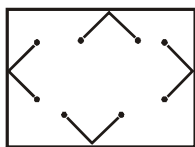


PARAMETERS TO DESCRIBE A GAS

☞ (a) Pressure :



☞ The force per unit area exerted on the wall of container due to constant bombardment of gas molecules on the wall of container is called pressure.

☞ **Units:** $1 \text{ N/m}^2 = 1 \text{ Pa}$

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

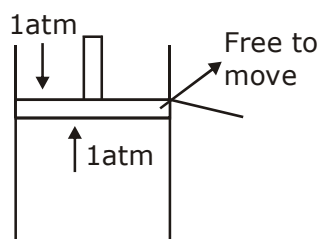
$$1 \text{ atm} = 76 \text{ cm} = 760 \text{ mm of Hg} = 760 \text{ torr}$$

$$1 \text{ torr} = 1 \text{ mm Hg}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

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

☞ **Constraints :** $P = \text{constant}$



☞ (b) Volume (V) :

Volume of a gas is equal to volume of container.

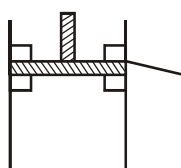
☞ **Units :**

$$1 \text{ cc} = 1 \text{ cm}^3 = 1 \text{ mL}$$

$$1000 \text{ cc} = 1000 \text{ cm}^3 = 1000 \text{ mL} = 1 \text{ L} = 1 \text{ dm}^3$$

$$1000 \text{ L} = 1000 \text{ dm}^3 = 1 \text{ m}^3$$

Volume = Constant



Piston hindered from moving

(c) Temperature :

$$T(K) = t^{\circ}(C) + 273.15$$

(d) no. of moles (n) :

$$n = \text{moles}$$

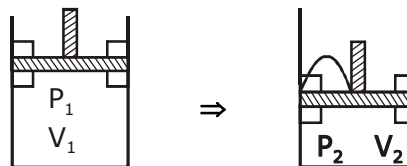
Gas Laws**(1)** Boyle's law**(2)** Charle's law**(3)** Gay-lussac's law (Amonton's law)**(4)** Avogadro's law**(1) Boyle's law**

$$P_1 < P_2$$

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

$$V_1 > V_2$$

$$P = \frac{k}{V}$$



$$PV = k \quad ; \quad T = \text{Constant}$$

$$P_1 V_1 = P_2 V_2 = \dots = P_n V_n$$

$$\therefore \rho = \frac{m}{V} \text{ Constant}$$

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

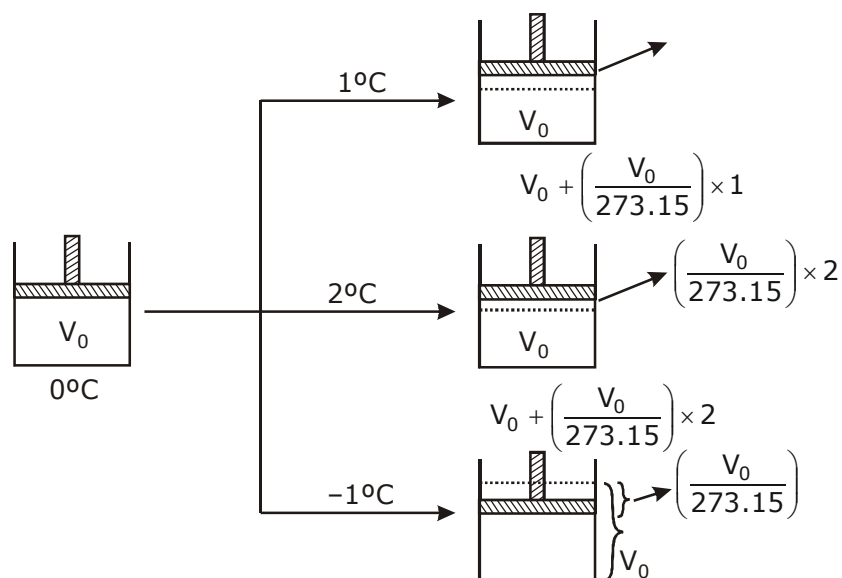
$$\therefore \rho \propto P$$

$$\frac{P}{\rho} = K \quad ; \quad T = \text{Constant}$$

$$\frac{P_1}{\rho_1} = \frac{P_2}{\rho_2} = \dots = \frac{P_n}{\rho_n}$$

“ For a fixed amount of gas at constant temperature, the gas volume is inversely proportional to the gas pressure”.

(2) Charle's law



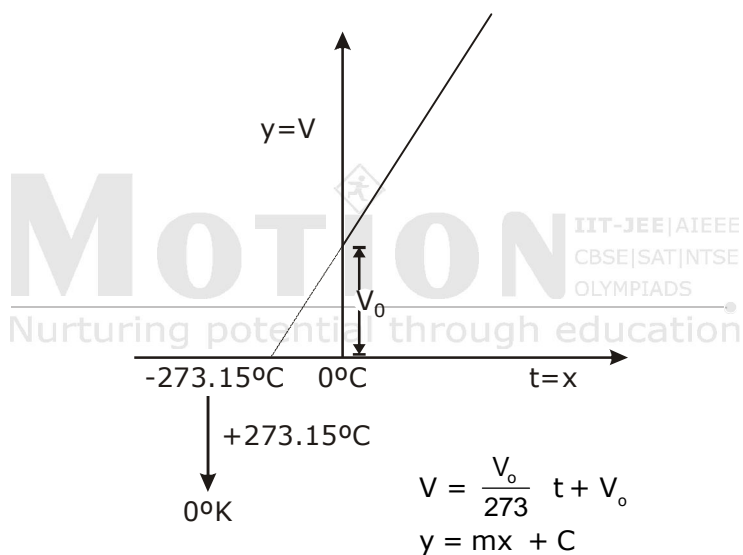
$$V_0 - \frac{V_0}{273.15}$$

$$= V_0 + \left(\frac{V_0}{273.15}\right) (-1)$$

$$V = V_0 + \frac{V_0}{273.15} \times t$$

V_0 = volume at 0°C

t = change in temp ($^\circ\text{C}$)



$$V = \frac{V_0}{273} t + V_0$$

$$y = mx + C$$

$$T = t + 273.15$$

From 1

2

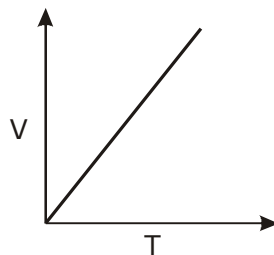
$$V = V_0 \left(1 + \frac{t}{273.15}\right), \quad V = V_0 \left(\frac{273.15 + t}{273.15}\right), \quad V = \left(\frac{V_0}{273.15}\right)$$

or, $\frac{V}{T} = \text{Constant}$

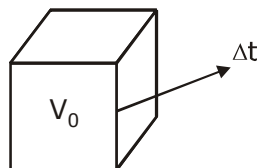
$V \propto T ; P = \text{Constant}$

$$[V = K T]$$

$$y = Kx$$



$V = V_0 + V_0 \gamma \Delta t$



Coefficient of superficial expansion

$V = V_0 (1 + \gamma t) \longrightarrow (\text{solid})$

$V = V_0 \left(1 + \frac{1}{273.15} \times t \right) \longrightarrow \text{Coefficient of superficial expansion of a gas}$

Charle's law states that, "volume of a gas increases by $\frac{1}{273.15}$ part of that volume which the gas had at 0°C for every 1° rise in temperature is called Charle's law "

OR

"Volume of a gas is directly proportional to absolute temp keeping pressure constant".

