

IIT – JEE SYLLABUS

Gaseous State : Tentative Lecture Flow

1	Ideal gas laws and Ideal gas equation
2	Problems on ideal gas equation, Dalton's law
3	Graham's law
4	Eudiometry
5	KTG
6	Real gas equation
7	Compressibility factor, virial equation

1. INTRODUCTION

The gaseous state is characterized by the following physical properties.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

2. EXPERIMENTAL GAS LAWS

Basic parameters associated with gas

(i) Pressure:-

Pascal: - It is SI unit for pressure; *Pascal* is very small amount of pressure

○ (10mg weight on 1cm^2 area)

○ $1\text{ Pa} = 1\text{ N/m}^2$

Atm: - $1\text{ atm} = 76\text{ cm of Hg} = 760\text{ torr} = 101325\text{ Pa} = 1.01325\text{ bar}$

(ii) Volume :- $1\text{ L} = 1000\text{ ml} = 10^{-3}\text{ m}^3 = 1000\text{ cc}$

(iii) Temperature :-

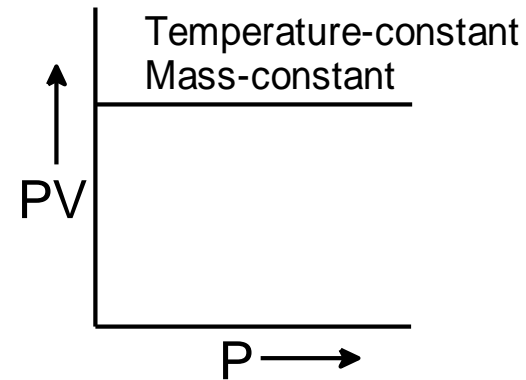
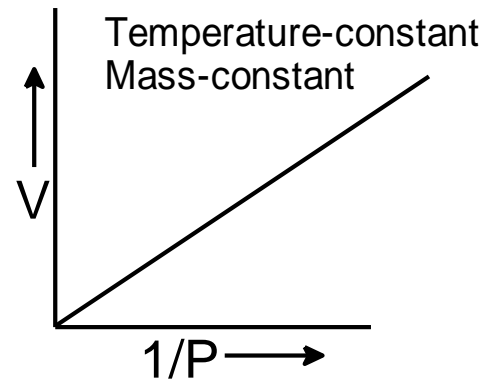
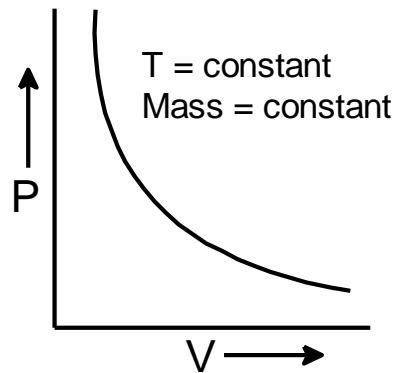
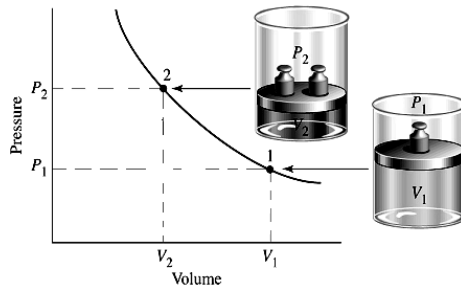
$$T\text{ K} = T^{\circ}\text{C} + 273$$

