0

GASEOUS STATE

INTRODUCTION

Matter is made up of atoms or molecules. The arrangement of these molecules determines the state of matter. There are three recognised state of matter : Solid, Liquid and Gas. Matter can change between states when the temperature or pressure is changed. State changes of matter are physical rather than chemical.

0

DIFFERENCE BETWEEN STATES OF MATTER

S. No.	Gas	Liquid	Solid
i.	Assumes the shape and volume	Assumes the shape of the	Retains a fixed volume and
	of its container.	part of the container which	shape.
		it occupies	
ii.	Particles can move past one	Particles can move/slide past	Rigid-particles locked into
	another.	one another.	place.
iii.	Compressible, lots of free space	Not easily compressible, little	Not easily compressible, little
	between particles	space between particles.	free space between particles.
iv.	Flows easily, particles can move	Flows easily, particles can	Does not flow easily, rigid-
	past one another.	move/slide past one another	particles cannot move/slide one
			past another
v.	Low density.	Intermediate density.	High density.
vi.	Very small intermolecular	Considerable intermolecular	Intermolecular forces are high,
	attraction but high kinetic	attraction, kinetic energy	vibrational motion only.
	energies.	is less.	

GASEOUS STATE

1. Important Properties of Gases

- (i) Mass : Mass in $gm = Moles \times Molecular mass.$
- (ii) Volume : Volume of the gas is the volume of container in which they are filled in.
- (iii) Temperature : Temperature of a gas is the measure of kinetic energy of gas.

Kinetic energy ∞ Temperature

(iv) **Pressure :** Pressure of gas is defined as the force exerted by the gas on the walls of its container. It is often assumed that pressure is isotropic, i.e. it is the same in all the three directions.

Pressure =
$$\frac{\text{Force}}{\text{Area}}$$
,

$$P = \frac{\text{Mg}}{\text{A}} = \frac{v \times d \times g}{\text{A}}$$

$$= \frac{A \times h \times d \times g}{\text{A}}$$

$$P = hdg$$
Where....
$$h = \text{height of the mercury column supported by the barometer.}$$

$$d = \text{density of mercury.}$$

$$g = \text{acceleration due to gravity.}$$



- 2. Units and Determination of Pressure of Gas
 - (a) In SI unit the unit of pressure is the pascal (N/m^2) instead, the unit bar, kPa or MPa is used. $1 \text{ bar} = 10^5 \text{ N/m}^2 = 100 \text{ kN/m}^2 = 100 \text{ kPa}$
 - (b) Pressure are also stated in mm or cm of mercury.

1 atm = 760 mm Hg =
$$1.01325$$
 bar = 1.01325×10^5 Pa = 101.325 KN/m² = 1.0332 Kgf/cm²

$$1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ Kgm}^{-1} \text{ S}^{-1}$$

 $1L = 1dm^3 = 10^{-3} m^3$ (SI unit)

1L atm = 101.325 J

$$1 \frac{\text{KN}}{\text{m}^2} = 1 \times 10^3 \frac{\text{N}}{\text{m}^2} = \frac{1 \times 10^3 \times \text{kg}}{9.8 \times 10^4 \text{ cm}^2} = \frac{1}{98} \text{ kgf/cm}^2$$

1Torr = $\frac{101325}{760}$ Pa = 133.322 Pa

(d) The pressure relative to the atmosphere is called gauge pressure. The pressure relative to the perfect vacuum is called absolute pressure.

Absolute pressure = Gauge pressure + Atmosphere pressure

(e) When the pressure in a system is less than atmospheric pressure, the gauge pressure becomes negative, but is frequently designated and called vacuum.

For example, 16 cm vacuum will be -

$$\frac{76-16}{76}$$
 × 1.013 = 0.80 bar

(f) Pressure is measured using a manometer which is a simple device with a horizontal arm and a U-tube carrying mercury or any other suitable liquid.





Ex. Calculate the mass of mercury in a uniform column 760 mm high and 1.00 cm² in cross-sectional area. Is there any change in.

(a) mass and

(b) pressure of column of same height but with 2.00cm² cross sectional area is taken ? (density of Hg = 13.6 g/cm³)

Sol.

$$V = 76 \times 1 = 76 \text{ cm}^3$$

760 mm = 76 cm

$$\therefore$$
 Mass = V × d = 76 × 13.6 = 1033.6 g

(a) If area of cross-section is 2 cm^2 (doubled) then volume is also doubled hence,

 \therefore Mass = 76 × 2 × 13.6 = 2067.2 g

(b) This mass would rest on twice the area and so exert the same pressure.

GAS LAWS

The gas laws are a set of laws that describe the relationship between thermodynamic temperature (T), pressure (P) and volume (V) of gases.

1. Boyle's Law

It states "at a constant temperature (T), the pressure (P) of a given mass (or moles, n) of any gas varies inversely with the volume (V)". Pressure (P) and volume (V) of gases.

i.e.
$$P \propto \frac{1}{V}$$
 (for given n and T)



PV = K = constantor, For two or more gases at constant temperature $P_1V_1 = P_2V_2 = \dots = K$ Also, density d $\propto \frac{1}{v}$ Hence $P \propto d$ $\frac{P_1}{d_1} = \frac{P_2}{d_2} = \dots = K$ or \mathfrak{G} **Graphical Representation** $> T_1$ 1/Pр log P log P log 1/V Р-

These plots drawn at constant temperature for a gas are called Isotherms.

- Ex. The diameters of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake-water and the atmosphere are equal, what is the depth of the lake ? (The density of lake-water and Hg are 1 gm/ml and 13.6 gm/ml respectively. Also neglect the contribution of pressure due to surface tension).
- Sol. The pressure on the bubble = 1 atm (when it is at the surface)

The pressure on the bubble = P atm (say) (when it is at the bottom)

The volume of the bubble =
$$\frac{1}{6}\pi (0.1)^3$$

$$P \times \frac{1}{6} \pi \times (0.1)^3 = 1 \times \frac{1}{6} \pi (0.4)^3$$

or P = 64 atm. Thus the pressure due to water is 63 atm (\therefore atmospheric pressure = 1 atm) Now, consider the depth of lake is h cm

$$63 \times 76 \times 13.6 \times g = h \times 1 \times g$$

or $h = 63 \times 76 \times 13.6$ cm = 65116.8 cm.





$$\therefore \quad \bullet_4 \times a \times \left(76 + \frac{8}{\sqrt{2}}\right) = 10 \times a \times 76$$
$$\therefore \quad \bullet_4 = \left(\frac{10 \times 76}{76 + 8/\sqrt{2}}\right) = 9.3 \text{ cm}$$

(fig. 4)

An iron tank contains helium at a pressure of 3.0 atm at 27°C. The tank can withstand a maximum pressure of Ex. 10 atm. The building in which tank has been placed catches fire predict whether the tank will blow up first or melt. (melting point of iron is 1535°C) 20 T - 200 V

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \implies \frac{3.0}{300} = \frac{P_2}{1808}$$
$$P_2 = \frac{3.0 \times 1808}{300} = 18.08 \text{ atm}$$

Since at melting point it is greater than the maximum pressure, therefore it will blow up.



So

Ex. A rubber balloon contains some solid marbles each of volume 10 ml. A gas is filled in the balloon at a pressure of 2 atm and the total volume of the balloon is 1 litre in this condition. If the external pressure is increased to 4atm the volume of Balloon becomes 625 ml. Find the number of marbles present in the balloon.

Sol. Let the no. of marbles be = n.

volume of marble = 10 n ml.

volume of balloon earlier = 1000 ml.

later = 625 ml.

Now for the gas inside the balloon temperature and amount of the gas is constant, hence boyles law can be applied

 $P_{1}V_{1} = P_{2}V_{2}$ $4 \times (625 - 10n) = 2 \times (1000 - 10n)$ $625 \times 4 = 2000 - 20n + 40n$ $625 \times 4 - 2000 = 20n$ $\frac{625 \times 4 - 2000}{20} = n. \qquad \frac{125}{5} = n \quad ; \qquad n = 25$

2. Charles' Law

It states "at constant pressure, the volume of a given mass of a gas, increases or decreases by $\frac{1}{273.15}$ th of its volume at 0°C for every rise or fall of one degree in temperature".

$$\frac{V_{t}}{V_{0}} = 1 + \frac{1}{273.15} t$$
 (at constant n and P)
$$V_{t} = V_{0} \left(1 + \frac{t}{273.15} \right)$$

or

or

 $V_t = \frac{V_0(273.15 + t)}{273.15}$

 $\frac{V_t}{T_t} = \frac{V_0}{T_0}$

0°C on the Celsius scale is equal to 273.15 K at the Kelvin or absolute scale. i.e. T_t (Temperature in Kelvin scale) = 273.15 + t

$$\therefore \quad \text{From the above equation we get } \frac{V_t}{V_0}$$

or

i.e. The volume of a given gas is proportional to the absolute temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ (at constant P)}$$

80 Graphical Representation



Graphs between V and T at constant pressure are called Isobars.



Ex. If the temp. of a particular amount of gas is increased from 27° C to 57° C, find final volume of the gas, if initial volume = 1 lt and assume pressure is constant.

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

 $\frac{1}{(273+27)} = \frac{V_2}{(273+57)}$ So $V_2 = 1.1$ lt.

Ex. An open container of volume 3 litre contains air at 1 atmospheric pressure. The container is heated from initial temperature 27°C or 300 K to t°C or (t + 273) K the amount of the gas expelled from the container measured 1.45 litre at 17°C and 1 atm.Find temperature t.

Sol. $\therefore T_{1}^{0} = 300 \text{ K}$

It can be assumed that the gas in the container was first heated to (t + 273), at which a volume ' ΔV ' escaped from the container

hence applying charles law :

$$\frac{3}{300} = \frac{3+\Delta V}{t+273}$$

Now, this volume ' Δ V' which escapes when the container get cooled

$$\therefore \qquad \frac{\Delta V}{t+273} = \frac{1.45}{290}$$

Solve the two equations and get the value of ΔV and t. determine ΔV & calculate t that will be the answer.

3. Gay-Lussac's Law : Dependence of Pressure on Temperature

It states "at constant volume, the pressure of a given mass of a gas is directly proportional to the absolute temperature of the gas".

$$P \propto T$$
 or $P = KT$

or
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

80 Graphical Representation



The plots drawn at constant volume for a gas is called as Isochore.

80 The Combined Gas Law

It states "for a fixed mass of gas, the volume is directly proportional to absolute temperature and inversely proportional to the pressure".

Boyle's Law,
$$V \propto \frac{1}{P}$$
 (at constant n, T)

Charle's Law, V \propto T (at constant n, P)

Therefore,
$$V \propto \frac{T}{P}$$
 or $V = K \frac{T}{P}$ or $\frac{PV}{T} = K$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$



& Volume Coefficient (αv) of a Gas

The ratio of increase in volume of a gas at constant pressure per degree rise of temperature to its volume at 0°C is the volume coefficient of the gas.

$$\alpha_{v} = \frac{V_{t} - V_{0}}{V_{0} \times t} \quad \text{or} \quad V_{t} = V_{0} (1 + \alpha_{v} t)$$

For all gases, $\alpha_{v} = \frac{1}{273}$

δ Pressure Coefficient (αp) of a Gas

The ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C is the pressure coefficient of the gas.

$$\alpha_{p} = \frac{P_{t} - P_{0}}{P_{0} \times t} \qquad \text{or} \quad P_{t} = P_{0} (1 + \alpha_{p} t)$$

For all gases, $\alpha_{p} = \frac{1}{273}$

4. Avogadro's Law

or,

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

V \propto n (At constant P and T) $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

Ex. The temperature of a certain mass of a gas is doubled. If the initially the gas is at 1 atm pressure. Find the % increase in pressure ?

Sol.
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
; $\frac{1}{T} = \frac{P_2}{2T}$

% increase = $\frac{2-1}{1} \times 100 = 100\%$

Ex. The temperature of a certain mass of a gas was increased from 27°C to 37°C at constant volume. What will be the pressure of the gas.

Sol.
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
; $\frac{P}{300} = \frac{P_2}{310}$; $P_2 = \frac{31}{30}$ P

THE IDEAL GAS EQUATION

An ideal gas is defined to be a system in which there are no inter molecular/interatomic forces. Such a system can only exist as a gas. Any real system will approach ideal gas behaviour in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.

An ideal gas is a gas to go which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures.

From Boyle's law we get,

 $V \propto 1/P$ (at constant n and T)

From charles law we get,

 $V \propto T$ (at constant n and P)



From Avogadro's law we get,

 $V \propto n$ (at constant T and P)

Combining the above three equations we get

$$V \propto \frac{nT}{P}$$
 or $V = R \frac{nT}{P}$

or PV=nRT

Ideal gas equation is a relation between four variables and it describes the state of any gas. For this reason, it is also called Equation of State.

[Where R = ideal gas constant]

80 Dimension of R

$$R = \frac{PV}{nT} = \frac{Pressure \times Volume}{Mole \times Temperature}$$
$$= \frac{(Force / Area) \times (Area \times Length)}{Mole \times Degree(K)}$$
$$= \frac{Force \times Length}{Mole \times Degree(K)} = \frac{Work \text{ or energy}}{Mole \times Degree(K)}$$

80 Physical Significance of R

The dimentions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1K.

EDUBULL KEY POINTS					
Units	Units of R				
(i)	In lit-atm	$R = \frac{1 \text{ atm} \times 22.4 \text{ lit}}{273 \text{ K}} = 0.0821 \text{ lit-atm} \text{ mol}^{-1} \text{K}^{-1}$			
(ii)	In C.G.S system	$R = \frac{1 \times 76 \times 13.6 \times 980 \text{ dyne } \text{cm}^{-2} \times 22400 \text{ cm}^{3}}{273 \text{ K}}$			
		$= 8.314 \times 10^7 \mathrm{erg \ mole^{-1} K^{-1}}.$			
(iii)	In M.K.S. system	$R = 8.314$ Joule mole ⁻¹ K^{-1} . [10 ⁷ erg = 1 joule]			
(iv)	In calories	$R = \frac{8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}}{4.184 \times 10^7 \text{ erg}}$			
		= 1.987 ≈ 2 calorie mol ⁻¹ K ⁻¹ .			

