# GASEOUS STATE

# Section (A) : Daltons law of partial pressure

## Partial pressure :

In a mixture of non reacting gases partial pressure of any component gas is defined as pressure exerted by this component gas if whole of volume of mixture had been occupied by this component only. Partial pressure of first component gas :



$$P_1 = \frac{n_1 \quad RT}{v} \qquad ; \qquad P_2 = \frac{n_2 \quad RT}{v} \qquad ; \qquad P_3 = \frac{n_3 \quad RT}{v}$$

Total pressure =  $P_1 + P_2 + P_3$ .

## Daltons law :

For a *non reacting* gaseous mixture total pressure of the mixture is the summation of partial pressure of the different components gases.

$$\frac{(n_1 + n_2 + n_3)RT}{V}$$

 $P_{Total} = P_1 + P_2 + P_3 = V$   $\frac{P_1}{P_T} = \frac{n_1}{n_T} = x_1$ (mole fraction of first component gas)  $\frac{P_2}{P_T} = \frac{n_2}{n_T} = x_2$ (mole fraction of second component gas)  $\frac{P_3}{P_T} = \frac{n_3}{n_T} = x_3$ (mole fraction of third component gas)

- **Ex.1** A mixture of gases at 760 torr contains 55.0% nitrogen, 25.0% oxyegn and 20.0% carbon dioxide by mole. What is the partial pressure of each gas in torr ?
- Ans.  $P_{N_2} = 418$  torr,  $P_{O_2} = 190$  torr,  $P_{CO_2} = 0.152$  torr, total pressure = 760.
- Sol. Let total moles of gas mixture be 100.

$$P_{N_{2}} = \left(\frac{n_{N_{2}}}{n_{T}}\right)_{\mathbf{x}} P_{T} = \frac{55}{100} \mathbf{x} \ 760 = 418 \ \text{torr.}$$
$$P_{O_{2}} = \left(\frac{n_{O_{2}}}{n_{T}}\right)_{\mathbf{x}} P_{T} = \frac{25}{100} \mathbf{x} \ 760 = 190 \ \text{torr.}$$

 $P_{CO_2} = (760 - 418 - 190) = 152 \text{ torr.}$ 

## Analysis of gaseous mixture :

## Vapour density :

Vapour density of any gas is defined as the density of any gas with respect to density of the  $H_2$  gas under identical conditions of temperature T and pressure P.

$$Vapour density = \frac{density of gas at T \& P}{density of H_2 under same P \& T}$$

$$P = \frac{m}{V} \cdot \frac{RT}{M} \implies P = \rho \cdot \frac{RT}{M} \implies \rho = \frac{PM}{RT}$$

$$=\frac{PM_{gas}RT}{RT PM_{H_2}} = \frac{PM_{gas}RT}{RT PM_{H_2}} = \frac{M_{gas}}{2}$$

Vapour density =  $M_{gas} = 2 \times vapour density$ 

# Average molecular mass of gaseous mixture :

total mass of the mixture divided by total no. of moles in the mixture

M<sub>mix</sub> = Total mass of mixture

If we have, ' $n_1$ ', ' $n_2$ ' and ' $n_3$ ' are moles of three different gases having molar mass ' $M_1$ ', ' $M_2$ ' and ' $M_3$ ' respectively.

$$M_{min} = \frac{ n_1 \quad M_1 + n_2 \quad M_2 + n_3 \quad M_3 }{ n_1 + n_2 + n_3 }$$

**Ex.2** Calculate the mean molar mass of a mixture of gases having 7 g of Nitrogen, 22 g of CO<sub>2</sub> and 5.6 litres of CO at STP.

Sol. Moles of N<sub>2</sub> = 7/28 = 1/4; Moles of CO<sub>2</sub> = 22/44 = 1/2; Moles of CO = 5.6 / 22.4 = 1/4  
mean molar mass = M<sub>min</sub> = 
$$\frac{n_1 \quad M_1 + n_2 \quad M_2 + n_3 \quad M_3}{n_1 + n_2 + n_3} = (7 + 7 + 22) / 1 = 36$$

# Section (B) : Grahams Law of diffusion

**Diffusion :** Net spontaneous flow of gaseous molecule from region of high concentration (higher partial pressure) to region of lower concentration or lower partial pressure



flow will be from both sides,  $N_2$  will try to equalise its partial pressure in both the vessels, and so will  $O_2$ .