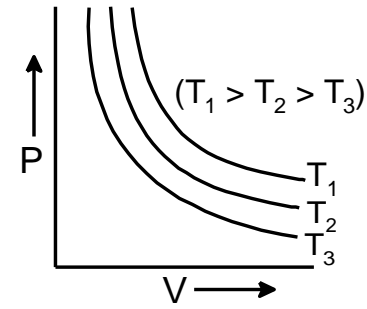
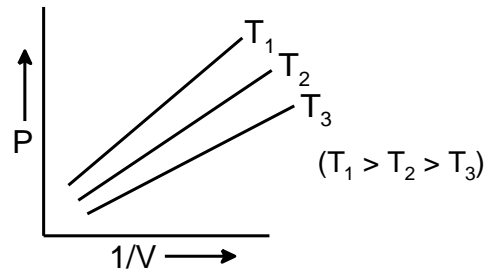
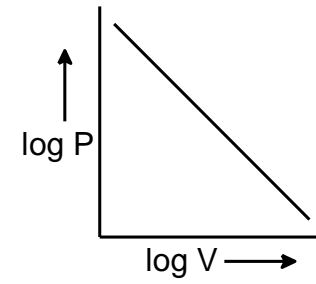
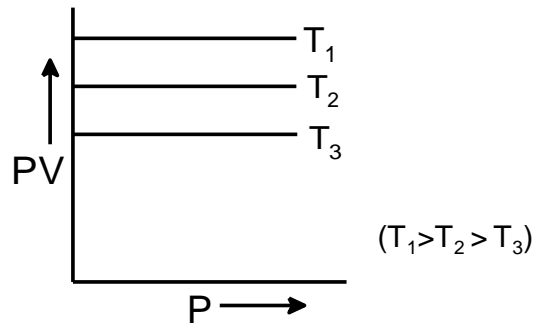
(iv) Amount of gas :- Generally measured in moles of gas

Boyle's Law

$$\therefore V \propto \frac{1}{P} \text{ (if } T \text{ and } n \text{ constant).} \quad \therefore PV = \text{Constant}$$

Graphical Representation: - Boyle's law can be graphically represented in following ways





Example 1: A 1.1 L flask containing nitrogen at a pressure of 710 mm is connected to an evacuated flask of unknown volume. The nitrogen, which acts ideally is allowed to expand into the combined system of both the flasks isothermally. If the final pressure of nitrogen is

583 mm, determine the volume of evacuated flask.

Solution: Applying Boyle's law: $p_1V_1 = p_2V_2$

Let V be the volume of evacuated flask

$$\Rightarrow 710 \times 1.1 = 583 (1.1 + V)$$

$$V = 0.24 \text{ L}$$

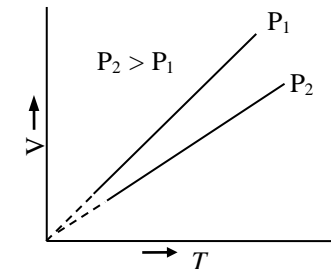
Charles law

Thus, $V_t = V_0 + \frac{V_0}{273} \times t = V_0 \left(1 + \frac{t}{273} \right)$

or $V_t = V_0 \left(\frac{273 + t}{273} \right)$ (since $K = ^\circ C + 273$) ... Eq(i)

by substituting T for $273 + t$ and T_0 for 273 in Eq. (i),

$$V_t = \frac{V_0 \times T}{T_0} \quad \text{or} \quad \frac{V_t}{T} = \frac{V_0}{T_0} \quad \text{or} \quad \frac{V}{T} = \text{constant (if pressure is kept constant)}$$



$$V \propto T \text{ (if pressure is kept constant)}$$

In fact, no substance exists as a gas at a temperature near Kelvin zero, through the straight-line plots can be extrapolated to zero volume. The temperature that corresponds to zero volume is -273.15°C .

- **Can you guess how the graph of volume vs Temperature ($^{\circ}\text{C}$) will look like**

Gay Lussac's Law

$$P_t = P_0 + \frac{P_0 \times t}{273} \quad \text{or} \quad P_t = P_0 \left(1 + \frac{t}{273} \right)$$

$$\text{or} \quad P_t = P_0 \left(\frac{273 + t}{273} \right) = P_0 \frac{T}{T_0}$$

$$\text{or} \quad \frac{P_t}{T} = \frac{P_0}{T_0} \quad \text{or} \quad P \propto T \text{ (if volume is kept constant)}$$

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

Example 3: A certain amount of ethane is confined in a bulb of 1 liter capacity. The bulb is so weak that it will burst if pressure exceeds 10 atm. Initially gas exerts 8 atm pressure at 27⁰ C.

Find temperature at which the bulb will burst?