(3) Amonton's law (Gay lussac's law)

$P = P_0 \left(1 + \frac{1}{273.15} t \right)$

$\frac{P}{T} = \text{Constant} \Rightarrow V = \text{constant}$

$\frac{1}{273.15} = \text{Coeff. of pressure change.}$

(4) Avogadro's law

$$\frac{V_1}{n_1}$$

$$\frac{V_2}{n_2}$$

$$n_2 > n_1$$

$$T = \text{constant}$$

$$V_2 > V_1$$

$$V \propto n \Rightarrow$$

$$P = \text{constant}$$

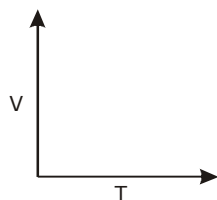
$$V = kn$$

$$\frac{V}{n} = \text{constant}$$

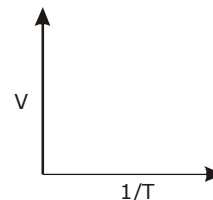
$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \dots = \frac{V_n}{n_n}$$

Avogadro's law states that, "volume of a gas is directly proportional to no. of moles keeping pressure and temp constant."

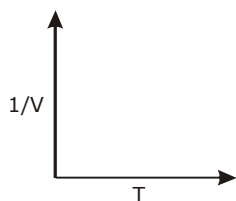
(I)



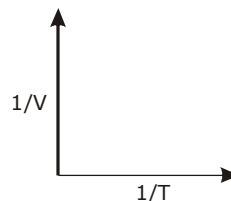
(II)



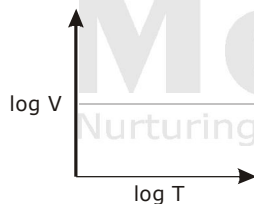
(III)



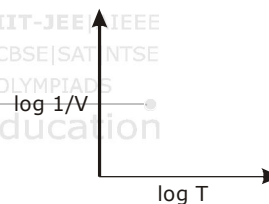
(IV)



(V)



(VI)

**Ideal gas equation**

$$V \propto \frac{1}{P} \text{ (Boyle's law) } \text{----- 1}$$

$$V \propto T \text{ (Charles' law) } \text{----- 2}$$

V \propto n (Avogadro's law)----- 3

from (1) (2) (3)

$$V \propto \frac{nT}{P} \Rightarrow V = \frac{KnT}{P}$$

$$[PV = KnT]$$

K = R = universal gas constant.

$$PV = nRT$$

$$\therefore n = \frac{W}{M}$$

$$PV = \frac{W}{M} RT$$

$$PM = \frac{W}{V} RT$$

$$PM = \rho RT$$

At S.T.P $\Rightarrow P = 1 \text{ atm}$

$$R = 0.0821$$

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

$$\rho = \frac{M}{\left(\frac{RT}{P}\right)} = \frac{M}{\left(\frac{(0.0821) \times 273}{1}\right)}$$

$$\rho_{\text{STP}} = \frac{M}{22.4}$$

Universal gas constant

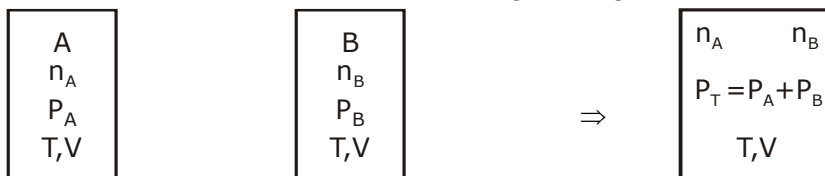
$$R = \frac{PV}{nT} = \frac{\frac{F}{A} \times A \times L}{n \times T} = \frac{\text{work}}{\text{mole} \times \text{temp}}$$

Is independent of P, V, n, T.

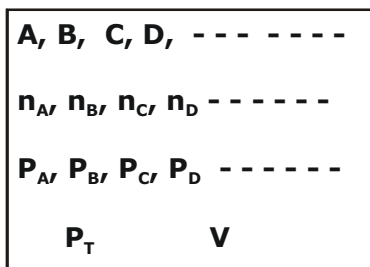
Value of 'R' depends on unit

P	V	R
Pa, N/m ²	m ³	8.31 J K ⁻¹ mol ⁻¹
atm	L	0.0821 Latm K ⁻¹ mol ⁻¹
---	---	1.97 cal K ⁻¹ mol ⁻¹ 2 cal K ⁻¹ mol ⁻¹
---	---	8.31 $\times 10^7$ ergs K ⁻¹ mol ⁻¹
---	---	5.189 $\times 10^3$ eV K ⁻¹ mol ⁻¹

Note : 1 atm L = 101.3 J

**Dalton's law of partial pressure**

Dalton's law of partial pressure states that " in a mixture of two non reacting gases taken in a closed volume & a constant temp behaves as if they are present alone in the container"

**Generalisation**

$$P_A V = n_A RT$$



$$P_A = n_A \frac{RT}{V} \text{----- (1)}$$



$$P_B = n_B \frac{RT}{V} \text{----- (2)}$$



$$P_C = n_C \frac{RT}{V} \text{----- (3)}$$



$$P_T \cdot V = (n_A + n_B + n_C + \text{-----}) RT$$



$$P_T = (n_A + n_B + n_C + \text{-----}) \frac{RT}{V} \text{----- (n)}$$

from (1) & (n) - - - - -



$$\frac{P_A}{P_T} = \frac{n_A \frac{RT}{V}}{(n_A + n_B + \text{-----}) \frac{RT}{V}}$$



$$P_A = \left[\frac{n_A}{n_A + n_B + \text{-----}} \right] \cdot P_T$$



$$P_A = X_A P_T$$

$$P_B = X_B P_T$$

$$P_C = X_C P_T$$



$$\left[X_A = \frac{n_A}{n_A + n_B + n_C + \text{-----}} \right]$$

$$X_A = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B} + \frac{W_C}{M_C} + \dots}$$

Amagat's law of Partial Volume

$$\begin{aligned} &A + B + C + \dots \\ &n_A + n_B + n_C + \dots \\ &P_A + P_B + P_C + \dots \\ &P_T, V_T \end{aligned}$$

$$P_T \cdot V_A = n_A RT \quad (1)$$

$$P_T \cdot V_T = (n_A + n_B + n_C + \dots) RT \quad (2)$$

from (1) & (2).