## Graham's Law :

"Under similar condition of pressure (partial pressure) the rate of diffusion of different gases is inversely proportional to square root of the density of different gases."

• Rate of diffusion  $r \propto \sqrt{d} d = density of gas$ 

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} =$$
V.D is vapour density  
r = volume flow rate =  $\frac{\sqrt{V.D_2}}{V.D_1}$   
r = mole flow rate =  $\frac{dn_{out}}{dt}$ 

dx

- r = distance travelled by gaseous molecule per unit time = dt
- The general form of the grahams law of diffusion can be stated as follows, when one or all of the parameters can be varied.

rate 
$$\propto \sqrt{TM} A$$
; P – Pressure, A – area of hole, T – Temp., M – mol. wt.

• If partial pressure of gases are not equal.

Then rate of diffusion is found to be proportional to partial pressure & inversely proportional to square root of molecular mass.

r ∝ P

$$r \propto \frac{1}{\sqrt{M}}$$
;  $\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$ 

## Selective diffusion :

If one or more than one components of a mixture are allowed to diffuse and others are not allowed then it is selective diffusion of those components.



#### Platinum allows only H<sub>2</sub> gas to pass through

Effusion : (forced diffusion) a gas is made to diffuse through a hole by application of external pressure.



**Ex-3.** In a tube of length 5 m having 2 identical holes at the opposite ends. H<sub>2</sub> & O<sub>2</sub> are made to effuses into the tube from opposite ends under identical conditions. Find the point where gases will meet for the first time.

Sol.  

$$\frac{r_1}{r_2} = \frac{ax}{dt} \times \frac{dt}{dx} = \sqrt{\frac{m_2}{m_1}} = \frac{dx_1}{dx_2} = \sqrt{\frac{32}{2}}$$

$$\frac{dx_1}{dx_2} = 4 \qquad \Rightarrow \qquad \frac{distance \quad travelled \quad by \quad H_2}{distance \quad travelled \quad by \quad O_2} = 4$$

$$\frac{x}{(5-x)} = 4 \qquad \Rightarrow \qquad x = (5-x) 4 \qquad \Rightarrow \qquad x = 20 - 4x$$

$$5x = 20 \qquad \Rightarrow \qquad x = 4 \quad \text{from } H_2 \text{ side}$$

## **GASEOUS STATE**

- The pressure in a vessel that contained pure oxygen dropped from 2000 torr to 1500 torr in 40 min as Ex-4 the oxygen leaked through a small hole into a vacuum. When the same vessel was filled with another gas, the pressure dropped from 2000 torr to 1500 torr in 80 min. What is the molecular weight of the second gas?
- Change in pessure = 2000-1500 = 500 torr; time-taken = 40 min Sol. 500 500

rate<sub>1</sub> = 40 torr/min; similarly rate<sub>2</sub> = 80 torr/min  $\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M}{32}}$ M = 128 g/mol Ans.

# Section (C) : Kinetic theory of gases

# Postulates / assumptions of KTG :

- 1. A gas consists of tiny spherical particles called molecules of the gas which are identical in shape & size (mass)
- 2. The volume occupied by the molecules is negligible in comparision to total volume of the gas. For an ideal gas, volume of the ideal gas molecule  $\geq 0$ .
- Gaseous molecules are always in random motion and collide with other gaseous molecule & with walls 3. of the container.
- Pressure of the gas is due to these molecular collisions with walls of the container 4.
- 5. These collisions are elastic in nature
- Molecular attraction forces are negligible. Infact, for an ideal gas attraction or repulsion forces are equal 6. to zero.
- 7. Newton's laws of motion are applicable on the motion of the gaseous molecule.
- 8. Effect of gravity is negligible on molecular motion.
- 9. The average K.E. of gaseous molecules is proportional to absolute temp of the gas.

$$\frac{1}{2} M^{(u^2)} \alpha T$$

Kinetic equation of gaseous state (expression for pressure of gas)