Ex. Some spherical balloons each of volume 2 litre are to be filled with hydrogen gas at one atm & 27° C from a cylinder of volume 4 litres. The pressure of the H₂ gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27° C.

Sol. No. of moles of gas taken initially =
$$\frac{20 \times 4}{R \times 400} = 2.43 \text{ L}$$

No. of moles of gas left in cylinder = $\frac{1 \times 4}{R \times 300} = 0.162L$

No. of moles of gas to be filled in balloons = 2.43 - 0.162 = 2.268



Let we have 'n' balloons that we can fill

No. of moles of gas that can be filled in 1 balloon = $\frac{1 \times 2}{0.082 \times 300} = 0.081$

 $\therefore 0.081 \times n = 2.268$

n = 28 balloons.

Ex. At room temperature following reaction goes to completion

 $2NO + O_2 \longrightarrow 2NO_2 \longrightarrow N_2O_4$

Dimer N_2O_4 at 262 K is solid. A 250 ml flask and a 100 ml flask are separated by a stop cock. At 300 K, the nitric oxide in the large flask exerts a pressure of 1.053 atm and the smaller on contains O₂ at 0.789 atm. The gases are mixed by opening the stop cock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of dimer. Find out the pressure and composition of gas remaining at 220 K (Assume gases behave ideally).

 0.32×10^{-2}

For NO gas :-Sol.

$$n_{NO} = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000} = 1.069 \times 10^{-2}$$

For O₂ gas :- $n_{O_2} = \frac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.32 \times 10^{-2}$

2NO

Now, Mole before reaction

 1.069×10^{-2} 0.32×10^{-2} $1.069 \times 10^{-2} - 2 \times 0.32 \times 10^{-2}$ Mole after reaction 0 $= 0.429 \times 10^{-2}$ Moles of NO left = 4.29×10^{-3} Given T = 220 K $P_{NO} \times V = nRT$ $V = \frac{250 + 100}{1000} = \frac{350}{1000}$ litre

 $P_{\rm NO} \times \frac{350}{1000} = 4.29 \times 10^{-3} \times 0.821 \times 220$

 P_{NO} (left) = 0.221 atm.

DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume in equal to the sum of the partial pressures of the component gases."

 $P_{Total} = p_1 + p_2 + p_3 + \dots$ (At constant V and T) $= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \dots\right) RT = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{nRT}{V}$

Where $n = n_1 + n_2 + n_3 + \dots =$ Total moles, V = Total volume

$$\mathbf{P}_{\text{Total}} = \sum \mathbf{p}_{i} = \frac{\mathbf{RT}}{\mathbf{V}} \sum \mathbf{n}_{i}$$

Dalton's law of partial pressure is applicable only to non-reacting gases.

If the two non-reacting gases A and B having n_A and n_B number of moles respectively are filled in a vessels of volume V at temperature T, Then



 $PV = (n_A + n_B) RT$ (i)

Partial pressure may be calculated as

 $p_A V = n_A RT$, $p_B V = n_B RT$ Total pressure $(p_A + p_B) V = (n_A + n_B) RT$ (ii) from (i) and (ii)

$$P = p_A + p_B$$

$$\frac{\mathbf{p}_{A}}{\mathbf{P}} = \frac{\mathbf{n}_{A}\mathbf{RT} / \mathbf{V}}{(\mathbf{n}_{A} + \mathbf{n}_{B})\mathbf{RT} / \mathbf{V}} = \frac{\mathbf{n}_{A}}{\mathbf{n}_{A} + \mathbf{n}_{B}} = \mathbf{x}_{A} \text{ (mole fraction of A)}$$

 $p_A = x_A \times P$, similarly $p_B = x_B \times P$

Partial pressure of a component = Mole fraction \times total pressure.

It has been observed that gases are generally collected over water and therefore are moist.

$$P_{dry gas} = P_{moist gas} - P_{water vapou}$$

The pressure exerted by water vapour is constant with water at a particular temperature is called as aqueous tension, which varies directly with the temperature and becomes 760 mm at 100°C.

Relative Humidity (RH) = $\frac{Partial pressure of water in air}{Vapour pressure of water}$

Pressure of dry gas = Pressure of moist gas – aqueous tension.



- Ex. The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing as ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure if the temperature remains same.
- Sol. After the opening of the stop cock the pressure of the each bulb will remain same.

At the beginning, the no. of moles of gas in A = $\frac{10 \times 6}{RT}$

At the beginning, the no. of moles of gas in B = $\frac{5 \times 9}{RT}$

 \therefore total no. of moles at the beginning = $\frac{105}{RT}$

Total no. of moles of gas before opening the stop cock

= total no. of moles of gas after opening stop $\operatorname{cock} = \frac{105}{RT}$

... pressure after the opening of the stop cock

$$P = \frac{105}{RT} \times \frac{RT}{V_{total}} = \frac{105}{10+5} = 7 \text{ atm}$$





- Ex. A mixture of NO_2 & CO having total volume of 100 ml contains 70 ml of NO_2 at 1 atm, mixture is left for some time and same NO_2 get dimerised to N_2O_4 such that final volume of the mixture become 80 ml at 1 atm, calculate the mole fraction of NO_2 in final equilibrium mixture.
- **Sol.** Initial volume of $NO_2 = 70 \text{ ml}$

Initial volume of CO = 100 - 70 = 30 ml

Final volume of mixture = 80 ml

Let the volume of NO_2 in final mixture be x

Let 'v' ml NO₂ be converted to N_2O_4

$$2NO_2 \longrightarrow N_2O_4$$

$$V \qquad V/2$$

Hence final volume

= volume of CO + volume of NO₂ left + volume of N_2O_4 formed

$$= 30 + 70 - V + V/2 = 80$$

$$V=40 \, ml$$

Hence volume of NO₂ left = 70 - V = 30 ml

Now as volume \propto moles

$$\therefore$$
 mole fraction = volume fraction = $\frac{30}{80} = \frac{3}{8}$

AMAGAT'S LAW OF PARTIAL VOLUME

According to this law at constant temperature and pressure, the total volume of mixture of gases which don't react is equal to the sum of partial volumes of each component present in mixture.

$$V_{T} = V_{1} + V_{2} + V_{3} + \dots$$

80 Partial Volume

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

PV = nRT

V ∝ n

80 Partial Volume

Let us consider a three non-reacting gases A, B and C are present in a container which have no. of moles n_A, n_B and n_C respectively. For each gas partial volume is

$$V_{A} = n_{A} \left(\frac{RT}{P}\right), \quad V_{B} = n_{B} \left(\frac{RT}{P}\right) \quad and \quad V_{C} = n_{C} \left(\frac{RT}{P}\right)$$

80 Total Volume

$$V_{T} = V_{A} + V_{B} + V_{C} = (n_{A} + n_{A} + n_{A}) \left(\frac{RT}{P}\right) = n_{T} \left(\frac{RT}{P}\right)$$



- Ex. A vessel of 2 lit capacity contains hydrogen at 380 mm pressure at 27°C. 16gm of O_2 is added to the container then find the total pressure and partial pressure where R = 0.0821 L atm mol⁻¹ k⁻¹.
- **Sol.** For H_2 gas :

Given

V = 2L and
$$p_{H_2} = \frac{380}{760} = \frac{1}{2}$$
 atm

пт

$$\mathbf{p}_{\mathrm{H}_2} \mathbf{v} = \mathbf{n}_{\mathrm{H}_2} \mathbf{K} \mathbf{I}$$

$$1 = n_{H_2} \times 0.0821 \times 300$$

$$n_{\rm H_2} = \frac{10000}{821 \times 300} = \frac{1}{24.6}$$

Moles of $O_2 = \frac{16}{32} = \frac{1}{2}$

Partial pressure of H₂ gas (p_{H2}) = $\frac{1}{2} = \frac{n_{H_2}}{n_{H_2} + n_{o_2}} \times P$

$$\frac{1}{2} = \frac{\frac{1}{24.6}}{\frac{1}{24.6} + \frac{1}{2}} \times P \quad \text{or} \quad P = 6.65 \text{ atm}$$

Ex. 1 mole of N_2 and 3 moles of H_2 are mixed in 8.21 lit container at 300 K to form NH_3 . If equilibrium average molecular mass was found to be 34/3 gram then find partial pressure of each component.

Sol.

 $N_2 + 3H_2 \ddagger \uparrow \uparrow \ddagger 2NH_3$ Initially 1 3 0 at equilibrium (1 - x) 3 (1 - x) 2x Total moles = 1 - x + 3 - 3x + 2x = (4 - 2x) moles

Given Average molecular mass = $\frac{34}{3}$

$$\frac{34}{3} = \frac{28(1-x) + 2(3-3x) + 17(2x)}{(4-2x)}$$
$$\frac{34}{3}(4-2x) = 34 \implies 4-2x = 3 \implies x = 1/2$$

So total no. of moles = 3

$$PV = nRT \implies P = \frac{nRT}{V} = \frac{3 \times 0.821 \times 300}{8.21} = 9 \text{ atm}$$
$$p_{N_2} = \frac{1 - x}{3} \times P = \frac{0.5}{3} \times 9 = 1.5 \text{ atm}$$
$$p_{H_2} = \frac{3 - 3x}{3} \times P = \frac{1.5}{3} \times 9 = 4.5 \text{ atm}$$



Ex. At constant temperature of 273K, $\frac{1}{V}$ Vs P are plotted for 2 ideal gases A and B as shown. Find out the number

of moles of gas A and B.

PV = nRT,

$$\frac{1}{V} = \frac{1}{nRT}P$$

Comparing by equation : y = mx + CC = 0

1

$$m = \frac{1}{nRT} \qquad (m = \tan \theta)$$

$$\tan \theta = \frac{1}{nRT} \qquad n_A = \frac{1}{RT\tan\theta}$$

$$n_A = \frac{1}{0.0821 \times 273 \times \tan45^\circ} \implies n_A =$$

$$n_B = \frac{1}{RT\tan60^\circ} = \frac{1}{22.4\sqrt{3}}$$

 $P = \frac{1}{V} nRT$



Ex. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mmHg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium ? Assume the temperature to be 50° C. Aqueous tension at 50° C = 93 mmHg.

22.4

Sol. The aqueous tension remains same in both the flask. Also flask are at same temperature

$$\therefore P_1 V_1 = P_2 V_2$$

where $P_1 = 200 - 93 = 107 \text{ mm}$
 $V_1 = 1 \text{ litre}$
 $V_2 = 2 \text{ litre}$
$$\therefore 107 \times 1 = P \times 2$$

P = 53.5 mm

V = 1 litre V = 1 litre

Since aqueous tension is also present in flask, equivalent to 93 mm. \therefore pressure of gaseous mixture = 93 + 53.5 = 146.5 mmHg.

Ex. A 500 ml bulb is filled with CH_4 at a pressure of 1 atm and oxygen at a pressure of 4 atm at 27°C. The mixture is then exploded, when the reaction $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ (•) occurs. Calculate the pressure if the final temperature is 27°C. Aqueous tension at 27°C is 26.7 mm.

Sol. Partial pressure of
$$CH_4$$
, $(p_{CH_4}) = 1$ atm
Partial pressure of O_2 , $(p_{O_2}) = 4$ atm
 \therefore moles of CH_4 present, $(n_{CH_4}) = \frac{1 \times 0.5}{RT} = \frac{0.5}{RT}$
 \therefore moles of O_2 present $(n_{O_2}) = \frac{4 \times 0.5}{RT} = \frac{2}{RT}$
 $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(\bullet)$
Initially $\frac{0.5}{RT}$ $\frac{2}{RT}$

GASEOUS STATE

Finally
$$\frac{1}{RT}$$
 $\frac{0.5}{RT}$

After the reaction, moles of residual $O_2 = \frac{2}{RT} - \frac{1}{RT} = \frac{1}{RT}$

After the reaction, moles of CO_2 produced = $\frac{0.5}{RT}$

Hence total no. of moles of O_2 and $CO_2 = \frac{1.5}{RT}$

$$\therefore$$
 total pressure due to O₂ and CO₂ = $\frac{1.5}{\text{RT}} \times \frac{\text{RT}}{0.5} = 3 \text{ atm}$

... pressure exerted by the entire gaseous components

$$= 3 + \frac{26.7}{760} = 3 + 0.03513 = 3.0513 \text{ atm}$$

Ex. What is the difference in the density of dry air at 1 atm and 25°C and moist air with 50% relative humidity under the same condition. The vapour pressure of water at 25°C is 23.7 Torr and dry air has 75.5% N₂ and 24.5% O₂.

