
- (b) Pressure P
- (c) Temperature T
- (d) No. of Molar, n of Gas

Units

Volume

$$1 \text{ - Litre} = 1000 \text{ ml}$$

$$1 \text{ - Litre} = 1 \text{ dm}^3 = 1000 \text{ cm}^3$$

$$1 \text{ dm} = 10 \text{ cm}$$

$$1 \text{ dm} = 0.1 \text{ metre}$$

Temp

$$K \text{ (NOT } ^\circ K) = ^\circ C + 273.15$$

$$\frac{^\circ F - 32}{9} = \frac{^\circ C}{5} \quad \text{Fahrenheit - to - Celsius}$$

In Numericals, ALWAYS convert to Kelvin.
[Absolute Temp].

Pressure

$$1 \text{ atmosphere} = 1 \text{ atm} = 760 \text{ mm of Hg column}$$

$$= 760 \text{ torr}$$

SI unit is Pascal (Pa)

$$1 \text{ atm} = 760 \text{ torr} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \times 10^5 \text{ Pa} = \text{Bar}$$

$$1 \text{ atm} = 1.013 \text{ Bar}$$

Moles of Gas

$$\text{moles of gas (n)} = \frac{\text{mass of gas sample (w)}}{\text{molecular wt. of gas (M)}} = \frac{w}{M}$$

Boyle's Law

At const. T, V of a fixed mass of gas is inversely proportional to its P, i.e.,

$$V \propto \frac{1}{P}$$

$$PV = \text{const.}$$

$$P_1 V_1 = P_2 V_2$$

$$P_i V_i = P_f V_f$$

Charles's Law

At constant P, V of a fixed mass of gas is directly proportional to Absolute Temp

$$V \propto T$$

$$\frac{V}{T} = \text{const.}$$

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

Gay Lussac's Law

At constant V

$$P \propto T$$

Avagadro's Law

at const. T and P

$$V \propto n$$

equal volumes of gases at same T and P contain equal number of moles or molecules.

Molar Gas Volume

At standard Temp and Pressure (1 atm/273 K)
(1 atm/0°C) one mole of gas occupies vol.
of 22.4 L, i.e.,
Molar volume at STP = 22.4 Litre

Boyle $V \propto \frac{1}{P}$

Charles $V \propto T$

Avagadro $V \propto n$

Combine

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

or $PV = nRT$

is Universal Gas Law / Ideal Gas Law

R is Gas Constant

Ideal gas eqn. is called an Equation of State for a gas because it contains all the variables (P , T , V and n) which describe completely the condition or state of any gas sample. If we know the three of these variables, it is enough to specify the system completely because the 4th variable can be calculated from ideal-gas eqn.

Numerical value of R

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

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

$$V = 22.4 \text{ L}$$

$$n = 1 \text{ mole}$$

$$T = 273 \text{ K}$$

$$R = \frac{(1 \text{ atm}) \times (22.4 \text{ L})}{(1 \text{ mole}) \times (273 \text{ K})}$$
$$= 0.0821 \text{ atm} \cdot \text{litre} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

It may be noted that unit for R is complex; it is composite of all the units used in calculating the constant.

If P is written as Force/area and V as area \times length

$$R = \frac{(\text{force/area}) \times (\text{area} \times \text{length})}{n \times T}$$
$$= \frac{\text{force} \times \text{length}}{n \times T} = \frac{\text{work}}{n \times T}$$

Hence R can be expressed in units of work or Energy per degree per mole.

The actual value of R depends on the units of P and V used in calculating it. The most important values of R are listed below below

- 0.0821 litre-atm $K^{-1} \text{mol}^{-1}$
- 82.1 ml-atm $K^{-1} \text{mol}^{-1}$
- 62.3 litre-mm of H_2 $K^{-1} \text{mol}^{-1}$
- 8.314×10^7 erg $K^{-1} \text{mol}^{-1}$
- 8.314 J $K^{-1} \text{mol}^{-1}$
- 1.987 cal $K^{-1} \text{mol}^{-1}$ (or 2 cal $K^{-1} \text{mol}^{-1}$)

Dalton's Law of Partial Pressures

Total pressure of a mixture of gases is equal to the sum of the partial pressures of all the gases present.

$$P_{\text{total}} = P_1 + P_2 + P_3$$

$$P_1 = n_1 \left(\frac{RT}{V} \right) \quad P_2 = n_2 \left(\frac{RT}{V} \right) \quad \dots$$

$$P_i = n_i \left(\frac{RT}{V} \right)$$

$$P_{\text{total}} = \sum_i n_i \left(\frac{RT}{V} \right)$$

Graham's Law of Diffusion

Under the same conditions of T and P , the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses.