# **Derivation:**

m = mass of one molecule

 $\ddot{U}_{=U_x}\hat{i}_{+U_y}\hat{j}_{+U_z}\hat{k}$ 

Consider collision with ABCD

 $P_{i} = mU_{x}\hat{i}$ initial

final change in momentum due to collision  $= 2 U_x m$ 



time taken between two successive collision with face ABCD = t =  $U_x$ 

frequency of collision =  $\overline{t} = \frac{-x}{2\ell}$ 

$$J_x \times U_x$$
 m  $U_x^2$ 

change in momentum in one sec. = force =  $2m \frac{2\ell}{2\ell}$  =

force due to all the molecules =  $\frac{m}{\ell} \{ U_{x_1}^2 + U_{x_2}^2 + \dots + U_{x_N}^2 \}$ 

average value of 
$$U_N^2 = \overline{U_N^2} = \frac{Ux_1^2 + U_{x_2}^2 + \dots U_{x_N}^2}{N}$$

 $F_x = \frac{m}{\ell} \{ N \quad \overline{U_x^2} \}$ 

all the three direction are equal as the motion is totally random in all directions, hence

$$\overline{U_x^2} = U_y^2 = \overline{U_z^2}$$
$$\overline{U^2} = \overline{U_x^2} + \overline{U_y^2} + \overline{U_z^2} = 3 \overline{U_x^2}$$
$$F = \frac{m}{\ell} = N \frac{1}{3} \overline{U^2}$$

Pressure =  $\frac{F}{\ell^2} = \frac{1}{3} \frac{mN}{\ell^3} \frac{1}{U^2}$  The volume of the container 'v' =  $\ell^3$ 

$$\therefore \qquad PV = \frac{1}{3} \text{ mN } \overline{U^2} \text{ Kinetic equation of gases}$$

where  $U^2$  is mean square speed

		$U_1^2 + U_2^2 + U_3^2 + \dots$	$U_N^2$
root mean square speed =	$U_{\rm rms} = \sqrt{U^2} = \sqrt{U^2}$	N	

# Verification of Gaseous Laws Using Kinetic Equation :

• From postulates ; 
$$PV = \frac{1}{3} mN \overline{U^2}$$
  
 $\frac{1}{2} m \overline{U^2} \propto T = \lambda T$  Where ' $\lambda$ ' is a proportionality constant  
 $PV = \frac{2}{3} \left(\frac{1}{2}m \overline{U^2}\right)_N$ ;  $PV = \frac{2}{3} \lambda NT$   
• Boyle's Law : N : constant  
T : constant  
PV = constant  
• Charles law : N : constant  
P : constant  
V  $\propto T$   
• Kinetic energy of gaseous molecule (translation K.E.)  
To calculate  $\lambda$  we have to use ideal gas equation (experimental equation)  
PV = nRT  
Kinetic equation PV = nRT =  $\frac{2}{3} \lambda NT = \frac{2}{3} \lambda (nN_A) T$   
On comparing  $\lambda = \frac{3}{2} \times \frac{R}{N_A}$   
 $\frac{3}{2} \qquad \frac{R}{14}$ 

 $\lambda = \overline{2}$  K where K =  $N_A$  = Boltzmann constant

Average K.E. of molecules =  $\frac{1}{2} m \overline{U^2} = \lambda T$ Average K.E. =  $\frac{3}{2} K T$  (only dependent on temperature not on nature of the gas.) Average K.E. for one mole =  $N_A \left(\frac{1}{2}m \quad \overline{U^2}\right) = \frac{3}{2} K N_A T = \frac{3}{2} RT$ **Root mean square speed (U**<sub>rms</sub>)

 $U_{rms} = \sqrt{U^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 R T}{m N_A}}$  Where m-mass of one molecule

## O Dependent on nature of gas i.e mass of the gas

$$U_{\text{rms}} = \sqrt{\frac{3 \quad \text{R} \quad \text{T}}{M}} \qquad \qquad M = \text{molar mass}$$

• Average speed (U<sub>av</sub>)

$$U_{av} = \frac{U_1 + U_2 + U_3 + \dots + U_N}{N}$$
$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}}$$

K is Boltzmann constant

## • Most probable speed (U<sub>mp</sub>) :

The speed possesed by maximum number of molecules at the given temperature.