Sol. M (dry air) =
$$\frac{M_1(O_2)X_1(\% \text{ of } O_2) + M_2(N_2)X_2(\% \text{ of } N_2)}{X_1 + X_2}$$

$$= \frac{32 \times 24.5 + 28 \times 75.5}{100} = 28.98 \text{ g mol}^{-1}$$

d (dry air) =
$$\frac{PM(air)}{RT} = \frac{1 \times 28.98}{0.0821 \times 298} = 1.184 \text{ g } \text{L}^{-1} = 1.184 \text{ kg m}^{-3}$$

 $\left(Q1gL^{-1} = \frac{10^{-3}kg}{10^{-3}m^3} = 1\text{kg m}^{-3}\right)$

relative humidity (50%) = $\frac{\text{partial pressure of } H_2 \text{O in air}}{\text{vapour pressure of } H_2 \text{O}}$

:.
$$P(H_2O) = 0.50 \times 23.7 \text{ Torr}$$

$$= 11.85 \text{ torr} = \frac{11.85}{760} \text{ atm} = 0.0156 \text{ atm}$$

% of H₂O vapour in air =
$$\frac{0.0156 \times 100}{1}$$
 = 1.56%

% of N_2 and O_2 in air = 98.44%

M (wet air) =
$$\frac{28.98 \times 98.44(air) + 18 \times 1.56(water vapour)}{100} = 28.81 \text{ g mol}^{-1}$$

d (wet air) = $\frac{PM(\text{wet air})}{RT} = \frac{1 \times 28.81}{0.0821 \times 298} = 1.177 \text{ g } \text{L}^{-1} = 1.177 \text{ kg m}^{-3}$ difference = 1.184 - 1.177 = 0.007 kg m⁻³



- A sample of butane gas C4H10 of unknown mass is contained in a vessel of unknown volume V at 25°C and Ex. a pressure of 760 mmHg. To this vessel 8.6787 g of neon gas is added in such a way that no butane is lost from the vessel. The final pressure in the vessel is 1920 mm Hg at the same temperature. Calculate the volume of the vessel and the mass of butane.
- Partial pressure of C_4H_{10} (p₁) = 760 mm Hg Sol.
 - By Dalton's law of partial pressure, $P_{total} = p_1 + p_2$

$$1920 = 760 + p_2$$
 or $p_2 = 1160$ mm Hg

$$p_2 = x_2 \times p_{total}$$

 $x_2 =$ mole fraction of Ne where

$$x_2 = \frac{P_2}{P_{total}} = \frac{1160}{1920} = 0.60$$
; Moles of Ne = $\frac{8.6787}{20.2} = 0.43$

$$x_2 = \frac{n_2}{n_1 + n_2}$$
; $0.60 = \frac{0.43}{0.43 + n_1} \Rightarrow n_1 = 0.28$

Molecular weight of $C_4H_{10} = 48 + 10 = 58$ so, amount of $C_4H_{10} = n_1 \times 58 = 16.24$ g again for C₄H₁₀

PV =
$$n_1 RT$$
; T = 273 + 25 = 298 K, P = $\frac{760}{760}$ atm = 1 atm
V = $\frac{n_1 RT}{P} = \frac{0.28 \times 0.0821 \times 298}{1} = 6.85 L$

- A mixture of CO and CO₂ is found to have a density of 1.50 g/litre at 30°C and 730 mm. Calculate the composition Ex. of mixture.
- Sol. For mixture, P = (730/760) atm,

T = 303 K, $d = 150 g litre^{-1}$

$$\therefore \qquad PV = nRT = (w/M) RT \Rightarrow P(w/VM) RT \Rightarrow P = \frac{d}{M} RT$$

$$\frac{730}{760} = \frac{1.50}{M} \times 0.0821 \times 303$$

Let n_1 moles of CO and $(100 - n_1)$ moles of CO₂ are present in 100 moles.

Average molecular weight (M) =
$$\frac{n_1 \times 28 + (100 - n_1) \times 44}{100} = 38.85 \implies n_1 = 32.19$$

mole % of CO = 32.19, and mole % of CO₂ = 67.81.

Ex.

An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant. Find

- (a) the temperature at which vessel was heated ?
- (b) the air escaped out if vessel is heated to 900 K?
- (c) temperature at which half of the air escapes out ?
- Sol. One should clearly note the fact that on heating a gas in a vessel there are the number of moles of gas which go out, the volume of vessel remains constant.



Let initial moles of air at 300 K be 'n'. On heating 3/5 moles of air are escaped out at temperature T.

- Moles of air left at temperature $T = \left(n \frac{3}{5}n\right) = \frac{2n}{5}$
- Under simillar conditions of P and V (a)

$$n_1 T_1 = n_2 T_2$$
$$n \times 300 = \frac{2n}{5} \times T \implies T = 750 \text{ K}$$

(b) On heating vessel to 900 K, let n_1 moles be left again $n_1T_1 = n_2T_2$

$$n_1 \times 900 = 300 \times n \implies n_1 = \frac{1}{3} n$$

 \therefore moles escaped out = $n - \frac{n}{3} = \frac{2}{3}n$ moles

Let n/2 moles are escaped out at temperature T then (c)

$$\mathbf{n}_1 \mathbf{T}_1 = \mathbf{n}_2 \mathbf{T}_2$$

$$n/2 \times T = n \times 300$$

T= 600 K

GRAHAM'S LAW OF DIFFUSION AND EFFUSION

Diffusion

The process of mixing of gases by random motion of the molecules is called diffusion.

Effusion

When gas is confined to a container at high pressure than in the surrounding atmosphere it will escape from a small hole which is opened in the container until the pressure outside and inside have been equalised. This process is called effusion.

The difference between diffusion and effusion is that in the former case, the gas spontaneously passes through a porous partition while in the case of effusion, the gas is passed out through a small orifice or hole by applying some external pressure.

Graham's law of diffusion states "under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses or their densities."

Mathematically,
$$\mathbf{r} \propto \sqrt{\frac{1}{M}}$$
 or $\sqrt{\frac{1}{d}}$ or, $\frac{\mathbf{r}_1}{\mathbf{r}_2} = \sqrt{\frac{\mathbf{M}_2}{\mathbf{M}_1}} = \sqrt{\frac{\mathbf{d}_2}{\mathbf{d}_1}}$

Where r_1 and r_2 are the rates of diffusion of gases 1 and 2.

M₁ and M₂ are their molecular masses.

 d_1 and d_2 are their densities.

Effect of Volume on Rate of Diffusion

Volume of gas diffused Rate of diffusion = $\overline{\text{Time taken for diffusion}}$

Let V_1 be the volume of gas 1 and V_2 be the volume of gas 2, then

$$r_{1} = \frac{V_{1}}{t_{1}} \qquad r_{2} = \frac{V_{2}}{t_{2}}$$
$$\frac{r_{1}}{r_{2}} = \sqrt{\frac{M_{2}}{M_{1}}} = \frac{V_{1}t_{2}}{V_{2}t_{1}}$$



(i) Comparison of Times Taken for the Same Volume of Two Gases Let the times of diffusion for the same volume of two gases be t₁ and t₂ respectively. Then

$$\frac{\mathbf{r}_{1}}{\mathbf{r}_{2}} = \frac{\mathbf{V} / \mathbf{t}_{1}}{\mathbf{V} / \mathbf{t}_{2}} = \sqrt{\frac{\mathbf{d}_{2}}{\mathbf{d}_{1}}} = \sqrt{\frac{\mathbf{M}_{2}}{\mathbf{M}_{1}}} \quad \text{or} \quad \frac{\mathbf{r}_{1}}{\mathbf{r}_{2}} = \frac{\mathbf{t}_{2}}{\mathbf{t}_{1}} = \sqrt{\frac{\mathbf{d}_{2}}{\mathbf{d}_{1}}} = \sqrt{\frac{\mathbf{M}_{2}}{\mathbf{M}_{1}}}$$

Comparision of the Volumes of the Gases that Diffuse in Same Time **(ii)** Let V_1 and V_2 be the volume of two gases that diffuse in same time t. Then,

$$\frac{r_1}{r_2} = \frac{V_1 / t}{V_2 / t} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(iii) **Effect of Pressure on Rate of Diffusion**

Rate of diffusion is proportional to the pressure of the gas in the container.

$$r \propto P$$
 ; again, $r \propto \frac{1}{\sqrt{M}}$

or
$$r \propto \frac{P}{\sqrt{M}}$$
 or $\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$

Application of Graham's Law of Diffusion in Enrichment of Isotopes **Enrichment of Light Component**

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas passing through will be enriched in lighter component by a factor $\sqrt{\frac{M_B}{M_A}}$, called enrichment factor because lighter molecules effuse more rapidly than heavier ones. The remaining gas will be enriched in the heavier component. Each passage gives an enrichment factor equal to $\sqrt{\frac{M_B}{M_A}}$ and so thousands of such barrier in succession are necessary to provide sufficient enrichment of heavier component.

Thus, enrichment factor for first barrier or operation $f_1 = \sqrt{\frac{M_B}{M_A}}$

 \therefore overall separation or enrichment factor $f = \frac{n_A^2 / n_B^2}{n_A^2 / n_B^2}$

Where n_A , n_B , and n_A , n_B are the concentration of two isotopically different components before and after processing. If required enrichment of gas A is attained in x-operation then,

or

or

$$x \log \left[\frac{M_{\rm B}}{M_{\rm A}}\right]^{1/2} = \log \left[\frac{n_{\rm A}^{'} / n_{\rm B}^{'}}{n_{\rm A}^{'} / n_{\rm B}^{\rm B}}\right]$$

 $(f_1)^x = \frac{n'_A / n'_B}{n_A / n_B} = f$

 $x \log f_1 = \log \left[\frac{n'_A / n'_B}{n_A / n_B} \right]$



or
$$\frac{x}{2} \log \left[\frac{M_{B}}{M_{A}}\right] = \log \left[\frac{n_{A}^{'}/n_{B}^{'}}{n_{A}^{'}/n_{B}}\right]$$

$$\mathbf{x} = \frac{2\log\left(\frac{\mathbf{n}_{A}^{'} / \mathbf{n}_{B}^{'}}{\mathbf{n}_{A}^{'} / \mathbf{n}_{B}^{'}}\right)}{\log\left(\frac{\mathbf{M}_{B}}{\mathbf{M}_{A}^{'}}\right)}$$

or

LIMITATIONS OF THIS LAW

- (i) The laws of diffusion and effusion are applicable only when the pressure difference is very small.
- (ii) Correctly speaking the rate of diffusion and effusion are not constant throughout the time interval, but these rates may be assumed constant for a small time interval.
- **Ex.** The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.
- Sol. The molar ratio of oxygen and the other gas in the evacuated bulb = 1 : 1 and the total pressure of the gas mixture is 4000 mm, hence the partial pressure of each gas is 2000 mm.

The drop in the pressure of oxygen after 74 minutes

$$=\frac{(2000-1500)\times74}{47}=787.2 \text{ mm of Hg}$$

After 74 minutes, the pressure of oxygen = 2000 - 787.2 = 1212.8 mm of Hg Let the rate of diffusion of other gas be r_n , then

$$\frac{\mathbf{r}_{n}}{\mathbf{r}_{0_{2}}} = \sqrt{\frac{32}{79}}$$

... Drop in pressure for the other gas $= 787.2 \times \sqrt{\frac{32}{79}} = 501.01 \text{ mm of Hg}$

 \therefore Pressure of the other gas after 74 minutes = 2000 - 501.01 mm = 1498.99 mm of Hg

Molar ratio =
$$\frac{\text{Moles of unknown gas}}{\text{Moles of O}_2} = \frac{1498.99}{1212.8} = 1.236 : 1$$

- Ex. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound.
- **Sol.** Rate of diffusion, $r \propto p$

$$\mathbf{r} \propto \sqrt{1/M} \text{ or } \mathbf{r} \propto \frac{\mathbf{p}}{\sqrt{M}}$$
$$\frac{\mathbf{r}_2}{\mathbf{r}_1} = \frac{\mathbf{p}_2}{\mathbf{p}_1} \left(\frac{\mathbf{M}_1}{\mathbf{M}_2}\right)^{1/2}$$
$$\approx \frac{1}{t}$$



or

Again, r ∝

or

$$\frac{t_1}{t_2} = \left(\frac{p_2}{p_1}\right) \left(\frac{M_1}{M_2}\right)^{1/2}$$

or

$$M_{2} = \left(\frac{p_{2}t_{2}}{p_{1}t_{1}}\right)^{2} M_{1}$$
$$M_{2} = \left(\frac{1.6}{0.8} \times \frac{57}{38}\right)^{2} \times 28 = 252 \text{ g mol}^{-1}$$

Let the molecular formula of the unknown compound be XeF_n .

or
$$M_{xe} + nM_F = 252$$

 $131 + 19 n = 252$
 $n = \frac{252 - 131}{19} = 6.36;$

Hence, the molecular formula of the gas is XeF_6 .

Ex. At 1200°C, mixture of Cl_2 and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atoms. M (Kr) = 83.8 g mol⁻¹.

6

Sol.
$$Cl_2 \ddagger \uparrow \uparrow \uparrow 2Cl$$

$$\frac{r(Cl_2 \text{ and } Cl \text{ mix})}{r(\text{Kr})} = 1.16 \sqrt{\frac{M(\text{Kr})}{M_{av}(\text{Cl}_2 + \text{Cl})}} = \sqrt{\frac{83.8}{M_{av}}}$$

$$\therefore M_{av} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$

$$Cl_2 \quad \hat{\ddagger} \land \hat{\cancel{}} \quad 2Cl$$
Initial mole 1 0
After dissociation (1 - x) 2x
(x = degree of dissociation)
Total moles after dissociation = 1 - x + 2x = (1 + x)
$$\therefore \frac{(1-x)M(\text{Cl}_2) + 2x M(\text{Cl})}{(1 + x)} = 62.28$$

$$\frac{(1-x) \times 71 + 2x \times 35.5}{1 + x} = 62.28$$

$$\frac{(1-x + x)71}{1 + x} = 62.28$$

$$\frac{1}{1 + x} = \frac{62.28}{71} = 0.88$$

$$1 + x = 1.14$$

$$x = 0.14$$

$$\therefore \qquad \% \text{ dissociation = 14\%}$$

Alternately, following formula can also be used to determine degree of dissociation when there is equilibrium mixture.

$$= \frac{m(normal) - m(average)}{m(average)} = \frac{71 - 62.28}{62.28} = 0.14$$



Х

Ex. In a tube of length 5 m having 2 identical holes at the opposite ends. $H_2 \& O_2$ are made to effuse into the tube from opposite ends under identical conditions. Find the point where gases will meet for the first time.



- Ex. Assume that you have a sample of hydrogen gas containing H_2 , HD and D_2 that you want to separate into pure components (H = ¹H and D = ²H). What are the relative rates of diffusion of the three molecules according to Graham's law?
- Sol. Since D_2 is the heaviest of the three molecules, it will diffuse most slowly, and let we call its relative rate 1.00. We can then compare HD and H_2 with D_2 .

Comparing HD with D_2 , we have

 $\frac{\text{Rate of HD diffusion}}{\text{Rate of } D_2 \text{ diffusion}} = \sqrt{\frac{\text{Molecular mass of } D_2}{\text{Molecular mass of HD}}} = \sqrt{\frac{4.0 \text{ amu}}{3.0 \text{ amu}}} = 1.15$

Comparing H_2 with D_2 we have

 $\frac{\text{Rate of H}_2 \text{ diffusion}}{\text{Rate of D}_2 \text{ diffusion}} = \sqrt{\frac{\text{Mass of D}_2}{\text{Mass of H}_2}} = \sqrt{\frac{4.0 \text{ amu}}{2.0 \text{ amu}}} = 1.41$

Thus, the relative rates of diffusion are $H_2(1.41) > HD(1.15) > D_2(1.00)$.