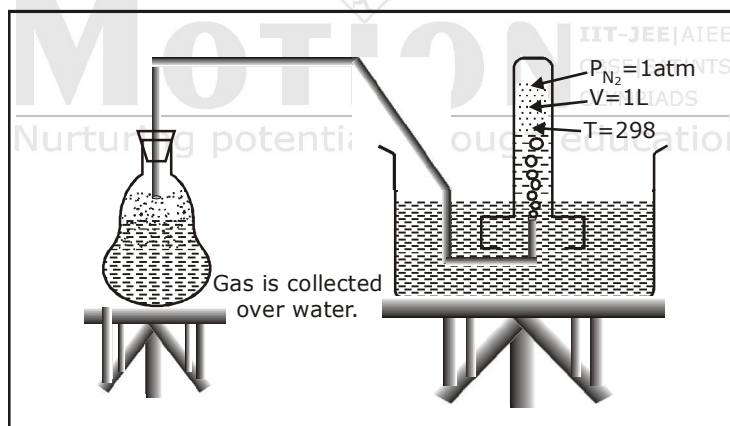
$$\frac{V_A}{V_T} = X_A$$

or $[V_A = X_A \cdot V_T]$

$$[P_A = X_A \cdot P_T]$$

$$\frac{V_A}{P_A} = \frac{V_T}{P_T}$$

Amagat's law of partial volume states that, "partial volume of any gas is equal to its mole fraction times its total volume."



$$P_{\text{wet gas}} = P_{\text{dry gas}} + P_{\text{H}_2\text{O}}$$

$$P_T = P_{\text{N}_2} + P_{\text{H}_2\text{O}}$$

$$1 \text{ atm} = P_{N_2} + P_{H_2O}$$

$$P_{N_2} = (1 \text{ atm} - P_{H_2O})$$

Whenever we apply ideal gas equation for a gas which is collected over water, take care that the pressure substituted is that of a dry gas.

(2) Relative humidity :

$$PV = \frac{w}{M} RT \Rightarrow P \propto w$$

$$RH = \frac{W_{H_2O} \text{ (present)}}{W_{\text{max } H_2O \text{ vapour}}}$$

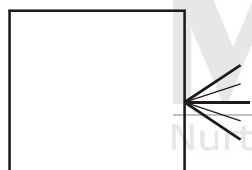
$$= \frac{\text{Partial vapour pressure of } H_2O}{\text{maximum partial pressure of } H_2O \text{ (Aqueoustension)}}$$

$$R.H\% = R.H \times 100$$

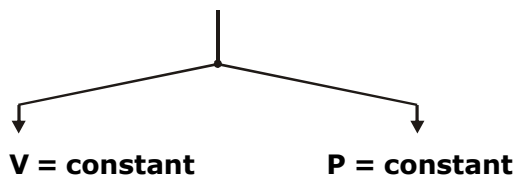
★ Effusion & Diffusion

EFFUSION

The process of leakage of a gas through a very fine hole is called effusion.

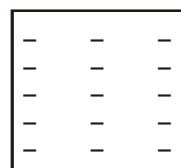
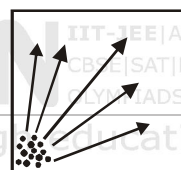


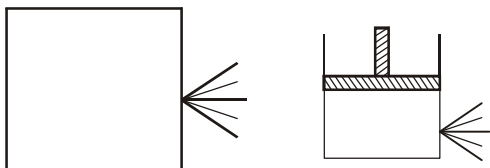
Effusion



DIFFUSION

⇒ The movement of molecules from a region of high conc. to low conc. is called diffusion.

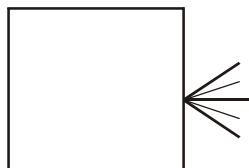




★

Definition of rates of Effusion & Diffusion

Effusion



$$\text{rate of} = \frac{\Delta n}{\Delta t}$$

V = Constant

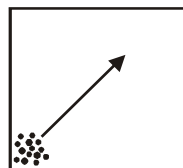


$$PV = nRT$$

$$\frac{\Delta P}{\Delta t} \propto \frac{\Delta n}{\Delta t}$$

$$\text{rate} = \frac{\Delta n}{\Delta t} = \frac{\Delta P}{\Delta t}$$

Diffusion



$$\text{rate of} = \frac{\text{distance}}{\text{time}}$$

P = Constant



$$PV = nRT$$

$$\frac{\Delta V}{\Delta t} \propto \frac{\Delta n}{\Delta t}$$

$$\text{rate of effusion} = \frac{\Delta n}{\Delta t} = \frac{\Delta V}{\Delta t}$$

★

Graham's law of diffusion or effusion

$$\text{rate} \propto P \text{ (Pressure of gas)} \dots\dots\dots (1)$$

$$\text{rate} \propto A \text{ (Area of hole)} \dots\dots\dots (2)$$

$$\text{rate} \propto \frac{1}{\sqrt{\rho}} \text{ (} \rho = \text{density of gas)} \dots\dots\dots (3)$$

$$\text{rate} \propto \frac{PA}{\sqrt{\rho}}$$

$$\text{rate} = \frac{KPA}{\sqrt{\rho}}$$

$$PM = \rho RT$$

$$M \propto \rho$$

$$\text{rate} = \frac{KPA}{\sqrt{\rho}} = \frac{KPA}{\sqrt{M}}$$

$$\text{rate} = \frac{K}{\sqrt{\rho}} = \frac{K}{\sqrt{M}}$$

Graham's law states that " the rate of diffusion or effusion of gas is directly proportional to the product of pressure & area of orifice and is inversely proportional to the density of gas "

Variations in Graham's law

Case - I (leaking alone)



Case - II (leak together)

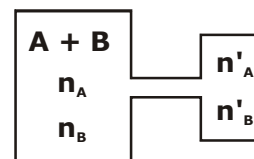


Case I - A

$V = \text{constant}$

Case I - B

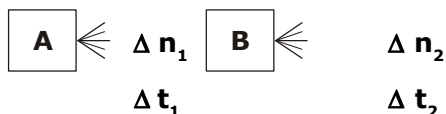
$P = \text{constant}$



Case I - A: ($V = \text{constant}$)