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

so a light molecule diffuses quicker than a heavy molecule.

When a gas escapes thro. a pin-hole into a region of low pressure or vacuum, the process is called Effusion.

The rate of effusion of a gas also depends on the molecular mass of gas.

Dalton's law when applied to effusion of a gas is called Dalton's law of effusion.

$$\frac{\text{Effusion rate of gas 1}}{\text{Effusion rate of gas 2}} = \sqrt{\frac{M_2}{M_1}} \quad (P, T \text{ const.})$$

The determination of rate of effusion is much easier compared to the rate of diffusion.

Therefore, Dalton's law of effusion is often used to find the molecular mass of a given gas.

Fig. 10-12: Diff. bet. (a) Diffusion (b) Effusion

- (a) Diffusion is mixing of gas molecules by random motion under conditions where molecular collisions occur.
(b) Effusion (thro. a pin-hole and w/o molecular collisions)

Kinetic Molecular Theory of Gases
by Maxwell - Boltzmann (1859)
is based on fundamental concept that a Gas is
made of a large no. of molecules in
perpetual motion

↳ hence Kinetic theory

Assumptions of Kinetic Molecular Theory

① A gas consists of extremely small (negligible vol.) of small discrete particles called molecules dispersed throughout vessel/container.

Fig 10.13 → dispersed gas molecules negligible

10.14 → Actual vol. of molecules negligible

10.15 → Gas molecules in constant motion in all directions

10.16 → Move in straight line, collide with walls or each other and change direction.

② Gas molecules are in constant motion with high velocities

③ The distance bet. molts. are very large and assumed that no van der Waals attractive forces.
↳ they move freely indep. of each other

④ All collisions are perfectly elastic. Hence no loss of K.E. during collision.

⑤ Pressure of gas is caused by the hits recorded by molecules on the walls of container.

⑥ Average K.E. ($\frac{1}{2}mv^2$) of the gas molecule is directly proportional to Absolute temp (K).
So avg. K.E. of molecules of ~~different~~ gases is same as a given temp

Van der Waals do talk about walls (force)

=

= T

How Does an Ideal Gas differ from Real Gas?

① No negligible vol.

② attractive forces bet. mole.

③ Molecular collisions are not perfectly Elastic

At very low T and very high P departure from Ideality

Derivation of kinetic Gas Eqn.

length of cubic box = l cm

total no. of gas mole. = n

mass of one mole. = m

v of mole. = v

① Resolution of velocity v of a single mole. along x, y, z

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

② No. of collisions per second on face A due to one mole.

$$\text{time bet. two collisions} = \frac{2l}{v_x} = \frac{1}{\frac{v_x}{2l}}$$

$$\text{no. of collisions per second} = \frac{v_x}{2l} = \frac{v_x}{l}$$

③ Total change of Momentum on all faces of box due to one molecule only

before impact $m v_x$

after impact $-m v_x$

$$\text{change of momentum} = m v_x - (-m v_x)$$

$$= 2 m v_x$$

But no. of collisions on face A due to one mole = $\frac{v_x}{l}$
 change in momentum per unit time $\frac{dp/dt}{dt}$

$$2 m v_x \times \frac{v_x}{l} = \frac{m v_x^2}{l}$$

$$\frac{2 m v_x^2}{l} + \frac{2 m v_y^2}{l} + \frac{2 m v_z^2}{l} = \frac{2 m v^2}{l}$$

→ pressure on 'y' & 'z' faces

$$= \frac{2 m v^2}{l}$$

The above was overall change of momentum per second on all faces of the box

- ④ Total change of momentum due to impacts of all the mole. on All faces of the box

$$= \frac{2m}{l} (v_1^2 + v_2^2 + v_3^2 + \dots)$$

Multiply and divide by mN

$$= \frac{2mN}{l} \left(\frac{v_1^2 + v_2^2 + v_3^2 + \dots}{N} \right)$$

$$= \frac{2mN}{l} \bar{v}^2 \quad \text{where } \bar{v}^2 \text{ is mean square velocity}$$