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

$$Molecular \text{ speed}$$

$$Most \text{ probable speed}$$

$$Average \text{ speed}$$

$$Root \text{ mean square}$$

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

$$\sqrt{\frac{8 \text{ RT}}{\pi M}} = \sqrt{\frac{8 \text{ KT}}{m}}$$

$$\sqrt{\frac{3 \text{ RT}}{M}} = \sqrt{\frac{3 \text{ KT}}{m}}$$

$$U_{mp} \colon U_{av} \colon U_{ms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

**Ex.5** In a container of capacity 1 litre there are 10<sup>23</sup> molecules each of mass 10<sup>-22</sup> g. If root mean square speed is 10<sup>5</sup> cm/sec then calculate pressure of the gas.

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

# Maxwell's distributions of molecular speeds :

Postulates/Assumptions of speed distributions

- It is based upon theory of probability.
- It gives the statistical averages of the speed of the whole collection of gas molecules.
- Speed of gaseous molecules of may vary from 0 to ∞. The maxwell distribution of speed can be plotted against fraction of molecules as follows.



• The area under the curve will denote fraction of molecules having speeds between zero and infinity • Total area under the curve will be constant and will be unity at all temperatures.

 $\odot$  Area under the curve between zero and  $u_1$  will give fraction of molecules racing speed between 0 to  $u_1$ . This fraction is more at  $T_1$  and is less at  $T_2$ .

O The peak corresponds to most probable speed.

O At higher temperature, fraction of molecules having speed less than a particular value decreases.

 $\odot\,\mbox{For Gases}$  with different molar masses will have following graph at a given temperature.



# Section (D) : Real gases

- Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- Real gases deviates from ideal behaviour because

O Real gaseous molecules have a finite volume.

{since on liquefication real gases occupies a finite volume}

 $\odot$  Inter molecular attraction forces between real gas molecules is not zero.

{Real gases can be converted into liquid where as ideal gases can't be}

• Deviation of real gases from ideal behaviour can be measured by using compressibility factor : (Z)





Variation of Z with pressure at different temperature (for a gas ) :



**Conclusions :** Z = 1 for ideal gas

Z > 1 at all pressures for He/H<sub>2</sub>

- Z < 1 at low pressure (for all other gases)
- Z > 1 at high pressure (for all other gases)

# Vander Waal Equation of real gases :

The ideal gas equation does not consider the effect of attractive forces and molecular volume. vander Waal corrected the the ideal gas equation by taking the effect of

(a) Molecular volume (b) Molecular attraction

• Volume correction :

Ideal gas equation :

 $P_i V_i = nRT$ ; In the equation 'V<sub>i</sub>' stands for the volume which is available for free movement of the molecules.

Videal = volume available for free movement of gasesous molecule

hence,  $V_i = V - \{volume not available for free movement\}$  For an ideal gas

 $V_i = V \{V = volume of container\}$ 

but for a real gas,  $V_i \neq V$ , as all the volume is not available for free movement

# Molecules have finite volume :

Excluded volume per molecule =  $\frac{1}{2} \left\{ \frac{4}{3} - \pi - (2r)^3 \right\}$  = Co-volume per molecule. The volume that is not available for free movement is called excluded volume. let us see, how this excluded volume is calculated.



Excluded volume (not available for free momement)

For above example, the entire shaded region is excluded, as its centre of mass cannot enter this region. If both molecules were ideal, then they would not have experienced any excluded volume but not in the case, of real gas as the centre of mass of '2' cannot go further.

Hence for this pair of real gas molecules,

Excluded volume per molecule = 
$$\frac{1}{2} \left\{ \frac{4}{3} \pi (2r)^3 \right\}_{=4} \left\{ \frac{4}{3} \pi r^3 \right\}_{=4}$$
  
= excluded volume per mole of gas (b) = N<sub>A</sub> 4  $\left\{ \frac{4}{3} \pi r^3 \right\}_{=4}$ 

= 4 x N<sub>A</sub> x Volume of individual molecule

for n moles, excluded volume = nb

 $V_i = V - nb$  volume correction

• Pressure correction or effect of molecular attraction forces :



Due to these attraction, speed during collision will be reduced

Momentum will be less

Force applied will be less

Pressure will be less.

 $P_{ideal} = P + \{correction term\}$ 

Correction term  $\alpha$  no. of molecules attracting the colliding molecule (n/v).