Case-II

$$\frac{n'_A}{n'_B} = \frac{n_A}{n_B} \times \sqrt{\frac{P_B}{P_A}}$$



$$\frac{\Delta n_1}{\Delta t_1} = \frac{k}{\sqrt{M_1}}, \quad \frac{\Delta n_2}{\Delta t_2} = \frac{k}{\sqrt{M_2}}$$

$$\frac{\Delta n_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta n_2} = \sqrt{\frac{M_2}{M_1}} \rightarrow \left[\frac{\Delta n_1}{\Delta n_2} = \sqrt{\frac{M_2}{M_1}} \right]$$

$$\rightarrow \left[\frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{M_2}{M_1}} \right]$$

as $\Delta n \propto \Delta P$

$$\frac{\Delta P_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta P_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\rightarrow \left[\frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{M_2}{M_1}} \right]$$

$$\left[\frac{\Delta P_1}{\Delta P_2} = \sqrt{\frac{M_2}{M_1}} \right]$$

Case I - B : (P = Constant)

$$\frac{\Delta n_1}{\Delta t_1} = \frac{k}{\sqrt{M_1}} ; \quad \frac{\Delta n_2}{\Delta t_2} = \frac{k}{\sqrt{M_2}}$$

$$\frac{\Delta n_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta n_2} = \sqrt{\frac{M_2}{M_1}} \longrightarrow \left[\frac{\Delta n_1}{\Delta n_2} = \sqrt{\frac{M_2}{M_1}} \right]$$

$$\left[\frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{M_2}{M_1}} \right]$$


as $\Delta n \propto \Delta V$

$$\frac{\Delta V_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta V_2} = \sqrt{\frac{M_2}{M_1}} \longrightarrow \left[\frac{\Delta V_1}{\Delta V_2} = \sqrt{\frac{M_2}{M_1}} \right]$$

$$\left[\frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{M_2}{M_1}} \right]$$

Kinetic theory of gases

Postulates of Kinetic Theory of gases :

(1)  Vol. of free space
 $V_{fs} = V - V_{\text{molecules}} \approx V$

The gases are composed of very small particles with their volume almost negligible as compared to the volume of the container.

(2) Gas molecules are in constant random motion.

(3) All the collisions in the gas molecules are assumed to be perfectly elastic.

(4) There is intermolecular attraction or repulsion between the gas molecules.

(5) The pressure exerted by the gas on the wall of the container is due to constt. bombardment of molecules on the wall of container.

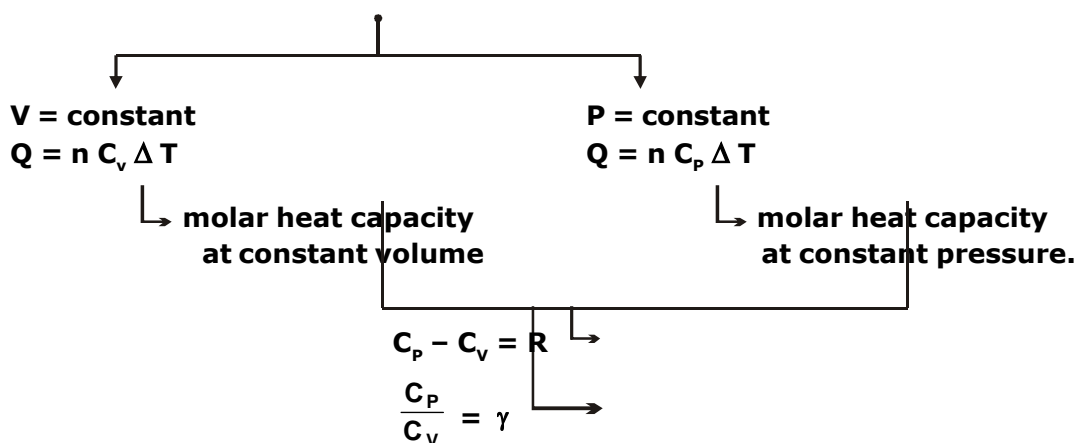
(6) It was assumed that the K.E. of the gas molecule is directly proportional to the absolute temperature.

$$K.E. \propto T$$

(7) There is no effect of gravity on the gas molecules.



Molar heat capacity of gases



Degree of freedom

- ☞ (1) The no. of terms in the expression of energy of a gas is known as "degree of freedom" symbol 'f'.
- ☞ (2) Monoatomic gas molecules possess only translational motion while diatomic & polyatomic molecules possess translational as well as rotational and vibrational energy.
- ☞ (3) At ordinary temp. the vibrational mode is neglected.
- ☞ (4) monoatomic Ne → f = 3
- diatomic Cl Cl → f = 5
- polyatomic O C O → f = 6



$$C_v = \frac{f}{2} R$$



$$C_p = \left(\frac{f}{2} + 1\right) R = \left(\frac{f+2}{2}\right) R$$

$$\left[\gamma = \frac{C_p}{C_v}\right] \Rightarrow \frac{\left(\frac{f+2}{2}\right) R}{\left(\frac{f}{2}\right) R} = 1 + \frac{2}{f}$$



$$\gamma = 1 + \frac{2}{f}$$



Energy of a molecule at T kelvin is $\left[\frac{1}{2} kT\right]$ per degree of freedom
where K = Boltzmann's constant.

$$= \frac{R}{N_A} = \frac{8.31}{6.023 \times 10^{23}} = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ mol}^{-1}$$

☞ K . E. of one gas molecule is equal to $\frac{f}{2} K T$

$$K . E = \frac{f}{2} K T$$

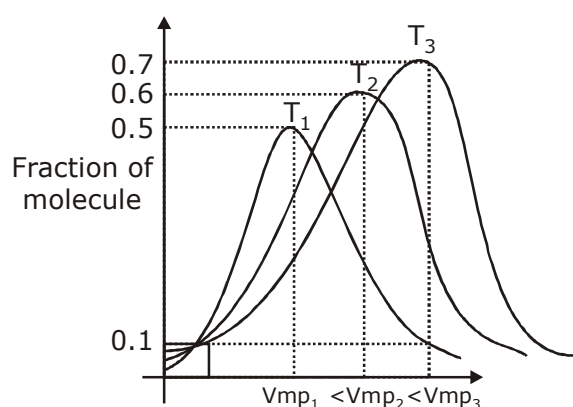
☞ Total energy of 1 mole of molecule is $\frac{f}{2} R T$

$$1 \text{ molecule} \rightarrow \frac{f}{2} \frac{R}{N_A} T$$

$$1 \text{ mole} \rightarrow \left(\frac{f}{2} \times \frac{R}{N_A} \times T \right) \times N_A = \frac{f}{2} R T$$

$$\text{Total energy} = \frac{f}{2} R T$$

Boltzmann Velocity Distribution Curve

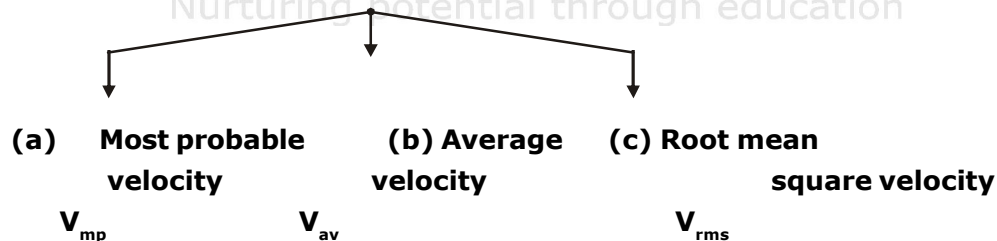


☞ The value of most probable velocity increases with temp.