- ⑤ Calculation of Pressure from Change of Momentum: Derivation of Kinetic Gas Eqn.

$$\text{Force} = \frac{2mN\bar{v}^2}{l}$$

$$P = \frac{\text{Total Force}}{\text{Total Area}} = \frac{2mN\bar{v}^2}{l} \times \frac{1}{(l)^2}$$

$$= \frac{1}{3} \frac{mN\bar{v}^2}{V}$$

$$\text{or } PV = \frac{1}{3} mN\bar{v}^2$$

$$v_{rms} = \sqrt{\bar{v}^2} = \text{root-mean-square velocity.}$$

$$P = \frac{2mN\bar{v}^2}{l}$$

Kinetic Gas Eqn. in terms of Kinetic Energy

$$PV = \frac{1}{3} m N \bar{v}^2$$

$$= \frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2 \right)$$

$$= \frac{2}{3} N (e) \quad \text{where } e = \begin{array}{l} \text{or Avg. energy} \\ \text{of one molecule} \end{array}$$

$$PV = \frac{2}{3} E \quad \text{where } E = \begin{array}{l} \text{Avg. energy of} \\ \text{All Molecules} \end{array}$$

$$\therefore PV = nRT$$

$$\therefore \frac{2}{3} E = nRT$$

$$\therefore E = \frac{3}{2} nRT$$

Since no. of gas molecules in one mole of gas is N_A

$$\therefore e = \frac{E}{N_A} = \frac{3RT}{2N_A}$$

$$= \frac{3}{2} k_B T$$

This or avg. energy of a molecule can be calculated.

$$\frac{e}{T} = \frac{2m\bar{v}^2}{T}$$

Deduction of Gas Law from Kinetic Gas Eqn.

(a) Boyle's Law

According to kinetic theory there is a direct proportionality between Abs. Temp. and Avg. K.E.

$$\frac{1}{2} m N \bar{v}^2 \propto T$$

$$\frac{1}{2} m N \bar{v}^2 = k T$$

$$\frac{2}{3} \times \frac{1}{2} m N \bar{v}^2 = \frac{2}{3} k T$$

$$\frac{2}{3} \times \frac{1}{2} m N \bar{v}^2 = \frac{2}{3} k T$$

$$\therefore PV = \frac{1}{3} m N \bar{v}^2$$

$$\therefore PV = \frac{2}{3} k T$$

(b) Charles's Law

$$PV = \frac{2}{3} k T$$

$$V = \frac{2}{3} \frac{k}{P} T$$

As const. P

$$V \propto T$$

(c) Avogadro's Law

$$PV = \frac{1}{3} m_1 N_1 \bar{v}_1^2 \quad [\text{molecule } 1]$$

$$PV = \frac{1}{3} m_2 N_2 \bar{v}_2^2 \quad [\text{molecule } 2]$$

$$\frac{1}{3} m_1 N_1 \bar{v}_1^2 = \frac{1}{3} m_2 N_2 \bar{v}_2^2$$

As T is same & K.E. is same

$$\therefore \frac{1}{3} m_1 \bar{v}_1^2 = \frac{1}{3} m_2 \bar{v}_2^2$$

$$N_1 = N_2$$

i.e., under same condition of T and P, equal volume of all gases contain same nos. of mol. (molecules)

$$\frac{1}{2} m \bar{v}^2 = \frac{2}{3} k T$$

(d) Graham's Law of Diffusion

for v_1, v_2 and m_1, m_2 and ρ_1, ρ_2

then in same P and V

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

By Avogadro's law $n_1 = n_2$

$$m_1 v_1^2 = m_2 v_2^2$$

$$\therefore \frac{v_1^2}{v_2^2} = \frac{m_2}{m_1} = \frac{M_2}{M_1} \quad \left[\text{where } M_2 \text{ and } M_1 \text{ are Molar Mass} \right]$$

Rate of diffusion $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

Overall char
faces of

$$= \frac{2}{T}$$

$$\frac{2}{T} + \frac{2m v_r^2}{T}$$

$$= \frac{2m v_r^2}{T}$$