Solution: Considering limiting condition

Since volume remain constant $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

Thus $8/300 = 10/T_2$

$\Rightarrow T_2 = 375 \text{ K}$

Ideal Gas Law

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad \text{i.e.} \quad \frac{pV}{T} = K$$

We thus have the general gas law

$$pV = nRT$$

The universal gas constant $R = pV/nT$.

Numerical Values of R

i) In liter atmosphere = $0.0821 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$ ii) In ergs = $8.314 \times 10^7 \text{ erg deg}^{-1} \text{ mole}^{-1}$

iii) In calories = $1.987 \text{ cal deg}^{-1} \text{ mole}^{-1}$

iv) In Joules = $8.314 \text{ J deg}^{-1} \text{ mole}^{-1}$

- Use the value of R depending on the units in which value of pressure and volume has been used in ideal gas equation.

Example 4 : What mass of ammonia will exert same pressure as 12 g of $\text{H}_2\text{S}(\text{g})$ in the same container under the similar conditions of temperature?

Solution: Under identical conditions of T and V , $p \propto n$

\Rightarrow equal moles of ammonia as that of $\text{H}_2\text{S}(\text{g})$ will exert same pressure, when confined in

the same container

\Rightarrow Moles of $\text{H}_2\text{S} = 12/34 = \text{moles of ammonia}$

\Rightarrow Mass of ammonia $= (12/34) \times 17 = 6\text{g}$

Example 5: 4 g of an ideal gas was confined in a 1.0 L flask at 1.0 atm. Increasing temperature of flask by 30°C increases gas pressure by 8%. Determine molar mass of gas.

Solution: Let the initial temperature be, TK.

Since, n and V are constants $P_1/T_1 = P_2/T_2$

$$\Rightarrow \frac{1}{1.08} = \frac{T}{T + 30} \Rightarrow T = 375K$$

Since $pV = nRT$ and $n = w/M$

$$\Rightarrow \frac{4}{M} = \frac{1 \times 1}{0.082 \times 375} \Rightarrow M = 123$$

Relation between Molecular Mass Density

From the ideal gas equation

$$P = \frac{nRT}{V} = \frac{w}{M \times V} RT = \frac{dRT}{M} \quad \therefore$$

$$M = \frac{d}{P} RT$$

M= Molecular mass, P = Pressure, T=Temperature, d= Density

- Vapour Density

$$W(\text{gas}) = \frac{PVM}{RT} \text{ and}$$

$$W_{H_2} = \frac{PV \times 2}{RT} (\because \text{mol. wt. of Hydrogen is 2})$$

$$\therefore \frac{W_{\text{gas}}}{W_{\text{H}_2}} = \frac{M}{2} = \text{Vapour density of gas}$$

$$\Rightarrow \text{Vapour Density} \times 2 = \text{Molecular wt.}$$

\Rightarrow

- **Vapour density of a gas is same at any temperature, pressure and volume.**

Example 6: Determine the density of carbon dioxide gas at the sublimation temperature of -78°C

and 1.0 atm, assuming ideal behaviour of the gas.

Solution: $\rho = \frac{pM}{RT} = \frac{1 \times 44}{0.082 \times 195} = 2.75 \text{ g L}^{-1}$

Example 7: Determine payload of a 1000,000 L balloon filled with He gas at 27°C and 1.0 atm. Composition of air can be considered to be 79% N₂ and 21% O₂ by volume and balloon is massless.

Solution: Moles of gas present in balloon

$$= \frac{pV}{RT} = \frac{1000,000}{0.082 \times 300} = 40650.4$$

$$\text{Payload} = W_{\text{air}} - W_{\text{gas}} = 40650.4 (M_{\text{air}} - M_{\text{He}}) \text{ g}$$

$$= \frac{40650.4}{1000} (28.84 - 4) \text{ kg} = 1009.75 \text{ kg}$$

2.6 Dalton's Law of Partial Pressure

The statement of Dalton's Law is “The total pressure of a mixture of non-reacting gases is equal to the sum of their partial pressures”.