☞ The fraction of molecules possessing the most probable velocity also increases with the temperature .

★

Velocities of gases



★

(a) **Most probable velocity** : (V_{mp}) :

☞ Possessed by maximum number of molecules .

$$V_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2PV}{nM}} = \sqrt{\frac{2PV_m}{M}}$$

$$PV = nRT \rightarrow RT = \frac{PV}{n}$$

$$PM = \rho RT \rightarrow \frac{P}{\rho} = \frac{RT}{M}$$

$$n \rightarrow V$$

$$1 \rightarrow \left[\frac{V}{n} = V_m \right].$$

★ (b) **Average velocity :**

$$V_{av} = \frac{V_1 + V_2 + V_3 + \dots + V_n}{n}$$

$$V_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8P}{\pi \rho}} = \sqrt{\frac{8PV}{\pi nM}} = \sqrt{\frac{8PV_m}{\pi M}}$$

★ (c) **Root mean square velocity (V_{rms}) :**

$$V_{rms} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \dots + V_n^2}{n}}$$

was defined for K E . of gas

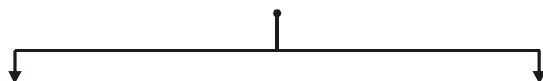
$$V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3PV_m}{M}}$$

$$V_{mp} < V_{av} < V_{rms}$$

$$\left[V_{mp} : V_{av} : V_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \right]$$

$$= 1 : 1.128 : 1.224$$

★ **Kinetic energy**



Total K . E of gas molecules

$$KE = \frac{3}{2} nRT = \frac{3}{2} \frac{W}{M} RT$$

$$n = n \text{ moles}$$

Average K E per molecules

$$n \text{ moles} \rightarrow \frac{3}{2} n RT$$

$$1 \text{ mole} \rightarrow \frac{3}{2} RT$$

K . E possessed by

n moles of any gas

$$N_A \text{ particle} \rightarrow \frac{3}{2} RT$$

$$1 \text{ particle} \rightarrow \frac{3}{2} \times \frac{R}{N_A} T = \frac{3}{2} K T$$

Boltzmann constant

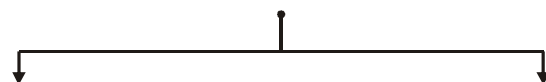
$$= 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K E (av) = \frac{3}{2} K T$$

(per molecule)

**Compressibility factor (Z)**

$$Z = \frac{PV}{nRT} = \frac{PV_n}{RT}$$

Z = 1 → Ideal gas**Z ≠ 1 → Real gas****Z > 1**

Real gas

Positive deviation from
ideal behaviour

intermolecular repulsion



can't be liquefied

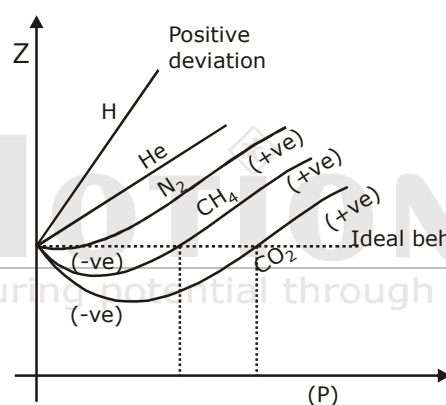
Z < 1

⇒ Real gas

⇒ Negative deviation from
ideal behaviour

⇒ intermolecular attraction

⇒ can be easily liquefied

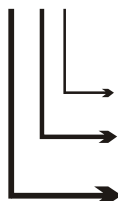


Question : Why H and He have Z always greater than 1?

Answer :

Vander Waals equation

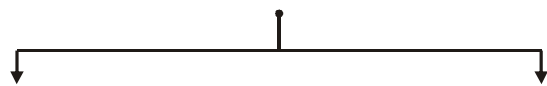
$$P_i V_{fs} = n R T$$



$$V - V_{\text{moles}} = V_{fs} \Rightarrow V_{fs} \approx V$$

assumed no intermolecular forces.

To be vander waal equation

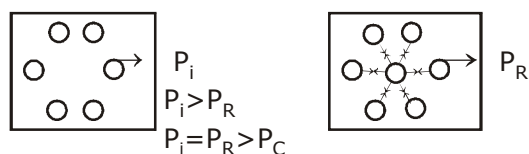


(a) Pressure Correction

(b) Volume Correction



(a) Pressure Correction



$P_C \propto \frac{n}{V} \Rightarrow$ Conc. of gas molecules colliding per unit time within the wall of container.



$P_C \propto \frac{n}{V} \Rightarrow$ Conc. of gas molecules behind every colliding molecule.

$$P_C \propto \frac{n^2}{V^2}$$



or , $P_C = \frac{an^2}{V^2}$ [a= Vander Waal's constant]

Unit of a = atm L² mol⁻²

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(b) Volume Correction

2 molecules

$$\frac{4}{3} \pi (2r)^3$$

2 molecules

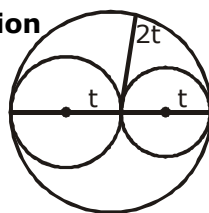
$$8 \times \frac{4}{3} \pi r^3$$

1 molecules

$$4 \times \frac{4}{3} \pi r^3$$

1 mole molecules

$$4 \times \frac{4}{3} \pi r^3 \times N_A$$



Let the volume occupied by 1 mole molecule



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

$$r = \sqrt[3]{\frac{3b}{16N_A\pi}}$$

$$b = 4 N_A \times V$$



Unit of $b = \text{L mole}^{-1}$

$$V_{\text{molecules}} (n \text{ moles}) = n b$$

$$V_{fs} = V_{\text{container}} - V_{\text{molecules}}$$

$$V_{fs} = V - nb$$

$$V_{fs} = V + V_c$$

$$V_c = nb$$



Vander Waal's equation can be written as :

$$P_i V_{fs} = nRT$$

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



Variations in Vander Waals equation



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

★ (a) **Low pressure :-**

$$P \downarrow \Rightarrow V \nearrow \Rightarrow V - nb \approx V \quad \nearrow \text{neglected}$$

$$V \nearrow \Rightarrow \frac{an^2}{V^2} \downarrow$$

$$P \downarrow \Rightarrow \text{hence, } \frac{an^2}{V^2} \text{ is net negligible}$$



Vander Waal's equation changes to

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

$$PV + \frac{an^2}{V} = nRT$$

$$\frac{PV}{nRT} + \frac{an^2}{V \times nRT} = 1$$

$$Z + \frac{an}{VRT} = 1$$

$$\left[Z = 1 - \frac{an}{VRT} \right]$$

for $n = 1$

$$Z = 1 - \frac{a}{VRT} \Rightarrow Z < 1$$



At low pressure :-

- (1) Intermolecular attraction
- (2) Can be liquify
- (c) Negative deviation from ideal behaviour



(b) High pressure :-

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

$P \uparrow \Rightarrow V \downarrow = V - nb \Rightarrow$ remain as it is

$V \downarrow = \frac{an^2}{V^2} \Rightarrow$ but it very less as compared to P hence $\frac{an^2}{V^2}$ can be neglected.