Correction term  $\alpha$  density of molecules (n/v).

$$\left(\frac{n}{v}\right)$$

;

net correction term  $\propto \left(\frac{n}{v}\right) \left(\frac{n}{v}\right)_{=} \frac{an^2}{v^2}$ 

no. of collision  $\alpha$  density of molecules (v)'a' is constant of proportionality and this is dependent on force of attraction

Stronger the force of attraction greater will be 'a' (Constant)

$$P_i = P + \frac{an^2}{v^2}$$

$$\left(1 + \frac{an^2}{v^2}\right)$$

Vander waal's equation is :

# Verification of Vander Waal's Equations

Variation of Z with P for vander waals' equation at any temp. Vander waal equation for 1mole

$$\left(\mathsf{P} + \frac{\mathsf{a}}{\mathsf{V}_m^2}\right)(\mathsf{V} - \mathsf{b}) = \mathsf{R}\mathsf{T}$$



• AT LOW PRESSURE (at separate temp.) At low pressure V<sub>m</sub> will be high.

а

Hence b can be neglected in comparision to  $V_m$ . but  $V_m^2$  cant be neglected as pressure is low. Thus equation would be

$$\begin{pmatrix} P + \frac{a}{V_m^2} \end{pmatrix}_{V_m} = RT \implies PV_m + \frac{a}{V_m} = RT$$

$$\Rightarrow \qquad \frac{PV_m}{RT} + \frac{a}{V_mRT} = 1 \implies Z = 1 - \frac{a}{V_mRT} \qquad Z < 1$$

Real gas is easily compressible in comparision to an ideal gas.

# • **AT HIGH PRESSURE** (moderate temp.)

 $\Rightarrow$  V<sub>m</sub> will be low

so b cant be neglected in comparision to  $V_m$ 

but  $V_m^2$  can be neglected in comparision to much high values of P.

Then vander Waals' equation will be

 $P(V_m - b) = RT$ 

 $PV_{m} - Pb = RT$   $\frac{PV_{m}}{RT} = \frac{Pb}{RT} + 1$   $Z = \frac{Pb}{RT} + 1 \quad (Z > 1)$ 

If Z > 1, then gas is more difficult to compress in comparision to an ideal gas.

At low pressure and very high temperature.
 V<sub>m</sub> will be very large

hence 'b' can be neglected and  $\frac{a}{V_m^2}$  can also be neglected as V<sub>m</sub> is very large PV<sub>m</sub> = RT (ideal gas condition)

• For  $H_2$  or  $H_2$ 

$$P(V_m - b) = RT$$
  
so 
$$Z = 1 + \frac{Pb}{RT}$$

- 'a' factor depends on inter molecular attraction forces.
  - 'a' factor for polar molecule > 'a' factor for non polar molecule.



# Critical constant of a gas :

When pressure increases at constant temp volume of gas decreases



AB  $\rightarrow$  gases BC  $\rightarrow$  vapour + liquid CD  $\rightarrow$  liquid

**Critical Point :** At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that Density of liquid = density of vapour

Tc or critical temp : Temperature above which a gas can not be liquified

$$T_{c} = \frac{\frac{8a}{27 Rb}}{$$

**P**<sub>c</sub> or critical pressure : Minimum pressure which must be applied at critical temp to convert the gas into liquid.

$$P_{C} = \frac{a}{27b^2}$$

 $V_{C} \mbox{ or critical volume}$  : Volume occupied by one mole of gas at  $T_{C} \mbox{ \& } P_{C}$ 

$$V_C = 3b$$

**Ex.6** Arrange following in decreasing 'a' factor (H<sub>2</sub>O, CO<sub>2</sub>, 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.7 Arrange following gases according to 'a'

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

O More 'a' factor means high boiling point.

## O liquification pressure :

Is the pressure required to convert gas into liquid.

for easy liquefaction  $a\uparrow$  and  $P\downarrow$ 

 $\Rightarrow$  easily liquifiable

Z > 1,  $V_m > V_{m, ideal} \implies$  more difficult to compress.

**Ex.8** Arrange the following according to liquification pressure.

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

n-pentane ; iso-pentane , neo pentane.

An-pentene > Aiso-pentane > Aneo-pentane

liquification pressure = LP

 $L_{P_{n-pentane}} < L_{P_{iso pentane}} < L_{P_{neo pentane}}$ 

- **Ex.9** 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.