$$p_{\text{total}} = p_1 + p_2 + \dots$$

$$p_1 = \frac{n_1}{n_{\text{total}}} p_{\text{total}} = x_1 p_{\text{total}}$$

$$p_2 = \frac{n_2}{n_{\text{total}}} p_{\text{total}} = x_2 p_{\text{total}}$$

x_1 , x_2 , and so on are the mole fraction of each gas respectively

Partial Pressure of a gas = Mole fraction of the gas \times Total Pressure of the gaseous mixture

- **Dalton's Law of Partial pressure is applicable only for non – reacting gases.**

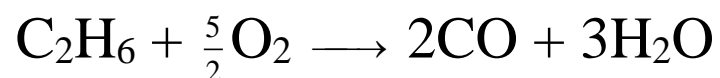
Example 8: Calculate partial pressure of nitrogen and oxygen in air assuming it to be composed of mostly nitrogen and oxygen. Volume percentage of oxygen and nitrogen in air are 20 and 80 respectively, and atmospheric pressure to be 1.0.

Solution: Mole fraction of $\text{N}_2(\text{g}) = 0.8$ and Mole fraction of $\text{O}_2(\text{g}) = 0.2$

Partial pressure of $\text{N}_2(\text{g}) = 0.8 \times 1 = 0.8 \text{ atm}$

Partial pressure of $\text{O}_2(\text{g}) = 0.2 \times 1 = 0.2 \text{ atm}$

Example 9: 0.1 mol of ethane gas and 0.3 mol of oxygen gas are taken in a flask at 27°C and 1.0 atm pressure and sealed. Now the flask is heated to 1000 K where the following reaction occurs quantitatively:



Calculate partial pressure of each component at the end of reaction.

Solution: The balanced chemical reaction (with states specified) is



Moles at start: 0.10 0.3 0 0

Moles at end: 0 0.05 0.2 0.3

Total moles $n_g = 0.55$

Now, applying gas laws at constant volume

$$\frac{p_1}{p_2} = \frac{n_1 T_1}{n_2 T_2} \Rightarrow p_2 = p_1 \left(\frac{n_2 T_2}{n_1 T_1} \right) = 1.0 \left(\frac{0.55 \times 1000}{0.4 \times 300} \right) = 4.58 \text{ atm}$$

$$\Rightarrow p_{\text{O}_2} = \left(\frac{0.05}{0.55} \right) \times 4.58 = 0.416 \text{ atm}$$

$$p_{\text{CO}_2} = \left(\frac{0.2}{0.55} \right) \times 4.58 = 1.664 \text{ atm} \quad \text{and}$$

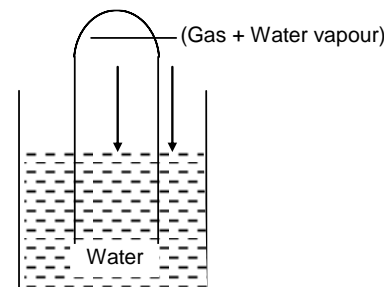
$$p_{\text{H}_2\text{O}} = \left(\frac{0.30}{0.55} \right) \times 4.58 = 2.5 \text{ atm}$$

Partial pressure and aqueous tension

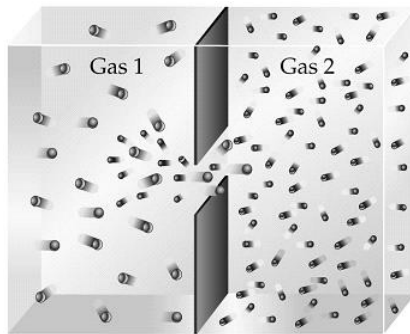
Dalton's law is used to calculate the pressure of a dry gas when it is collected over water at atmospheric pressure. By Dalton's law.

Pressure of dry gas = atmospheric pressure – aqueous tension

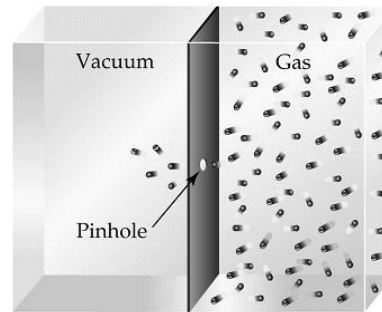
Aqueous tension is partial pressure of water vapour in air and it depends only on temperature. It increases with temperature and becomes 760 mm at 100°C.