Now, Vander Waal's equation changes :

$$P(V - nb) = nRT \quad PV - nPb = nRT$$

$$\frac{PV}{nRT} - \frac{nPb}{nRT} = 1 \quad Z - \frac{Pb}{RT} = 1$$

$$Z = 1 + \frac{Pb}{RT} \Rightarrow Z > 1$$



Rx

\rightarrow Pressure $\uparrow \Rightarrow$ Real gas

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(a) intermolecular repulsion



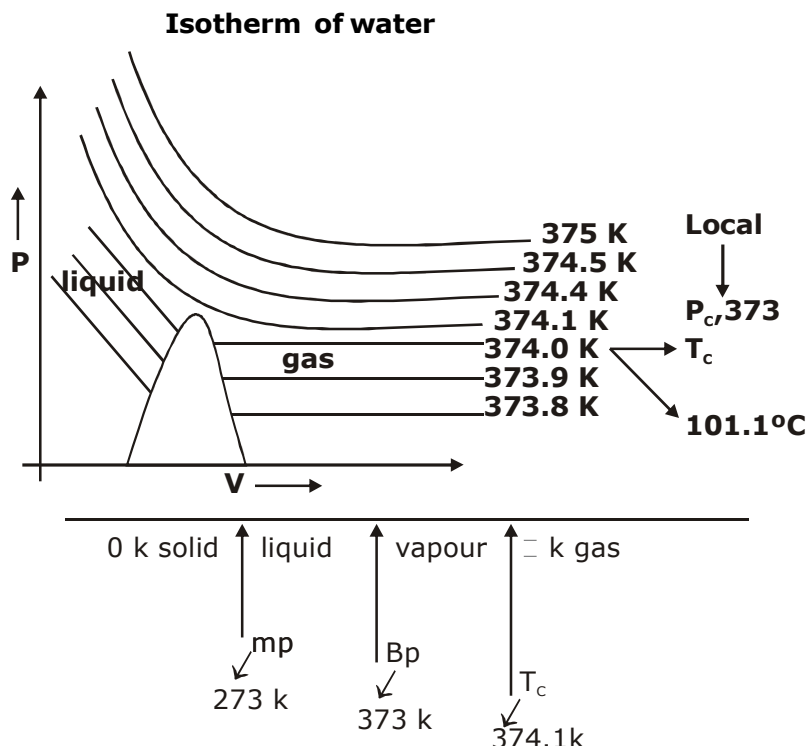
(b) cannot liquefy



(c) positive deviation from ideal behaviour



Isotherm : A plot between pressure and volume keeping temperature constant called isotherm.



☞ **Critical temp (T_c) :** The temp above which a gas can never be liquify is called critical temp.

☞
$$T_c = \frac{8a}{27Rb} \quad a, b = \text{Vander waal constant.}$$

☞ **Critical Pressure (P_c) :**
$$P_c = \frac{a}{27b^2}$$

☞ **Critical Volume (V_c) :** Volume of one mole of gas at critical point is called critical volume.

$$V_c = 3b$$

Calculation of Critical Constants

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

$$(V^2P + a)(V - b) = V^2RT$$

$$PV^3 - PbV^2 + aV - ab = V^2RT$$

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

At critical point

$$V^3 - \left(\frac{b + RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0$$

At Critical Point :

$$(V - V_c)^3 = 0$$

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \dots (II)$$

By (i) and (ii)

$$3V_c = b + \frac{RT_c}{P_c}$$

$$3V_c^2 = \frac{a}{P_c}$$

$$V_c^2 = \frac{ab}{P_c}$$

$$\frac{V_c^3}{3V_c^2} = \frac{ab/P_c}{a/P_c}$$



$$V_c = 3b$$

$$P_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

Virial equation

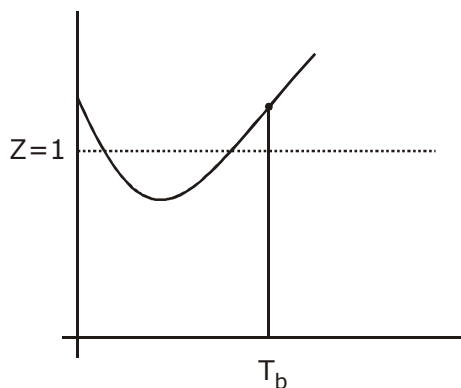


Whenever compressibility factor of a gas is expanded in the terms of $1/V_m$ or P , the expansion is called **Virial equation**

$$Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots \infty$$

$$Z = \frac{PV_m}{RT} = 1 + B \left(\frac{P}{RT} \right) + C \left(\frac{P}{RT} \right)^2 + D \left(\frac{P}{RT} \right)^3 + \dots \infty$$

Boyle's temperature (T_b)



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



The temperature at which a real gas behaves like an ideal gas is called "Boyle's temperature."

Inversion temperature (T_i)

gas expand \Rightarrow warms up



----- (T_i)



gas expand \Rightarrow cools down

$$T_i = \frac{2a}{Rb} = 2T_b$$



A temp below which a gas is expanded, it cools down and vice versa happens above that temperature, is called "**inversion temperature**"

SOLVED EXAMPLES

Ex.1 When 2 gm of a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1 atm. 3 gm another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights of A and B.

Sol. Let M_A and M_B be the molecular weights of A and B.

Using $PV = nRT$ for A, we get :

$$1 = \frac{\frac{2}{M_A} RT}{V} \quad \dots(i)$$

$$\text{and using Dalton's Law : } P_{\text{Total}} = \frac{(n_A + n_B)RT}{V} \Rightarrow 1.5 = \frac{\left(\frac{2}{M_A} + \frac{3}{M_B}\right)RT}{V} \quad \dots(ii)$$

$$\text{Solving (i) and (ii), we get } \frac{M_A}{M_B} = \frac{1}{3}$$

Ex.2 Which of the two gases, ammonia and hydrogen chloride, will diffuse faster and by what factor ?