Connecting Containers

- (1) When we are connecting two or more containers then the movement of any component of gas occurs in other container till the final pressure of that component in all the container become equal (that means partial pressure becomes equal).
- (2) To calculate composition of gaseous mixture in any container, we will use law of diffusion.
- Ex. A 10 liter container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 liter and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

(a) Moles and pressure of gas in both the containers before heating.

(b) Moles and pressure in two containers after heating. (assume that initially the larger container is completely evacuated.)

Sol. (a) Before heating :

PV = nRT



$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$X = 0.8 \text{ moles}$$
Pressure = $\frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$
(b) After heating :
 $\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$

$$X_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$
Pressure = $\frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times .0821 \times 600}{40} = 0.821 \text{ atm}$



Ex. A mixture containing 1.12 litre D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D_2 . Determine the % by weight of the gases in second bulb.

Sol. At STP

Before diffusion
$$\begin{array}{l} D_2 = 1.12 \text{ lit.at STP} = 0.2 \text{ g} = 0.05 \text{ mole} \\ H_2 = 2.24 \text{ lit.at STP} = 0.2 \text{ g} = 0.1 \text{ mole} \end{array}$$
in I bulk



When these moles are placed in the bulb, the partial pressure of gas will be different because V and T are constant. Also $P \propto n$

Thus,

 $\frac{P_{D_2}}{P_{H_2}} = \frac{0.05}{0.10} = \frac{1}{2}$ After diffusion D₂ left in I bulb = 0.1 g

or D_2 diffuses from I into II (bulb) = 0.2 - 0.1 = 0.1 g Now for diffusion of D_2 and H_2

$$\frac{r_{D_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{D_2}}} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\Rightarrow \quad \frac{w_{D_2}}{t_{D_2}} \times \frac{t_{H_2}}{w_{H_2}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\therefore \qquad \frac{0.1}{t} \times \frac{t}{w_{H_2}} = \sqrt{\left(\frac{4}{2}\right)} \times \frac{1}{2}$$

$$\therefore \qquad w_{H_2} = 0.14 \text{ g}$$

$$\therefore \qquad Wt. \text{ of gases in II bulb = wt. of } D_2 + \text{ wt. of } H_2$$

$$= 0.10 \text{ g} + 0.14 \text{ g} = 0.24 \text{ g}$$

$$0.10$$

%
$$D_2$$
 by wt. = $\frac{0.10}{0.24} \times 100 = 41.66$ %
% H_2 in bulb II = 58.33%



Ex. Calculate the relative rates of diffusion for ${}^{235}\text{UF}_6$ and ${}^{238}\text{UF}_6$ in gaseous form. Also if naturally occurring uranium ore having U²³⁵ and U²³⁸ in the ratio 0.72 and 99.28%, and if it is desired to enrich the U²³⁵ to 10% of the sample, making use of relative rates of diffusion of UF₆ having U²³⁵ and U²³⁸ isotopes, how many diffusion stages are required ?

Sol.

M.wt of ²³⁵U $F_6 = 235 + 19 \times 6 = 349$ M.wt of ²³⁸U $F_6 = 238 + 19 \times 6 = 352$

From Graham's law at same P and T

$$\frac{r_1}{r_2} = \sqrt{\left(\frac{M_2}{M_1}\right)}$$
$$\frac{r_{U^{235}F_6}}{r_{U^{238}F_6}} = \sqrt{\left(\frac{352}{349}\right)} = 1.0043$$

Also
$$x = \frac{2\log\left(\frac{n_A / n_B}{n_A / n_B}\right)}{\log\left(\frac{M_B}{M_A}\right)}$$

Here,
$$n_A = U^{235}$$
 in $U^{235}F_6 = 0.72$
 $n_B = U^{238}$ in $U^{238}F_6 = 99.28$
 $n'_A = U^{235}$ in $U^{235}F_6 = 10$
 $n'_B = U^{238}$ in $U^{238}F_6 = 90$
 $x = \frac{2\log\left(\frac{(10/90)}{(0.72/99.28)}\right)}{\log\left(\frac{352}{349}\right)} = 638$ steps

and $M_B = M_U^{238}_{F_6}$ and $M_A = M_U^{235}_{F_6}$

BAROMETRIC PRESSURE DISTRIBUTION

In case of air (ideal gas) density depends on pressure. So we can not calculate pressure difference between two points directly as 'hdg'.

Assume in case of air, composition of air and temperature is constant throughout.

Suppose pressure at height 'h' from the ground level is 'P' and as height increase by 'dh' the pressure decreases by 'dP'. So the pressure difference between two points is :

$$-dP - dP = dh \times d \times g$$

$$-dP = dh \times \frac{PM}{RT} \times g \qquad [PM = dRT]$$

$$\int_{P_0}^{P} \frac{-dP}{P} = \frac{Mg}{RT} \int_{0}^{H} dh$$

$$[1_n P]_{P_0}^{P} = \frac{-Mg}{RT} [h]_{0}^{H}$$





$$\ln \frac{P}{P_0} = \frac{-MgH}{RT}$$

$$P = P_0 e^{-\frac{MgH}{RT}}$$

$$M = \text{molar mass of air (kg/mole)}$$

$$g = 9.8 \text{ m/sec}^2$$

$$H = \text{height in meter}$$

$$R = 8.314 \text{ J/mole/K}$$

Calculate the expression for density of air at any height 'H' metre from the ground level. If at the ground level Ex. atmospheric pressure is P₀ atm and average molar mass of air is 'M' and temperature is 'T' kelvin. Given that average molar mass and temperature are constant.

Sol.

$$P = P_0 e^{-\left(\frac{MgH}{RT}\right)}$$
$$\frac{dRT}{M} = P_0 e^{-\left(\frac{MgH}{RT}\right)}$$
(MdH

$$\mathbf{d} = \left(\frac{P_0 \mathbf{M}}{\mathbf{R}T}\right) \mathbf{e}^{-\left(\frac{\mathbf{M} \mathbf{g} \cdot \mathbf{I}}{\mathbf{R}T}\right)}$$

Density at ground level = $d_0 = \frac{P_0 M}{RT}$) $\left(\frac{MgH}{RT}\right)$

$$\therefore \qquad \mathbf{d} = \mathbf{d}_0 \ \mathbf{e}^{-(-1)}$$

PAYLOAD OF BALLOON

Payload of a balloon is defined as maximum weight which a bolloon can carry with it upward direction.

$$V = Volume of Balloon, d_{out} = density of autside air,$$

 d_{in} = density of gas inside, m = mass of balloon.

$$Payload = d_{out} \times V \times g - [d_{in} V \times g + mg]$$

= [Buoyancy force] – [effective wt. of Balloon]



Calculate payload of a balloon having volume 100 litre. It is filled with helium gas at 0.2486 atm pressure and 300 K. Ex. Density of air is 1.3 gm./litre and mass of material of bolloon is 20 gm.

$$PM = dRT$$

$$d_{in} = \frac{PM_{He}}{RT} = \frac{0.2486 \times 4}{0.0821 \times 300} = \frac{1}{25}$$
Payload = 1.3 × 100 × 10 - $\left[\frac{1}{25} \times 100 \times 10 + 20 \times 10\right]$

$$= \frac{13}{10} \times 100 \times 10 - [4 \times 10 + 200] = 1300 - 240 = 1060$$

Sol.

(A) CALCULATION OF PAYLOAD OF BALLOON AT CONSTANT HEIGHT

(1) At constant volume of balloon

Payload =
$$d_{out}$$
 V. g - [w]
 $d_{out} = d_0 e^{\left(-\frac{Mgh}{RT}\right)}$
Payload = $d_0 e^{-\frac{Mgh}{RT}}$ V.g - w

Density of outside air decreases with increase in height so buoyancy force decreases and payload of balloon decreases with increase in height.

(2) At variable volume of balloon

$$PV = nRT$$

$$PV = constant$$

$$P_0V_0 = P_h \times V_h$$

$$P_0V_0 = P_0 e^{\left(-\frac{Mgh}{RT}\right)} \times V_h$$

$$V_h = V_0 e^{\left(\frac{Mgh}{RT}\right)}$$
Now payload = d_{out} × V × g - w
$$= d_0 e^{-\frac{Mgh}{RT}} V_0 e^{\left(\frac{Mgh}{RT}\right)} xg - w = d_0 V_0 g + c_0$$
= constant

In this case buoyancy force at any height is same so payload will remain constant throughout.

(B) MAXIMUM HEIGHTAT WHICH BALLOON WILL BURST

Maximum volume = V_{max}

$$V_{max} = V_0 e^{\left(\frac{Mgh_{max}}{RT}\right)}$$
$$\frac{V_{max}}{V_0} = e^{\left(\frac{Mgh_{max}}{RT}\right)}$$
$$h\left(\frac{V_{max}}{V_0}\right) = \left(\frac{Mgh_{max}}{RT}\right)$$
$$h_{max} = \frac{RT}{Mg} ln\left(\frac{V_{max}}{V_0}\right)$$

Ex. Calculate the payload of balloon of diameter 20 meter weight 100 kg. If it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kgm^{-3} . [R = 0.082 dm³ atm K⁻¹ mol⁻¹]

Sol. Weight of balloon = $100 \text{ kg} = 10 \times 10^4 \text{ g}$

Volume of balloon =
$$\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{20}{2} \times 100\right)^3$$

= 4190 × 10⁶ cm³ = 4190 × 10³ litre

Weight of gas (He) in balloon = $\frac{PV}{RT} = \frac{1 \times 4190 \times 10^3 \times 4}{0.082 \times 300} = 68.13 \times 10^4 \text{ g}$



Total weight of gas and balloon = $68.13 \times 10^4 + 10 \times 10^4 = 78.13 \times 10^4$ g

Weight of air displaced = $\frac{1.2 \times 4190 \times 10^6}{10^3} = 502.8 \times 10^4 \text{ g}$

- \therefore Payload = wt. of air displaced (wt. of balloon + wt. of gas)
- $\therefore \qquad \text{Payload} = 502.8 \times 10^4 78.13 \times 10^4 = 424.67 \times 10^4 \text{ g} = 4.2467 \times 10^6 \text{ g}$
- Ex. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atmpsphere at 27°C. If the cylinder can hold 2.82 litre of water at NTP, calculate the number of balloons that can be filled up.
- Sol. Radius of the balloon $=\frac{21}{2}$ cm = 10.5 cm Volume of the balloon $=\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10.5)^3$ cc = 4851 cc Pressure $= 1 \times 76 \times 13.6 \times 981 = 1.014 \times 10^6$ dynes/cm²

$$\therefore \qquad \text{No. of mole of H}_2, \text{ the balloon can contain at NTP} = \frac{\text{PV}}{\text{RT}} = \frac{1.014 \times 10^6 \times 4851}{8.314 \times 10^7 \times 273} = 0.2167$$

No. of mole in the cylinder = $\frac{20 \times 76 \times 13.6 \times 981 \times 2820}{8.314 \times 10^7 \times 300} = 2.2929$

When the balloons are being filled, the pressure in the cylinder will decreases, when the pressure of the cylinder will drop to 1 atm, gas cannot be withdrawn.

Now, no. of moles of H₂ remaining in the cylinder unused =
$$\frac{1.014 \times 10^6 \times 2820}{8.314 \times 10^7 \times 300} = 0.1146$$

 \therefore No. of balloons that can be filled = $\frac{\text{No.of moles of H}_2 \text{ in the cylinder that can be used}}{\text{No.of moles of H}_2 \text{ in one balloon can contain}}$
= $\frac{2.2929 - 0.1146}{10} = 10$

- Ex. (a) How much H₂ (in moles) is needed to inflate a balloon of radius 3.0 m to a pressure of 1.0 atm in an ambient temperature of 25°C at sea level ?
 - (b) What mass can the balloon lift at sea level, where the density of air is 1.22 kg m⁻³?
 - (c) What would be the payload if He were used instead of H_2 ?

Sol. (a) $PV = n_{H_2} RT$

where P = 1 atm = 1.0132×10^5 N m⁻²,

0.2167

$$V = \frac{\tau}{3} \times \pi \times (3)^3 \text{ m}^3,$$

1

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, T = 298 \text{ K}$$

$$_{\rm H_2} = \frac{\rm PV}{\rm RT} = \frac{1.0132 \times 10^5 \times \frac{4}{3} \times \frac{22}{7} \times (3)^3}{8.314 \times 298} = 4.62 \times 10^3 \, \rm mol$$



(b) Density of air = 1.22 kg m^{-3}

hence, mass of air = volume of balloon \times density

$$= \frac{4}{3}\pi r^{3} \times d = \frac{4}{3} \times \frac{22}{7} \times (3)^{3} \times 1.22 \text{ kg} = 138.03 \text{ kg}$$

mass of $H_2 = n_{H_2} \times M_w$ of $H_2 = 4.62 \times 10^3 \times 2 = 9.24$ kg

hence, the mass that the balloon can lift

= mass of air – mass of $H_2 = 138.03 - 9.24 = 128.79 \text{ kg}$

(c) Payload if He were used instead of $H_2 = 138.03 - 18.48 = 119.55 \text{ kg}$

[Mass of He = $n_{He} \times M_w$ of He = 4.62 × 10³ × 4 = 18.48 kg]

0

CALCULATION OF VAPOUR DENSITY OF MIXTURE IN REACTION

It is given that initially only reactant A is present with vapour density (D). It has degree of dissociation α and finally vapour density 'd'

A	\longrightarrow	nΒ
- ` n		

Moles before dissociation 1

Moles after dissociation $1 - \alpha$ $n\alpha$

 \therefore total no. of moles after dissociation = 1 + (n - 1) α

Since, mol. wt.
$$\propto \frac{1}{\text{no. of particles present}}$$

 $\therefore \frac{1}{\text{Normal mol. wt}} \propto \text{no. of particles before dissociation}$

 \therefore $\frac{1}{\text{Experimental mol. wt}} \propto \frac{1}{1} \cos \frac{1}{1}$

 $\therefore \qquad \frac{\text{Normal mol. wt.}}{\text{Experimental mol. wt}} \propto \frac{\text{no. of particles after dissociation}}{\text{no. of particles before dissociation}}$

$$\frac{M_{\text{Normal}}}{M_{\text{max}}} = \frac{1 + (n-1)\alpha}{1}$$

The entire conclusion can represented in a general way as -

$$\frac{P_{\text{Normal}}}{P_{\text{experimental}}} = \frac{D_{\text{Normal}}}{D_{\text{experimental}}} = \frac{M_{\text{Normal}}}{M_{\text{experimental}}} = 1 + (n-1)\alpha$$

KINETIC THEORY OF GASES

The theoretical model for all the experimental gas laws can be analys with the help of kinetic theory of gases which is based on following assumptions :

- (a) All the gases consists of very small molecules or atoms whose volume is negligible compared to volume of container (in case volume of container is very small, then this assumption will be violated)
- (b) There is no interaction between gaseous particles (the interaction may appreciably affected under certain conditions of temperature and pressure).



- (c) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as brownian motion)
- (d) Due to the continuous motion, collision between gaseous molecules with the wall of cantainer occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.
- (e) The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.
- (f) All the collision occuring are considered to be perfectely elastic which implies that there is no loss of energy.
- (g) The average kinetic energy of gas will depends on absolute temperature only.

Derivation of Equation for Kinetic Molecular Theory

Let us consider a cube of side L, that has N_0 molecules each of mass m moving with velocity u in all direction and thus colliding with one each other and against sides of the container. Velocity u can be resolved into three components u_x , u_y and u_z along there axes such that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$
 (assume velocity in ms⁻¹ and distance in meter)



For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity u_x . After collision against face B it moves towards face A with velocity $(-u_x)$ collissions being elastic (which results in change in direction but not velocity)

Momentum before collision on face $B = mu_x$

Momentum after collision on face $B = -mu_x$

Change in momentum due to one collision on face B

 $= mu_x - (-mu_x) = 2mu_x$

To strike face B again distance travelled = 2L



Time taken to strike face B again = $\frac{2L}{u_x}$ seconds

 \therefore Number of collisions per second on face B along x-axis = $\frac{u_x}{2L}$

 $\therefore \qquad \text{Change in momentum due to } \frac{u_x}{2L} \text{ collisions per second on face B along x-axis} = 2mu_x \cdot \frac{u_x}{2L} = \frac{mu_x^2}{L}$

Change in momentum per second due to collisions of one molecule on opposite faces A and B along x-axis = $\frac{2mu_x^2}{L}$

Similarly for y-axis change in momentum per second = $\frac{2mu_y^2}{L}$ and for z-axis = $\frac{2mu_z^2}{L}$

Total change in momentum per second due to collisions of a single molecule on six faces along three axes

$$= \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L}$$
$$= \frac{2m}{L}(u_x^2 + u_y^2 + u_z^2) = \frac{2mu^2}{L}$$

But rate of change in momentum per second = Force

$$\therefore \qquad \text{Force} = \frac{2\text{mu}}{\text{L}}$$

$$\therefore \qquad \text{Pressure} = \frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{2\text{mu}^2}{\text{L}}}{6\text{L}^2} = \frac{\text{mu}^2}{3\text{L}^3} = \frac{\text{mu}^2}{3\text{V}} \qquad [\text{L}^3 = \text{volume V}]$$

 \therefore Pressure due to collisions of N₀ molecules on six faces of a cube = $\frac{1}{3}$ mN₀u²

$$PV = \frac{1}{3} mN_0 u^2 = \frac{1}{3} Mu^2$$

 $mN_0 = M \text{ (molar mass)}$ $N_0 = Avogadro's number$

u = root mean square velocity (U_{rms})

Translational Kinetic Energy of n Moles

$$\frac{1}{2}$$
 Mu² = $\frac{3}{2}$ PV = $\frac{3}{2}$ nRT

Average Translational Kinetic Energy Per Molecule

$$=\frac{3}{2}\frac{RT}{N_0}=\frac{3}{2}KT$$

Where $K\left(=\frac{R}{N_0}\right)$ is called Boltzmann's constant.

Its numerical value is 1.38×10^{-16} erg K⁻¹ molecule⁻¹ Thus average K.E. is proportional to absolute temperature. If T = 0 K (i.e., -273.15°C), then average KE = 0 Thus, absolute zero (0 K) is the temperature at which molecular motion ceases.



DIFFERENT TYPES OF MOLECULAR VELOCITIES

$$\mathfrak{E} \mathbf{P} \mathbf{V} = \frac{1}{3} \mathbf{M} \mathbf{U}_{\rm rms}^2$$

(i) Root mean square velocity (U_{rms}) : It is defined as the square root of the mean of the squares of the velocities possessed by all the molecules present in the given sample of gas

$$U_{\rm rms} = \sqrt{\frac{U_1^2 + U_2^2 + ...U_n^2}{N}}$$

 \therefore U_{rms} (root mean square velocity) = $\sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$

Where d is the density.

 \mathfrak{W} If N₁ molecules have velocity u₁ and N₂ molecules have velocity u₂, then

$$U_{\rm rms} = \sqrt{\frac{N_1 u_1^2 + N_2 u_2^2}{N_1 + N_2}}$$

(ii) Average velocity (U_{av}) : It is given by the arithmetic mean of square of the different velocities possessed by the molecules of the gases at a particular temperature.

$$U_{av} = \frac{U_1^2 + U_2^2 + \dots U_n^2}{n}$$

 \mathfrak{W} U_{av} (average velocity)

$$\sqrt{\frac{8RT}{\pi M}}$$

(iii) Most probable velocity (U_{mp}) : It is defined as the velocity possessed by the maximum number of molecules of a gas at a given temperature.

$$\mathfrak{W}$$
 U_{mp} (most probable velocity) = $\sqrt{\frac{2RT}{M}}$

80 If P and T both are given, use equation in terms of temperature i.e. use

$$U_{\rm rms} = \sqrt{\frac{3RT}{M}}$$
 and not $\sqrt{\frac{3PV}{M}}$

80 To have velocity in ms⁻¹ (MKS) take $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$, M in kg.

80 If density is in kg m⁻³ and P in N m⁻², velocity will be in ms⁻¹.

Relation between rms velocity, average velocity and most probable velocity.

$$U_{\text{rms}} : U_{\text{av}} : U_{\text{mp}} = \sqrt{\frac{3\text{RT}}{M}} : \sqrt{\frac{8\text{RT}}{\pi M}} : \sqrt{\frac{2\text{RT}}{M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.2248 : 1.1284 : 1$$

$$U_{\text{rms}} = 1.2248 U_{\text{mp}}$$

$$U_{\text{av}} = 1.1284 U_{\text{mp}}$$

$$U_{\text{mp}} = 1.0854 U_{\text{av}}$$



Distribution of Molecular Speeds

- (a) The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus, the net result is that we cannot speak of the speed of individual molecule; hence must consider the statistical averages of the speeds of the whole collection of gas molecules.
- (b) The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

$$dN = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mu^2}{2\pi KT}} u^2 du$$

- (c) The above expression gives the no. of molecules dN having speeds between U and U + du in terms of total no. of molecules, N present in the gas m is mass of single gas molecule and T is the absolute temperature of gas.
- (d) The Maxwell distribution of speeds is customarily plotted with the fraction $\frac{1}{N} \left(\frac{dNu}{dU} \right)$ as the ordinate and U as the abscissa.



So, the term, $\frac{1}{N}\frac{dN}{dU}$ represents the fraction of molecules in the speed range of u to u + du per unit interval

of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between u and (u + du). The distribution of two temperatures is shown in the fig.

- (c) The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u, however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed (U_{mps}). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.
- (f) It can be seen from the given figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers. The total area under the curve gives the total no. of molecules in the collection i.e. the no. of molecules comprising of all speeds. The area under the curve between any two speeds, for example, U₁ and U₂, gives the total no. of molecules having speed between these two values.
- (g) The given figure illustrates the distribution of speeds at two temperatures T_1 and T_2 . Since the total no. of molecules is the same at both temperatures, increases the K.E. of the molecules, it follows that fraction of molecules having lower speed range decreases whereas fraction of molecules having higher speed range increases on increasing the temperature.
- (h) Also the curve at the higher temperature T_2 has its U_{mps} shifted to a higher value compared with that for T_1 , whereas corresponding fraction of molecules has decreased. But at the same time, the curve near U_{mps} has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.



The value of U_{mps} can be calculated easily, based on the concept of maximum or minimum value of a (i) function.

$$dN = 4\pi N \left(\frac{m}{2\pi RT}\right)^{\frac{3}{2}} e^{-mU^2/_{2KT}} u^2 du$$
$$\frac{1}{N} \frac{dN}{du} = 4\pi \left(\frac{m}{2\pi RT}\right)^{\frac{3}{2}} e^{-mU^2/_{2KT}} u^2$$

or

Differentiating both sides with respect to U

$$\frac{\mathrm{d}}{\mathrm{d}u} \left(\frac{1}{\mathrm{N}} \frac{\mathrm{d}\mathrm{N}}{\mathrm{d}u}\right) = 4\pi \left(\frac{\mathrm{m}}{2\pi \mathrm{RT}}\right)^{\frac{3}{2}} \left[2\mathrm{u} \ \mathrm{e}^{-\mathrm{m}u^{2}/_{2\mathrm{KT}}} + \mathrm{u}^{2} \left(-\frac{2\mathrm{m}u}{2\mathrm{KT}}\right) \mathrm{e}^{-\mathrm{m}u^{2}/_{2\mathrm{KT}}}\right]$$

For maximum

$$\frac{\mathrm{d}}{\mathrm{d}u} \left(\frac{1}{\mathrm{N}} \frac{\mathrm{d}\mathrm{N}}{\mathrm{d}u}\right) = 0$$

$$\therefore \qquad 4\pi \left(\frac{\mathrm{m}}{2\pi\mathrm{RT}}\right)^{\frac{3}{2}} \left[2\mathrm{u} \ \mathrm{e}^{-\mathrm{mu}^{2}/2\mathrm{KT}} + \mathrm{u}^{2} \left(-\frac{2\mathrm{mu}}{2\mathrm{KT}}\right) \mathrm{e}^{-\mathrm{mu}^{2}/2\mathrm{KT}}\right] = 0$$

$$-\mathrm{mu}^{\frac{1}{2}} \left[-\mathrm{mu}^{2}\right]$$

or
$$2u e^{-mU^2/2KT} \left[1 - \frac{mu^2}{2KT}\right] = 0$$

Now at the condition of mps, $U \neq 0$ and $e^{-mU^2/2KT} = 0$ when $U = \infty$, but at the condition of U_{mps} , $U \neq \infty$.

$$\therefore \qquad e^{-mU^2/_{2KT}} = 0$$

$$\therefore \qquad 1 - \frac{mU^2}{2KT} = 0 \implies \frac{mU^2}{2KT} = 1$$

or
$$\qquad U = \sqrt{\frac{2KT}{m}}$$

or

$$U_{mps} = \sqrt{\frac{2KT}{m}} = \sqrt{\frac{2RT}{M}}$$

Maxwell Distribution Curve for Energy \mathfrak{G}

$$E = \frac{1}{2}MU^{2}$$
$$U = \sqrt{\frac{2E}{M}}$$
$$dE = \frac{1}{2}M \times 2 UdU$$
$$dE = MU dU$$
$$UdU = \frac{dE}{M}$$

By Maxwell equation :

$$dN = 4\pi N \left(\frac{M}{2\pi RT}\right)^{3/2} \cdot e^{\frac{-Mu^2}{2RT}} U. UdU$$



$$dN_{E} = 4\pi N \left(\frac{M}{2\pi RT}\right)^{3/2} \cdot e^{-\left(\frac{E}{RT}\right)} \sqrt{\frac{2E}{M}} \frac{dE}{M}$$

$$dN_{E} = 2\pi N \left(\frac{1}{\pi RT}\right)^{3/2} \cdot e^{\frac{-E}{RT}} \sqrt{E} dE$$

$$\frac{1}{N} \left(\frac{dN_{E}}{dE}\right) = 2\pi \left(\frac{1}{\pi RT}\right)^{3/2} \sqrt{E} e^{-E/RT}$$

$$\frac{1}{N} \left(\frac{dN_{E}}{dE}\right) = 2\pi \left(\frac{1}{\pi RT}\right)^{3/2} \sqrt{E} e^{-E/RT}$$

The shaded area of this graph indicates the fraction of particle having energy between E_1 and E_2 .

From maxwell equation we are able to calculate the total no. of particles which are having energy greater than threshold energy (Activation energy) [for a chemical reaction to occur, reactant need some minimum amount of energy which is called as threshold energy or activation energy].

$$dN_{E} = 2\pi N \left(\frac{1}{\pi RT}\right)^{3/2} \int_{E_{a}}^{\infty} \sqrt{E} e^{-\sqrt{\frac{E}{RT}}} dE$$

From the above equation we calculate the total no. of particles which will participate in chemical reaction.

- Ex. (a) Calculate the pressure exerted by 10^{23} gas molecules, each of mass 10^{-25} kg, in a container of volume 1×10^{-3} m³ and having root mean square velocity of 10^3 ms⁻¹.
 - (b) Also calculate total kinetic energy and
 - (c) temperature of the gas.
- **Sol.** (a) By kinetic theory

$$P = \frac{1}{3} \frac{mNu^2}{V} = \frac{1 \times 10^{-25} \times 10^{23} \times (10^3)^2}{3 \times 10^{-3}} = 3.33 \times 10^6 \text{ N m}^{-2}$$

(b) Total KE = $\left(\frac{1}{2}mu^2\right) \times N$

$$= \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4 = 0.5 \times 10^4 \text{ J}$$

c) Also total KE =
$$\frac{3}{2}$$
 nRT, where n (mole) = $\frac{10^{23}}{N_A} = \frac{10^{23}}{6.023 \times 10^{23}}$

$$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415 \text{ K}$$



- Ex. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 Nm⁻². Calculate the root mean square velocity of the gas molecules.
- **Sol.** No. of gas molecules = 2×10^{21}

 6.023×10^{23} molecules of nitrogen weight = 28 g

2 × 10²¹ molecules of N₂ weights =
$$\frac{28 \times 2 \times 10^{21}}{6.023 \times 10^{23}}$$
 g = 0.093 g

Density =
$$\frac{\text{Mass}}{\text{Volume}} = \frac{0.093}{1} \text{ g/L} = \frac{0.093 \times 10^{-3}}{10^{-3}} = 0.093 \text{ kg/m}^3$$

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}} = U_{rms} = \sqrt{\frac{3 \times 7.57 \times 10^3}{0.093}} = 494.16 \text{ m/s}$$

Ex. In a container of capacity 1 litre there are 10^{23} molecules each of mass 10^{-22} gms. If root mean square speed is 10^5 cm/ sec then calculate pressure of the gas.