Sol. By Graham's Law :

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} \approx 1.46 \Rightarrow r_{\text{NH}_3} = 1.46 r_{\text{HCl}}$$

Thus, ammonia will diffuse 1.46 times faster than hydrogen chloride gas.

Ex.3 The ratio of rate of diffusion of gases A and B is 1 : 4 and their molar mass ratio is 2 : 3. Calculate the composition of the gas mixture initially effusing out.

Sol. By Graham's Law :

$$\frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{1}{4} = \frac{P_A}{P_B} \sqrt{\frac{3}{2}} \Rightarrow \frac{P_A}{P_B} = \frac{1}{4} \sqrt{\frac{2}{3}}$$

$$\Rightarrow \text{Mole ratio of gas A and B effusing out} = \frac{1}{4} \sqrt{\frac{2}{3}} \quad [\text{moles} \propto \text{pressure}]$$

Ex.4 At 30°C and 720 mm of Hg, the density of a gas is 1.5 g/lit. Calculate molecular mass of the gas. Also find the number of molecules in 1 cc of the gas at the same temperature.

Sol. Assuming ideal behaviour and applying ideal gas equation :

$$PV = nRT$$

$$\text{Another form of gas equation is } PM_0 = dRT$$

$$\Rightarrow M_0 = \frac{dRT}{P} = \frac{1.5 \times 0.0821 \times 303}{720/760} \quad (T = 30 + 273 \text{ K})$$

$$\Rightarrow M_0 = 39.38$$

$$\text{Now number of molecules} = n \times N_0$$

$$= \frac{PV}{RT} \times N_0 = \frac{720/760 \times 1 \times 10^{-3}}{0.0821 \times 303} \times 6.023 \times 10^{23}$$

$$= 2.29 \times 10^{19}$$

Ex.5 The pressure exerted by 12 gm of an ideal gas at temperature $t^{\circ}\text{C}$ in a vessel of volume V litre is one atm. When the temperature is increased by 10° at the same volume, the pressure rises by 10% calculate the temperature t and volume V . (molecular mass of the gas = 120 gm/mole)

Sol. Using Gas equation : $PV = nRT$

We have, $P \times V = 0.1 \times R \times t \dots(1)$

and $1.1 P \times V = 0.1 \times R \times (t + 10) \dots(2)$

Using (i) and (ii), we have : $\frac{t}{t+10} = \frac{1}{1.1}$

$\Rightarrow t = 100 \text{ K or } t = -173^{\circ}\text{C}$

Putting the value of t in (i), we get :

$\Rightarrow 1 \times V = 0.1 \times 0.0821 \times 100 \Rightarrow V = 0.821 \text{ L}$

Ex.6 Assuming that the air is essentially a mixture of nitrogen and oxygen in mole ratio of 4 : 1 by volume. Calculate the partial pressures of N_2 and O_2 on a day when the atmospheric pressure is 750 mm of Hg. Neglect the pressure of other gases.

Sol. From Dalton's Law of partial pressure, we have

Partial pressure of nitrogen = $p_{\text{N}_2} = \chi_{\text{N}_2} \times P$ and Partial pressure of oxygen = $p_{\text{O}_2} = \chi_{\text{O}_2} \times P$

Now, $\chi_{\text{N}_2} = 4/5$, and $\chi_{\text{O}_2} = 1/5$

$\Rightarrow p_{\text{N}_2} = \frac{4}{5} \times 750 = 600 \text{ mm of Hg}$ and $p_{\text{O}_2} = \frac{1}{5} \times 750 = 150 \text{ mm of Hg}$

Ex.7 An open vessel at 27°C is heated until three fifth of the air has been expelled, Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.

Sol. In the given questions, volume is constant. Also, as the vessel is open to atmosphere, the pressure is constant. This means that the gas equation is simply reduced to the following form :

$nT = \text{constant (Use } PV = nRT)$

or $n_1 T_1 = n_2 T_2$

Now let n_1 = initial moles and n_2 = final moles

$\Rightarrow n_2 = 2/5 \times n_1$ (as 3/5th of the air has been expelled)

$\Rightarrow T_2 = \frac{n_1 T_1}{n_2} = \frac{n_1 T_1}{2/5 n_1} = \frac{5}{2} T_1$

$\Rightarrow T_2 = \frac{5}{2} (300) = 750 \text{ K} = 477^{\circ}\text{C}$

Ex.8 When 3.2 gm of sulphur is vaporized at 450°C and 723 mm pressure, the vapour occupies a volume of 780 m, what is the formula for the sulphur under these conditions ?

Sol. The molecular weight = no. of atoms \times atomic mass

So let us find the molecular weight of S from the data given.

$M_0 = \frac{gRT}{PV} = \frac{3.2 \times 0.082 \times 723}{(723 \times 760) \times (780/1000)} = 256$

$\Rightarrow \text{Number of atoms} = \frac{256}{32} = 8$

Hence, molecular formula of sulphur = S_8

Ex.9 A spherical balloon of 21 cm diameter is to be filled with H_2 at NTP from a cylinder containing the gas at 20 atm at $27^\circ C$. If the cylinder can hold 2.80L of water, calculate the number of balloons that can be filled up.

Sol. The capacity of cylinder = 2.80 L

Let n = moles of hydrogen contained in cylinder and n_0 = moles of hydrogen required to fill one balloon.

$$n = \frac{PV}{RT} = \frac{20 \times 280}{0.0821 \times 300} = 2.273$$

$$n_0 = \frac{\text{volume of balloon}}{22400} \quad (\text{Note : the balloons are being filled at S.T.P.})$$

$$= \frac{4/3 \pi r^2}{22400} = \frac{4/3 \times 3.14 \times (10.5)^3}{22400} = 0.2164$$

$$\Rightarrow \text{Number of balloons that can be filled} = \frac{n}{n_0} = 10.50 \approx 10$$

Ex.10 A mixture containing 1.12L of H_2 and 1.12L of D_2 (deuterium) at S.T.P. is taken inside a bulb connected to another bulb by 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 found to contain 0.05 gm of H_2 . Determine the % age composition by weight of the gases in the second bulb.

Sol. In the first bulb :

$$\text{Initial moles of } H_2 = 1.12 / 22.4 = 1/20$$

$$\text{Initial moles of } D_2 = 1.12/22.4 = 1/20$$

Now after opening of stop-cock, mass of H_2 left in the first bulb = 0.05

$$\Rightarrow \text{Moles of } H_2 = 0.05/2 = 1/40$$

$$\Rightarrow \text{Moles of } H_2 \text{ effused into second bulb} = 1/20 - 1/40 = 1/40$$

Let n be number of moles of D_2 effused.