Sol.
$$PV = \frac{1}{3} MN \overline{U^2}$$

 $P = ?$
 $V = 10^{-3} m^3$
 $m = 10^{-25} kg$
 $N = 10^{23}$
 $\sqrt{U^2} = 10^5 cm/sec = 10^3 m/sec$
 $\overline{U^2} = 10^6 m^2/sec^2$
 $P \times 10^{-3} = \frac{1}{3} \times 10^{-25} \times 10^{23} \times 10^6$
 $P = \frac{1}{3} \times 10^{-2} \times 10^6 \times 10^3$
 $P = \frac{1}{3} \times 10^7 pascals$

COLLISION THEORY

Collision Diameter : It is the closest distance between the centres of two molecules taking part in collision.

collision diameter (σ) = $r_A + r_B$

Collision Frequency

It is the number of molecular collisions taking place per second per unit volume of the gas.

Determination of Number of Bimolecular Collisions

(a) While considering the molecules among themselves the molecules to be rigid, non-interacting and spherical with diameter σ . It is also assumed that all the molecules move with the same speed. The arithmetic mean of speed is \overline{U} .



(b) Two identical molecules of diameter σ will just touch each other when the distance separating their centres is σ . Thus, a moving molecule will collide with other molecules whose centres come within a distance of σ from its centre. The quantity $\pi\sigma^2$ is called the collision cross-section for the rigid spherical molecule. It is obvious that this collision cross-section is an area of an imaginary sphere of radius σ around the molecule within which the centre of another molecule cannot penetrate.



- (c) If the molecule is moving with an average speed \overline{U} , then in a unit time area swept out by a single molecule is $\pi\sigma^2 \overline{U}$. If N* is the no. of molecules within the volume $\pi\sigma^2 \overline{U}$, the no. of collisions by a single molecule in a unit time will be $\pi\sigma^2 \overline{U}$ N*.
- (d) So, far, we have assumed that only one molecule is moving and all other are stationary. In practice however, this is not true. In order to account for the movements of all molecules, we must consider the average velocity along the line of centres of two colliding molecules instead of average velocity of a single molecule. If it is assumed that, on an average, molecules collide while approaching each other perpendicularly, then the average velocity along their centre is $\sqrt{2}$ U as shown below.



The no. of collisions made by a single molecule with other molecules per unit time (collision number) are given by

$$z_1 = \sqrt{2} \pi \sigma^2 \overline{U} N^*$$

(e) The total number of bimolecular collision per unit time is given as z_{11} (collision frequency)

$$z_{11} = \frac{1}{2}(z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2} \pi \sigma^2 \overline{U} N^*$$
$$= \frac{1}{\sqrt{2}} \pi \sigma^2 \overline{U} N^{*2}$$

(f)

If the collisions involve two unlike molecules, the no. of bimolecular collision is given as
$$z_{12}$$
.

$$z_{12} = \frac{1}{\sqrt{2}} \pi \sigma_{12}^2 < u_0 > N_1 N_2$$

Where N_1 and N_2 are the no. of molecules per unit volume of the two types of gases, σ_{12} is the average diameter of two molecules, that is

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \text{ or } < u_0 > = [u_1^2 + u_2^2 \ 7]^{1/2} \text{ and}$$
$$u_1^2 = \frac{8RT}{\pi M_1} , \qquad u_2^2 = \frac{8RT}{\pi M_2}$$



80 Determination of Mean free Path and Its Dependence on Pressure and Temperature

(a) The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collsions made by single molecule per unit time}}$$

$$\lambda = \frac{\overline{U}}{z_1} = \frac{\overline{U}}{\sqrt{2}\pi\sigma^2\overline{U}N^*} = \frac{1}{\sqrt{2}\pi\sigma^2N^*}$$

(b) According to ideal gas equation,

$$PV = nRT = \frac{N^{1}}{N_{A}}RT$$

or
$$P = \left(\frac{N^{1}}{V}\right)\left(\frac{R}{N_{A}}\right)T = \left(\frac{N^{1}}{V}\right)KT$$

Now $\frac{N^{1}}{V} = N^{*},$
$$\therefore P = N^{*}KT \text{ or } N^{*} = \frac{P}{KT}$$

(where K is known as Boltzmann's constant)

(c)
$$\lambda = \frac{1}{\sqrt{2\pi\sigma^2 N^*}}$$

 $\lambda = \frac{1}{N^*}$ or $\lambda \propto \frac{T}{P}$

Since, according to gas law $P \propto T$ at constant volume

\therefore λ = constant at constant volume.

Thus there will no effect of changing T or P on λ , if the volume of the gas is kept constant.

 $N^* \propto \frac{P}{T}$

or

(d) Now
$$z_1 = \sqrt{2} \pi \sigma^2 \overline{U} N^*$$

$$\overline{U} \propto \sqrt{T} \qquad \therefore \quad \overline{U} = K_1 \sqrt{T}$$
$$N^* \propto \frac{P}{T} \qquad \therefore \quad N^* = K_2 \frac{P}{T}$$

$$\therefore z_1 = \sqrt{2} \pi \sigma^2 K_1 K_2 \frac{r}{\sqrt{T}}$$
$$\therefore z_1 = K' \frac{P}{\sqrt{T}}$$

Now $z_1 \propto P$ when T constant and $z_1 \propto \frac{1}{\sqrt{T}}$ when pressure is held constant.

At constant volume $P \propto T$ or P = K'' T

$$z_1 = \frac{K'K''T}{\sqrt{T}}$$

or $z_1 \propto \sqrt{T}$ when volume is constant.

Again $z_1 \propto \sqrt{P}$ when volume is constant.



(c) $z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 \overline{U} N^{*2}$ or $z_{11} \propto \overline{U} N^{*2}$ or $z_{11} \propto \sqrt{T} \left(\frac{P}{T}\right)^2$ or $z_{11} \propto \frac{P^2}{T^{3/2}}$ Thus $z_{11} \propto p^2$ when temperature is held constant and $z_{11} \propto T^{-3/2}$ when pressure is held constant At constant volume $z_{11} \propto T^{-1/2}$ and $z_{11} \propto P^{1/2}$.

IDEALAND REAL GAS

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

Real gases do not obey the ideal gas laws exactly under all conditions of tamperature and pressure.

Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

- (i) The volume of gas particle is negligible compared to volume of container (while the real gas particle have some significant volume).
- (ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

& Deviation from Ideal Behaviours

Compressibility Factor

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z), where Z is

$$Z = \frac{V_{m}}{V_{m(ideal)}} = \frac{PV_{m}}{RT} \quad [V_{m} = \text{molar volume}]$$

When Z > 1, $V_m > 22.4$ lit at STP ; When Z < 1, $V_m < 22.4$ lit at STP

Plots of Compressibility Factor vs Pressure

- (i) For an ideal gas Z = 1 and is independent of temperature and pressure.
- (ii) Exceptional behaviour of H_2 and He:

for these gases Z > 1. For such gases repulsive forces predominants.

(iii) Effect of pressure :

At very low P, $PV \approx RT$ i.e. $Z \approx 1$

At low P, PV < RT i.e. Z < 1

At moderate P, $PV \approx RT$ i.e. $Z \approx 1$

- At high P, PV > RT i.e. Z > 1
- (iv) For the gases which are easily liquefied (e.g. CO₂) Z dips sharply below the ideal line in the low pressure region.
- (v) Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours i.e. PV approaches unity or Z approaches unity with increase in temperature.





Boyle's Temperature

The temperature at which a real gas behaves like an ideal gas over an appreciable range of pressure is known as Boyle's temperature (T_B) . It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e. Boyle's Law is abeyed. Mathematically we may express the Boyle temperature or Boyle point

as the temperature where $\frac{\partial (PV)}{\partial P} = 0$ when $P \rightarrow 0$.

So to use ideal gas equation for real gas, we will use some correction factor for volume as well as for pressure.

(A) Volume Correction : Anil ahlawat (Page 154-)

In the ideal gas equation, $P_iV_i = nRT$, V_i represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume V_i is the total volume V minus the volume occupied by the gas molecules.

excluded

volume

i.e. Real volume of gas = Actual volume of container – volume occupied by N molecules in motion.

 $V_i = V - b$ for one mole of gas

 $V_i = V - nb$ for n mole of gas

Where b is termed the 'excluded volume' or 'co-volume'.

It is constant and characteristic for each gas.

$$\mathbf{b} = \left(\frac{4}{3}\pi r^3\right) \times 4\mathbf{N}$$

[where r = radius of gas molecule, N = Avogadro's number]

(B) Pressure Correction

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A is the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical

manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.



Illustration of excluded volume



Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on one side of the vessel, i.e. towards its centre, with the result that this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Van der Walls noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules, n/V. However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration n/V. Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to n^2/V^2 . Letting a be the proportionality constant, we can write

- $P (actual) = P(ideal) n^2 a/V^2$
- or P (ideal) = P(actual) + n^2a/V^2

'a' is a constant which depends upon the nature of the gas, V is the volume of 1 mole of gas. Combining the two corrections, for 1 mole of gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

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

The Constants 'a' and 'b'

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

- (i) The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.
- (ii) For a given gas van der Waals constant of attraction 'a' is always greater than van der Waals constant of volume 'b'.
- (iii) The gas having higher value of 'a' can be liquefied easily and therefore H₂ and He are not liquefied easily.
- (iv) Unit of 'a' is lit^2 mole⁻² atm or cm⁴ mole⁻² dyne.
- (v) Unit of 'b' is lit $mole^{-1}$ or $cm^3 mole^{-1}$.
- (vi) At low pressure, volume correction for 1 mole of gas is negligible,
 - $\therefore b = 0$

The gas equation can be written as

$$\left(P + \frac{a}{V^2}\right)V = RT$$
 or $Z = \frac{PV_m}{RT} = 1 - \frac{a}{V_m RT}$

where $V_m = molar$ volume

where Z is known as the compressibility factor.

(vii) At higher pressures, the pressure correction for 1 mole of gas is negligible

 $\therefore \frac{a}{V^2} = 0$ or (P + 0) (V- b) = RT or P (V_m - b) = RT or PV_m = RT + Pb or, Z = $\frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$



Gas	a (dm ⁶ atm mol ⁻²)	b (dm ³ mol ⁻¹)
Ammonia	4 17	0.0271
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethanol	2.56	0.087
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0433
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	3.71	0.0564
Water	5.44	0.0305

The Van der Walls Vonstants for Some Common Gases

LIQUEFACTION OF GASES AND CRITICAL POINTS

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that exist in the liquid. A gas can be liquefied by : (a) Increasing Pressure : An increase in pressure results in an increase in attraction among molecules. (b) Decreasing Temperature : A decrease in temperature results in a decrease in kinetic energy of molecules.

ANDREW'S ISOTHERMS

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P-V-T relationship for CO₂. The types of isotherms are shown in figure.





Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141

Observations from Figure

(a) At Low Temperatures : For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B).

At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density).

At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium.

CF represent liquid state.

The pressure corresponding to the line BC is there vapour pressure of the liquid.

- (b) At Higher Temperatures : Similar type of curve as in case (a) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.
- (c) At High Temperatures : (like 48°C), the isotherms are like those of ideal gas.
- (d) At Temperature (31.1°C) : The horizontal portion is reduced to a point.

The isotherm at $T_{\rm C}$ is called critical isotherm.

At point O,
$$\frac{dP}{dV} = 0$$
.

The point O is called the point of inflection.

Critical Temperature (T_c) : The maximum temperature at which gas can be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exit is called the critical temperature T_{C} .

Critical Pressure (P_C) :The minimum pressure required to liquefy the gas at the temperature T_C is called the critical pressure P_C .

Critical Volume (V_C) :The volume occupied by one mole of the gas at critical temperature, T_C and critical pressure, P_C is called the critical volume (V_C) of the gas.

Determination of Value of P_C, V_C and T_C

(a) The vander waal's equation is

$$\left(P + \frac{a}{V_m^2}\right) (V_m - b) = RT$$

 $PV_m + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$

or

or

$$V_{m} + \frac{a}{P} \times \frac{1}{V} - b - \left(\frac{ab}{P}\right) \frac{1}{V^{2}} =$$

or
$$V_{m}^{3} + \frac{a}{P}V_{m} - bV_{m}^{2} - \frac{ab}{P} = \frac{RTV_{m}^{2}}{P}$$

$$V_{m}^{3} - \left(b + \frac{RT}{P}\right)V_{m}^{2} + \frac{a}{P}V_{m} - \frac{ab}{P} = 0$$
 (1)

RΤ



or

- (b) This equation has three roots in V_m for given values of a, b, P and T. It is found that either all the three roots are real or one is real and the other two are imaginary.
- (c) The main characteristics of the figure are as follow :



- (i) At higher temperature than T_C the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g., V_1 , V_2 and V_3 at pressure P_1 .
- (ii) On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation V_m can be written as

$$(V_m - V') (V_m - V'') (V_m - V''') = 0$$

At the critical point $V' = V'' = V''' = V_C$

 \therefore the equation becomes,

$$(V_{m} - V_{C})^{3} = 0$$

or
$$V_m^3 - V_C^3 - 3V_C V_m^2 + 3V_C^2 V_m = 0$$

from eq. (1)

$$V_{m}^{3} - \left(b + \frac{RT}{P}\right)V_{m}^{2} + \frac{a}{P}V_{m} - \frac{ab}{P} = 0$$

(d) By comparing the coefficients

$$3V_{C} = b + \frac{RT_{C}}{P_{C}}, \ 3V_{C}^{2} = \frac{a}{P_{C}}, \ V_{C}^{3} = \frac{ab}{P_{C}}$$

By solving,
$$V_c = 3b$$
, $P_c = \frac{a}{27b^2}$ and $T_c = \frac{8a}{27Rb}$

(e) Therefore the value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_{\rm c}V_{\rm c}}{RT_{\rm c}} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{\frac{a}{9b}}{\frac{8Ra}{27Rb}} = \frac{\frac{a}{9b}}{\frac{8Ra}{27Rb}}$$

$$Z = \frac{P_{\rm c}V_{\rm c}}{RT_{\rm c}} = \frac{a}{9b} \times \frac{27b}{8a} = \frac{3}{8} = 0.375$$

(f) If we compart the value of $\frac{P_c V_c}{RT_c} = 0.375$, with the experimental values, it has been found that the agreement

is very poor.

(g) Boyle temperatures in terms of van der Waals constant :

$$T_B = \frac{a}{Rb}$$



Gas	P _C (atm)	V _{m,c} (cm ³ mol ⁻¹)	Т _С (К)
Не	2.26	57.9	5.2
Ne	26.9	41.7	44.4
Ar	48.1	75.2	150.7
Xe	58.0	119.0	289.7
Н,	12.8	65.5	33.3
0, 0,	50.1	78.2	154.8
N ₂	33.5	90.1	126.2
CO,	72.8	94.0	304.2
H ₂ Õ	218.0	55.6	647.3
NH ₃	111.5	72.5	405.0
CH ₄	45.6	98.7	190.6
$C_{2}H_{6}$	48.2	148.0	305.4

CRITICAL CONSTANTS OF GASES

EQUATION OF CORRESPONDING STATE

All the equation defined for real gases involved gas dependent constant, hence if for two real gases n,P, V are same then the fourth parameter need not to be same and can be calculated only when the gas dependent constant is known. However instead of pressure, temperature, moles and volume, new reduced parameter are defined such that-

$$P_{r} = \left(\frac{P}{P_{c}}\right) \implies \text{Reduced Pressure}$$

$$T_{r} = \left(\frac{T}{T_{c}}\right) \implies \text{Reduced temperature}$$

$$V_{r} = \left(\frac{V}{V_{c}}\right) \implies \text{Reduced volume}$$

$$\left(P + \frac{a}{V_{m}^{2}}\right) (V_{m} - b) = RT$$

$$\left[P_{r}P_{c} + \frac{a}{(V_{r}V_{c})^{2}}\right] (V_{r}V_{c} - b) = R \times T_{r}T_{c}$$

$$\left(P_{r} + \frac{3}{V_{r}^{2}}\right) (3V_{r} - 1) = 8 T_{r}$$

From this equation the law of corresponding state can be stated two real gas having same no. of moles are at same reduced temperature and same reduced volume then they have same reduced pressure.

Ex. For 1 mole gas reduced temperature is 3 and reduced volume is 10. If critical pressure is 42 atm then calculate the pressure exerted by 1 mole of real gas.

$$\begin{pmatrix} P_r + \frac{3}{V_r^2} \end{pmatrix} (3V_r - 1) = 8 T_r$$

$$\begin{pmatrix} P_r + \frac{3}{(10)^2} \end{pmatrix} (3 \times 10 - 1) = 8 \times 3 \implies P_r = \frac{24}{29} - \frac{3}{100}$$

$$P = P_r P_c = \left(\frac{24}{29} - \frac{3}{100}\right) 42 = 33.49 \text{ atm}$$



Law of Equiparition of Energy

This law states that is energy of the molecule (due to translational, rotational, vibrational motion) is represented as a sum of independent significant terms (which are proportional to v^2 (velocity), ω^2 (angular velocity) and x^2

(displacement) then each of the significant term contribute to $\frac{RT}{2}$ in average K.E. per mole of the system).

DEGREE OF FREEDOM

Number of independent co-ordinates or axis required to represent position or motion of the molecules is called as degree of freedom (for a system comprising of N atoms, total 3N degree of freedom are available, out of which some of translational, some are rotational and the other are vibrational).

Translation Degree of Freedom

Motion of any molecule can be represented along three independent coordinates or axis so translational degree of freedom is always three (these are significant at all temperatures for the gas).

T.E. =
$$\frac{1}{2} mV_x^2 + \frac{1}{2} mV_y^2 + \frac{1}{2} mV_z^2$$

T.E. (per mole) = $\frac{RT}{2} + \frac{RT}{2} + \frac{RT}{2} = \frac{3RT}{2}$

Each degree of freedom contributes to $\frac{RT}{2}$ in average K.E. per mole.

Rotational Degree of Freedom

- (i) For monoatomic molecule rotational energy is $\frac{1}{2}$ I ω^2 will be insignificant (if rotation is about its own axis.)
- (ii) For polyatomic gases :
- (a) Non-linear complete rotation can be represented along three perpendicular axis (this is significant at moderate temperature).
- (b) Linear : only two independent axis are required to represent total energy due to rotation. For non Linear (NL) :

R.E.
$$= \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 + \frac{1}{2}I\omega_z^2$$
 (Here I = moment of Inertia)
R.E. per mole $= \frac{RT}{2} + \frac{RT}{2} + \frac{RT}{2} = \frac{3RT}{2}$

For Linear :

R.E.
$$=\left(\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2\right)$$
 or $\left(\frac{1}{2}I\omega_y^2 + \frac{1}{2}I\omega_z^2\right)$ or $\left(\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_z^2\right)$
R.E. per mole $=\frac{RT}{2} + \frac{RT}{2} = RT$

These are influencial only at moderate temperature.

Vibrational Degree of Freedom

- (a) For linear molecule = 3N 5.
- (b) For non-linear molecule = 3N 6.

where N is no. of atoms present in a molecule.

Each vibrational degree of freedom comprises of two energy terms.

V.E. =
$$\frac{1}{2}mv^2 + \frac{1}{2}Kx^2$$

vibrational degree of freedom contributes RT to average K.E. per mole. These are significant only at a very high temperature.



HEAT CAPACITY

It is the amount of heat required to raise the temperature of 1 mole or 1 gram of a substance through 1°C or 1 K. If it is measured per mole of substance then it is called as molar heat capacity.

(where a, b, c are constant)

If it is measured in per gram of substance then it is called as specific heat.

$$C = \frac{q}{n \times \Delta T}$$
 (C = molar heat capacity, q = Heat given)

(i) Heat capacity at constant pressure

$$C_{\rm P} = \frac{q_{\rm p}}{n \times \Delta T} = \frac{\Delta H}{n \Delta T}$$

 $q_p = \Delta H = Enthalpy$ change.

(ii) Heat capacity at constant volume

$$C_{V} = \frac{q_{p}}{n\Delta T} = \frac{\Delta U}{n \times \Delta T}$$

 $q_V = \Delta U =$ change in internal energy

molar heat capacity is a function of temperature.

$$C = f(T)$$

$$C = (a + bT + CT2 +)$$

$$q = n \int_{T_1}^{T_2} C dT$$

$$q_{\rm V} = C_{\rm V} (T_2 - T_1) = \text{K.E./ mole}$$

K.E./ mole = C_V (Δ T)

$$C_V = \frac{K.E / mole}{\Delta T}$$

at T temperature :

$$C_V = \frac{K.E / mole}{T}$$

For ideal gas $C_p - C_V = R$ (here R = ideal gas constant)

	C _V	Cp	$C_P/C_V = \gamma$ (Poission's Ratio)
Monoatmic gas	$\frac{3}{2}$ R	$\frac{5}{2}$ R	$\frac{5}{3} = 1.66$
Diatomic gas	$\frac{7}{2}$ R	$\frac{9}{2}$ R	$\frac{9}{7} = 1.28$

For 'N' atomic molecules the degree of dissociation is 3N.

(i) If the gas is monoatomic :

(a) It will have three degree of freedom for K.E. since each degree of freedom provides $\frac{1}{2}$ KT amount of energy therefore total K.E. is $\frac{3}{2}$ KT (It will not have any rotational or vibrational degree of freedom).



- **(ii)** If gas is diatomic : Total degree of freedom is six.
- Out of which 3 is translational degree of freedom, therefore total energy $\frac{3}{2}$ KT. (a)
- Out of which 2 will be rotational degree of freedom -**(b)**

R.E. =
$$\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 = \frac{1}{2}KT + \frac{1}{2}KT = KT$$

Remaining is vibrational degree of freedom is one. (c)

> Energy concerned with the vibration motion corresponds to energy because of relative motion + change in position from equilibrium position.

V.E. =
$$\frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}K(r_o - r)$$

= $\frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}Kx^2$ (Here x is displacement from equilibium position)

$$= \frac{1}{2}KT + \frac{1}{2}KT = KT$$

So each vibrational degree of freedom will provide KT amount of energy.

We consider the vibrational degree of freedom at very high temperature.

- If gas is triatomic : Total degree of freedom is nine. (iii)
- Out of which $\frac{3}{2}$ KT is translational. (a)
- If linear then it will have two degree of freedom of rotational. **(b)**

Vibrational will have four degree of freedom (c)

$T.E. = \frac{3}{2}KT + K$	$KT + 4KT = \frac{13}{2}K$	Т	
	Cv	C _P	$C_P/C_V = \gamma$ (Poission's Ratio)
Triatomic (linear)	$\frac{13}{2}R$	$\frac{15}{2}$ R	$\frac{15}{3} = 1.15$
Non linear	6R	7R	$\frac{7}{6} = 1.16$
If vibration is ignored a	at lower temperat	ure.	
	C _V	Cp	$C_P/C_V = \gamma$
Diatomic	$\frac{5}{2}R$	$\frac{7}{2}$ R	$\frac{7}{5} = 1.4$
Triatomic (linear)	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.4$
Triatomic (Non linear)	3R	4R	$\frac{4}{3} = 1.33$



Temperature above which gases gives heating effect and below this cooling effect in process of adiabatic expansion.

 $T_{exp.} > T_{i} \longrightarrow \text{heating}$ $T_{exp.} < T_{i} \longrightarrow \text{Cooling}$ $T_{exp.} = T_{i} \longrightarrow \text{No cooling, No heating}$ $T_{i} = \frac{2a}{Rb} = 2 \times T_{b}$ $T_{i} \text{ for } H_{2} \text{ gas} = 193 \text{ K}$ $T_{i} \text{ for He gas} = 33 \text{ K}$ $T_{i} \text{ for He gas} = 33 \text{ K}$

Ex. Arrange following in decreasing 'a' factor (H_2O, CO_2, Ar)

 $H_2O > CO_2 > Ar$ polar

For Non Polar Molecules

Greater the size or surface area, greater will be vander waals' forces, so greater will be 'a' constant.

Ex. Arrange following gases according to 'a'

He, Ar, Ne, Kr.

$$a_{Kr} > a_{Ar} > a_{Ne} > a_{He}$$

• More 'a' factor means higher will be boiling point.

liquification Pressure

Is the pressure required to convert gas into liquid.

for easy liquefaction a^{\uparrow} and $P\downarrow$

When Z < 1, $V_m < V_{m, ideal}$ Z > 1, $V_m > V_{m, ideal}$

easily liquifiable more difficult to compress.

Ex. Arrange the following according to liquification pressure.

n-pentane ; iso-pentane , neo pentane.

 $a_{n-pentene} > a_{iso-pentane} > a_{neo-pentane}$

liquification pressure = LP

L_{Pn-pentane} < L_{Piso pentane} < L_{Pneo pentane}

b is roughly related with size of the molecule. (Thumb rule)

$$b = N_A 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

- Ex.
- Two vander waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions ?
- Sol. If two gases have same value of 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume. This is because the gas with a larger value of 'a' will have larger force of attraction and hence lesser distance between its molecules.



Ex. Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that $a = 3.592 \text{ atm} \text{It}^2 \text{ mol}^{-2}$, b = 0.0427 L/mol. Also, if the volume occupied by CO₂ molecules is negligible, then calculate the pressure exerted by one mole of CO₂ gas at 273 K.

Sol. Vander waal's equation

$$\left[p + \frac{n^2 a}{V^2}\right] [V - nb] = nRT$$

 $n_{CO_2} = 5$, V = 1 litre, T = 320 K, a = 3.592, b = 0.0427

$$\therefore \qquad \left[P + 25 \times \frac{3.592}{1} \right] [1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

 \therefore P = 77.218 atm

For ideal behaviour of gas, PV = nRT

$$\therefore \qquad \mathbf{P} \times \mathbf{1} = 5 \times 0.0821 \times 320$$

$$\therefore$$
 P = 131.36 atm

For one mole
$$\left[P + \frac{a}{V^2}\right] [V - b] = RT$$

$$\therefore \qquad \mathbf{P} = \frac{\mathbf{RT}}{\mathbf{V}} - \frac{\mathbf{a}}{\mathbf{V}^2}$$
$$0.0821 \times 273 \qquad 3.$$

P =
$$\frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

$$P = 0.9922 \text{ atm}$$

The volume occupied by 1 mole at 273 K is 22.4 litre if b is negligible.

Two moles of ammonia gas are enclosed in a vessel of 5 litre capacity at 27°C. Calculate the pressure exerted by the gas, assuming that

(i) the gas behaves like an ideal gas (using ideal gas equation).

(ii) the gas behaves like a real gas (using van der Waal's equation)

Given that for ammonia, a = 4.17 atm litre² mol⁻² and b = 0.037 litre mol⁻¹.

Sol. Given,

Ex.

```
n = 2 moles

V = 5 litres

T = 27°C = (27 + 273) K = 300 K

a = 4.17 atm litre<sup>2</sup> mol<sup>-2</sup>

b = 0.037 litre mol<sup>-1</sup>

Also, we know that

R = 0.0821 litre atm K<sup>-1</sup> mol<sup>-1</sup>
```

If the gas behaves like an ideal gas, we have

PV = nRT

$$P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300}{5} = 9.85 \text{ atm}$$



(i)

(ii) If the gas behaves like a real gas, we apply van der Waal's equation i.e.

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

or
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.037} - \frac{4.17 \times (2)^2}{(5)^2} = 9.33$$
 atm.