From Graham's Law :

$$\frac{n}{1/40} = \sqrt{\frac{2}{4}}$$

$$\Rightarrow n = \frac{\sqrt{2}}{80} = \text{moles of } D_2 \text{ in second bulb.}$$

In the second bulb :

$$\text{The mass of } H_2 \text{ gas} = 1/40 \times 2 = 0.05 \text{ gm}$$

$$\text{The mass of } D_2 \text{ gas} = \sqrt{2}/80 \times 4 = 0.07 \text{ gm}$$

$$\Rightarrow \text{Total mass} = 0.05 + 0.07 = 0.12 \text{ gm}$$

$$\Rightarrow \% \text{ of } H_2 = 0.05/0.12 \times 100 = 41.67 \%$$

$$\Rightarrow \% \text{ of } D_2 = 0.07/0.12 \times 100 = 58.33 \%$$

Ex.11 The pressure in a bulb dropped from 2000 mm to 1500 mm of Hg in 47 min when the contained O_2 leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas (B) of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min.

Sol. Now as $P \propto n$ (moles), we define the rate of diffusion as the drop in the pressure per second. First we try to find the rate of diffusion of the gas B.

The rate of diffusion of $O_2 = R_0 = (2000 - 1500)/47 = 10.638 \text{ mm/min}$.

Assuming that gas B was present alone in the bulb. Let the rate of diffusion of B = R_B .

From Graham's Law of diffusion, we have :

$$\frac{R_B}{R_O} = \sqrt{\frac{M_{O_2}}{M_B}} = \sqrt{\frac{32}{79}} = 0.636$$

$$\Rightarrow R_B = 10.638 \times 0.636 = 6.77 \text{ mm/min}$$

Now the bulb contains mixture of O_2 and B in the mole ratio of 1 : 1 at total pressure of 4000 mm Hg.

$$\Rightarrow P_{O_2} = P_B = 2000 \text{ mm of Hg}$$

As the pressure and temperature conditions are same for both gases in the second case (same bulb), so the rate of diffusion will remain same in the second case also.

Let X_0 and X_B be the final pressure in the bulb after leakage for 74 minutes.

$$R_O = \frac{2000 - X_0}{74} = 10.638$$

$$\Rightarrow X_0 = 1212.78$$

$$R_B = \frac{2000 - X_B}{74} = 6.77 \Rightarrow X_B = 1498.96$$

As $P \propto n$

$$\Rightarrow \text{Ratio of moles is given as : } X_0 : X_B = 1 : 1235$$

Ex.12 A 672 ml of a mixture of oxygen-ozone at N.T.P. were found to be weigh 1 gm. Calculate the volume of ozone in the mixture.

Sol. Let V ml of ozone are there in the mixture

$$\Rightarrow (672 - V) \text{ m; = vol. of oxygen}$$

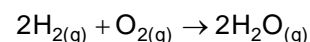
$$\text{Mass of ozone at N.T.P.} = \frac{V}{22400} \times 48$$

$$\text{Mass of oxygen at N.T.P.} = \frac{672 - V}{22400} \times 32$$

$$\Rightarrow \frac{V}{22400} \times 48 + \frac{672 - V}{22400} \times 32 = 1 \Rightarrow \text{On solving we get: } V = 56 \text{ ml}$$

Ex.13 A 20 L flask contains 4.0 gm of O_2 & 0.6 gm of H_2 at 100°C . If the contents are allowed to react to form water vapors at 100°C , find the contents of flask and there partial pressures.

Sol. H_2 reacts with O_2 to form water [$H_2O_{(g)}$]



$$\Rightarrow 2 \text{ moles of } H_2 = 1 \text{ mole of } O_2 = 2 \text{ moles of } H_2O$$

Here masses of H_2 and O_2 are given, so one of them can be in excess. So first check out which of the reactants is in excess.

Now, Moles of $O_2 = 4/32 = 0.125$ and Moles of $H_2 = 0.6/2 = 0.3$

Since 1 mole of $O_2 = 2$ moles of H_2

$$\Rightarrow 0.125 \text{ moles of } O_2 = 2 \times 0.125 \text{ moles of } H_2$$

i.e. 0.25 moles of H_2 are used, so O_2 reacts completely whereas H_2 is in excess.

$$\Rightarrow \text{Moles of } H_2 \text{ in excess} = 0.3 - 0.25 = 0.05 \text{ moles.}$$

Also, 2 moles of $H_2 \equiv$ 2 moles of H_2O

\Rightarrow 0.25 moles of $H_2 \equiv$ 0.25 moles of H_2O are produced.

\Rightarrow Total moles after the reaction = 0.05 (moles of H_2) + 0.25 (moles of H_2O) = 0.3

\Rightarrow The total pressure P_{Total} at the end of reaction is given by :

$$P_{\text{Total}} = \frac{nRT}{V} = \frac{0.3 \times 0.0821 \times 373}{20} = 0.459 \text{ atm}$$

Now partial pressure of A = mole fraction of A $\times P_{\text{Total}}$

$$\Rightarrow P_{H_2} = 0.05/0.3 \times 0.459 = 0.076 \text{ atm}$$

$$\Rightarrow P_{H_2O} = 0.25/0.3 \times 0.459 = 0.383 \text{ atm}$$

Ex.19 The compressibility factor for 1 mole of a van Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecular is negligible, calculate the van der Waals constant 'a'.

Using van der Waal's equation of state :

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

Now : $V - nb \approx V(\text{given})$

$$\Rightarrow \text{The equation is reduced to : } \left(P + \frac{a}{V^2}\right)V = RT$$

$$\text{or } Z = \frac{PV}{RT} = \frac{V}{RT} \left(\frac{RT}{V} - \frac{a}{V^2}\right) = 1 - \frac{a}{RTV}$$

$$0.5 = \frac{100 \times V}{0.0821 \times 273} \Rightarrow V = 0.112 \text{ L}$$

$$\text{Also, } 0.5 = 1 - \frac{a}{RTV}$$

Substitute the values of V and T :

$$\Rightarrow a = 1.25 \text{ litre}^2 \text{ mol}^{-2} \text{ atm.}$$

Ex.20 Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der waals equation. Also report the pressure of gas if it behaves ideally in nature.

($a = 3.592 \text{ atm litre}^2 \text{ mol}^{-2}$, $b = 0.0427 \text{ litre mol}^{-1}$)

Using van der waals equation of state :

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

$$\text{Substituting the given values, we get : } \left(P + \frac{3.592 \times 5^2}{1^2}\right)(1 - 5 \times 0.0427) = 5 \times 0.0821 \times 320$$

$$\Rightarrow P = 77.218 \text{ atm}$$

If the gas behaves ideally, then using : $PV = nRT$

$$\Rightarrow P = \frac{5 \times 0.0821 \times 320}{1} \text{ atm} = 131.36 \text{ atm}$$