- Ex. 1 mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If vander waal's constants are a = 20.39 L² atm mol⁻² and b = 0.1383 L mol⁻¹, calculate compressibility factor Z under,
 - (a) low pressure region. (b) high pressure region.
- Sol. (a) Under low pressure region, V is high

$$(V-b) \approx V$$

$$\left(P + \frac{a}{V^2}\right) V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV}\right) = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.9$$

(b) Under high pressure region, P is high,

$$\left(P + \frac{a}{V^2}\right) \approx P$$

$$\therefore P(V-b) = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$\left(Q \frac{PV}{RT} = 1, \text{ or } \frac{P}{RT} = \frac{1}{V}\right)$$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

- Ex. One way of writing the equation of state for real gases is $PV = RT \left[1 + \frac{B}{V} + ...\right]$ where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.
- Sol. According to van der Waal's equation

$$\left[P + \frac{a}{V^2}\right] [V - b] = RT$$

or
$$P = \frac{RT}{(V - b)} - \frac{a}{V^2}$$



Multiply by V, then

$$PV = \frac{RTV}{(V-b)} - \frac{a}{V}$$

or
$$PV = RT \left[\frac{V}{V-b} - \frac{a}{VRT} \right]$$

or
$$PV = RT \left[\left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

$$\Rightarrow \qquad \left[1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V} \right)^{2} + \dots$$

$$\therefore \qquad PV = RT \left[1 + \frac{b}{V} + \dots - \frac{a}{VRT} \right]$$

$$PV = RT \left[1 + \left(b - \frac{a}{RT} \right) \cdot \frac{1}{V} + \dots \right]$$

$$\therefore \qquad B = b - \frac{a}{RT}$$

The critical temperature and pressure of CO₂ gas are 304.2 K and 72.9 atm respectively. What is the radius of Ex. CO_2 molecule assuming it to behave as vander Waal's gas ?

Sol.
$$T_C = 304.2 \text{ K P}_C = 72.9 \text{ atm}$$

$$T_{\rm C} = \frac{8a}{27Rb} \qquad P_{\rm C} = \frac{a}{27b^2}$$
8a

$$\frac{T_{\rm c}}{P_{\rm c}} = \frac{\overline{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

or
$$b = \frac{RT_c}{8P_c} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

-23

$$b = 4 N_A \times \frac{4}{3} \pi r^3 = 42.77 \text{ cm}^3$$

$$\therefore \qquad 4 \times N_A \times \frac{4}{3}\pi r^3 = 42.77$$

or
$$r^3 = \frac{3 \times 42.77 \times 10^{-23}}{16 \times 6.023 \times 3.14}$$

or
$$r^3 = 0.424 \times 10^{-23} = 4.24 \times 10^{-24}$$

or
$$r = (4.24)^{1/3} \times 10^{-8} \text{ cm} = 1.62 \times 10^{-8} \text{ cm}$$

radius of CO_2 molecule = 1.62 Å



Ex. The vander waals constant for HCI are a = 371.843 KPa.dm⁶ mol⁻² and b = 40.8 cm³ mol⁻¹ find the critical constant of this substance.

The critical pressure, $P_C = \frac{a}{27b^2} = \frac{371.843 \times 10^3}{27 \times (40.8)^2 \times 10^{-6}} = \frac{371.843 \times 10^9}{27 \times (40.8)^2} = 8.273 \times 10^6$ Sol.

 $P_{C} = 8.273 \text{ MPa}$

The critical pressure,
$$T_C = \frac{8a}{27Rb}$$

 $R = 8.314 \text{ KPa } \text{dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

$$\Gamma_{\rm C} = \frac{8a}{27Rb} = \frac{8 \times 371.843}{8.314 \times 27 \times 40.8 \times 10^{-3}} = 324.79 = 324.8 \,{\rm K}$$

The critical volume, $V_{C} = 3b = 3 \times 40.8 = 122.4 \text{ cm}^{3}$

Ex. The vander waals constant for gases A, B and C are as follows :

Gas	a/dm ⁶ KPa mol ⁻²	b/dm ³ mol ⁻
А	405.3	0.027
В	1215.9	0.030
С	607.95	0.032

Which gas has

(i) Highest critical temperature

(ii) The largest molecular volume

(iii) Most ideal behaviour around STP?

 $T_{c} = \frac{8a}{27Rb}$ Since, R is constant, higher the value of a/b, higher will be critical temperature. Sol.

 $V_{c} = 3b$ and $V_{c} \propto V_{m}$ (for a particular gas) therefore higher the value of V_{c} , higher will be molar volume of the gas.

If the critical temperature is close to 273 K, gas will behave ideally around the STP. Let us illustrate the result in a tabular form.

Gas	a/dm ⁶ KPa mol ⁻²	b/dm ³ mol ⁻¹	T _C	V _C	a/b
А	405.3	0.027	534.97 K	0.081	$1.501 \ge 10^4$
В	1215.9	0.030	1444.42 K	0.09	$4.053 \ x \ 10^4$
С	607.95	0.032	677.07 K	0.096	$1.89 \ge 10^4$

(i) B gas has the largest critical temperature.

(ii) C gas has the largest molecular volume.

(iii) A gas has the most ideal behaviour around STP

In a container of capacity 1 litre, air and some liquid water is present in equilibrium at total pressure of 200 mm of Hg. This container is connected to another one litre evacuated container. Find total pressure inside the container when equilibrium is again stablised (aqueous tension or vapour pressure at this temp. is 96 mm Hg).

Sol.

Ex.

Total pressure = 200 mm of Hg =
$$P_{gas} + P_{vapot}$$

 $\Rightarrow P_{ras} + 96 = 200$

 $P_{max} = 104 \text{ mm of Hg}$ Initially

when second container is connected



 $P_1 = 104 \text{ mm of Hg}$ $P_{2} = ?$ $V_{1} = 1$ $V_2 = 2$ litre $P_1V_1 = P_2V_2$ $104 \times 1 = P_2 \times 2$ $52 = P_{2}$ After equilibrium is established $P_{total} = 52 + 96 = P_{eas} + P_{water} = 148 \text{ mm of Hg at equilibrium.}$ Ex. Carbon dioxide gas (CO₂) measuring 1 litre is passed over heated coke the total volume of the gases coming out becomes 1.6 litre. Find % conversion of CO₂ into carbon monoxide. $CO_2 + C \longrightarrow 2CO$ Sol. CO, CO 1 0 at time t 1 - x2x Initial volume = 1 litre final volume = 1.6 litre Final volume = (1 + x) litres 1 + x = 1.6x = 0.6x = 0.6 $\frac{0.6}{1}$ × 10 = 60% of CO₂ will be converted into CO

Ex. 100 ml of hydrocarbon is mixed with excess of oxygen and exploded. On cooling, the mixture was reported to have a contraction of 250 ml. The remaining gas when passed through a solution of aqueous KOH, the mixture shows a further contraction of 300 ml. Find molecular formula of the hydrocarbon.

Sol.
$$C_x H_y + \left(x + \frac{Y}{4}\right) O_2 \longrightarrow x CO_2 + \frac{y}{2} H_2 O_2$$

100 ml

x 100 $\frac{y}{2} 100.$

mixture contains CO_2 , H_2O & excess O_2

on cooling, H_0 is separated, volume of H_0 = 250 ml

$$\frac{y}{2} \times 100 = 250; y = 5,$$

as KOH absorbs CO₂, hence 300 ml contraction is because of CO₂ that has been absorbed.

Volume of $CO_2 = 100 x = 300$; x = 3

Empirical formula = C_3H_5 ; molecular formula = C_6H_{10} .

Note: If water is already condensed out then total contraction in reaction mixture = {volume of reactants} - {volume of products + volume of unused species excluding volume of H_2O }.



Ex. 100 ml of an hydrocarbon is burnt in excess of oxygen in conditions so that water formed gets condensed out the total contraction in volume of reaction mixture was found to be 250 ml when the reaction mixture is further exposed to aqueous KOH a further contraction of 300 ml is observed find molecular formula of hydrocarbon.

```
\rightarrow CO<sub>2</sub> + H<sub>2</sub>O
C_x H_v +
                Ο,
100\,\mathrm{ml}
                                    300 ml
                excess
By POAC on 'C' atoms
  x \times 100 = 300
          x = 3
POAC on 'H' atoms
y \times 100 = 2 \times moles of H_2O
POAC on O atoms
2 \times v = 2 \times 300 + 1 \times H_2O
                                    \{V = volume of O_2 consumed\}
2 \times v = 600 + 50 y
v = \frac{600 + 50y}{2} volume of O_2 consumed
The total volume contraction is 250 ml.
Hence,
                      100 + V - 300 = 250
                      -200 + V = 250
                2 \times 450 - 600 = 50 y
                      \frac{300}{50} = y = 6
Hydro carbon will be C<sub>3</sub>H<sub>6</sub>
```



Sol.

PLEASE TORNEL ST

1. GASLAW (I) Boyle's Law

 $\Re \propto \frac{1}{p} (n, 1 - const.)$

 $P_1V_1 - P_2V_2$

(II) Clurie's Law

 $\frac{V \propto T (n, P + const)}{V_{t}} = \frac{T_{z}}{T_{t}}$

(III) Gay hossed's Law $P \approx \Gamma(n, V - const)$

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

(DV) Avogadro's Law

 $\label{eq:Variable} \begin{array}{l} V < moles < number of molecules (P, T = cosnt)\\ Ideal gas equation PV = inRT\\ R = 0.0821 \mbox{ fit atminol}^{-1} K^{-1}\\ R = 8.314 \mbox{ J} K^{-1} \mbox{ mol}^{-1} \mbox{ or } 8.314 \mbox{ M} \times K^{-1} \mbox{ mol}^{-1}\\ R = 2 \mbox{ cat } K^{-1} \mbox{ mol}^{-1}\\ R = 8.314 \times 10^{7} \mbox{ erg } K^{-1} \mbox{ mol} \end{array}$

2. GRAHAM'S DIFFUSION LAW

It is applicable for non-reacting gases

$$r < \frac{1}{\sqrt{d}}$$

$$r \approx \frac{1}{\sqrt{v(t)}}$$

$$r \approx \frac{1}{\sqrt{Mw}}$$

$$(P, 1 - \cos w)$$

$$r \approx - Mw$$

VD cgas vo dtt. 2

rate of diffusion r

Lans yr Inrealen

(Where, • + distance travelled by differed gas)

n<u>d Jusedger</u> Langetager

3. DALTON'S LAW OF FARTIAL PRESSURE



GASEOUS STATE

$$P_{\text{mixture}} = P_1 + P_2 + P_3 \dots (T \& V \text{ const})$$
$$P_t = P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapours}}$$

It is applicable for non racting gases.

Methods of determination of partial pressure

 $(P_A \& P_B are partial pressure)$

(I) from ideal gas equation

$$P_A V = n_A RT$$
 and $P_B V = n_B RT$

(II) In the form of mole fraction.

$$P_{A} = X_{A}P_{T} = \frac{n_{A}}{n_{t}}P_{T}$$

$$\mathbf{P}_{\mathrm{B}} = \mathbf{X}_{\mathrm{B}} \mathbf{P}_{\mathrm{T}} = \frac{\mathbf{n}_{\mathrm{B}}}{\mathbf{n}_{\mathrm{t}}} \mathbf{P}_{\mathrm{T}}$$

 P_{T} = sum of partial pressure of al gases

(III) In the form of volume fraction

$$P_A = \frac{V_A}{V} P_T$$
 and $P_B = \frac{V_A}{V} P_T$

(IV) In individual pressure and individual volume are given

$$P_A = \frac{V_A}{V} P_1$$
 and $P_B = \frac{V_B}{V} P_2$

 $P_1, P_2 =$ pressure of gases before mixing

 $P_A, P_B =$ pressure of gases after mixing

4. Kinetic gtas equation

$$PV = \frac{1}{3} mN V^2 rms$$

5. Average KE (KE_{av})

$$KE_{av} = \frac{3}{2} nRT$$
 (m moles)

$$XE_{av} = \frac{3}{2} RT$$
 (1 mol or N_A molecules)

$$KE_{av} = \frac{3}{2} KT$$
 (1 molecules)

$$K = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$$



CHEMISTRY FOR JEE MAIN & ADVANCED

6.	$V_{\rm rms} = \sqrt{\frac{V_1^2 + V_2^2}{N}}$	$\frac{V_{n}^{2} + V_{n}^{2}}{N}$		$V_{av} = -$	$V_1 + V_2 + \frac{V_1}{N}$	V ₃ V _n
	$V_{rms} = \sqrt{\frac{3RT}{Mw}}$			$V_{av} = $	$\frac{8RT}{\pi Mw}$	
	$V_{rms} = \sqrt{\frac{3PV}{Mw}}$			$V_{av} = $	$\frac{8PV}{\pi Mw}$	
	$V_{\rm rms} = \sqrt{\frac{3P}{d}}$			$V_{av} = $	$\frac{8P}{\pi d}$	
	$V_{rms}: V_{av}: V_{mp}$	$=\sqrt{3}$:	$\sqrt{\frac{8}{\pi}}$:	$\sqrt{2}$
		= 1	:	0.92	:	0.82
	$V_{mp}: V_{av}: V_{ms}$	$=\sqrt{2}$:	$\sqrt{\frac{8}{\pi}}$:	$\sqrt{3}$
		=1	:	1.128	:	1.224

$$V_{mp} = \sqrt{\frac{2RT}{Mw}}$$
$$V_{mp} = \sqrt{\frac{2PV}{Mw}}$$
$$V_{mp} = \sqrt{\frac{2P}{d}}$$

7. Compressibility factor $(z) = \frac{(V_m)obs}{V_i} = \frac{P(V_m)obs}{RT}$ If z=1, the gas show ideal gas behaviour. If z>1, the gas show positive deviation.

If z < 1, the gas show negative deviation.

8. Vanderwaal's Sequation

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

$$P_i = P_R + \frac{an^2}{V^2} \implies P_i > P_R$$

 $_a \uparrow \,$ force of attraction \uparrow , liquification \uparrow

 $b\uparrow$, effective size of molecule \uparrow

incompressible vol \uparrow , compressible vol \downarrow

At high pressure, Vanderwaal's equation is
$$PV_m - Pb = RT$$

(II) At low pressure Vanderwaal's equation is
$$PV_m + \frac{a}{V_m} = RT$$



(I)