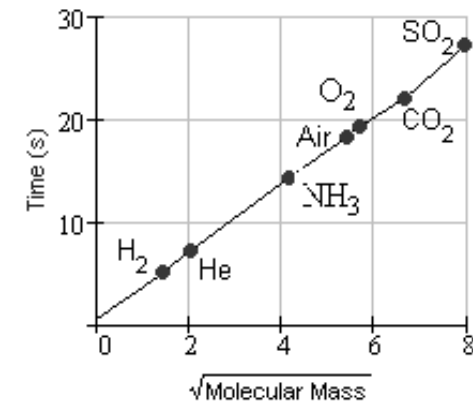
Graham's Law of Diffusion



Diffusion: mixing of gas molecules to a concentration gradient



Effusion: escape of a gas through a pinhole



$$r \propto \sqrt{\frac{1}{M}} \text{ at constant P \& T} \quad \therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \text{ at constant P \& T}$$

$$r_i \propto p_i \text{ and } r_i \propto \frac{1}{\sqrt{M_i}}$$

$\Rightarrow r_i \propto \frac{p_i}{\sqrt{M_i}}$, if rate of effusion is linearly related to its partial pressure.

Under the above conditions, $\frac{r_1}{r_2} = \frac{p_1}{p_2} \sqrt{\frac{M_2}{M_1}}$

- **Rate can be expressed in following terms**

$$r = \frac{\text{Volume diffused (V)}}{\text{time taken}} = \frac{\text{moles diffused(n)}}{\text{time taken}}$$

$$r = \frac{\text{distance travelled in a narrow tube(d)}}{\text{time taken}}$$

Example 10: Rate of effusion of ethane is 1.53 times faster than rate of a hydrocarbon containing 14.27% hydrogen by weight, under identical conditions. Deduce the molecular formula of hydrocarbon.

Solution: $\frac{r(\text{ethane})}{r(\text{hydrocarbon})} = \sqrt{\frac{M}{30}} = 1.53 \quad \Rightarrow \quad M = 70.23$

Empirical formula	C	H
Wt. %	85.73	14.27
Mol %	85.73 / 12	14.27
SR	1	2

Empirical formula = CH_2 ;

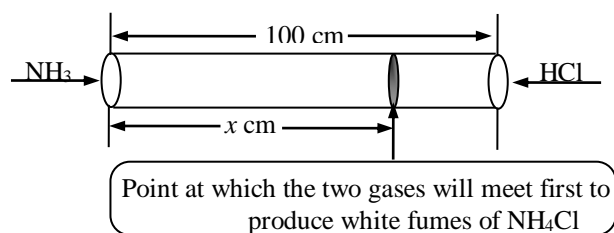
Molecular weight = 70.23

= Empirical formula weight $\times n = 14 n$

$n = 5$; hence, molecular formula of hydrocarbon is C_5H_{10} .

Example 11: Ammonia gas and HCl gas from the two flasks, at same temperature and pressure were injected simultaneously through pinholes of similar geometry, attached at the two ends of a 1.0 m long glass tube. At what distance from the ammonia end, the first flash of white fume would be observed?

Solution:



$$\frac{r_{(\text{NH}_3)}}{r_{(\text{HCl})}} = \frac{x}{100 - x} = \sqrt{\frac{36.5}{17}} \Rightarrow x = 59.43 \text{ cm}$$

Example12 : Diffusion of a certain volume of $N_2(g)$ at 1.0 atm and 300 K, takes 25s, while same volume of an unknown gas of Xenon and Fluorine at 2.0 atm and 300 K takes 34 s for diffusion through the same pinhole. Deduce the molecular formula of the unknown gas.

Solution: $\text{Rate} \propto \frac{1}{\text{time}} \Rightarrow \frac{r_{(N_2)}}{r_{(gas)}} = \frac{34}{25} = \frac{P_{N_2}}{P_{gas}} \sqrt{\frac{M}{28}} = \frac{1}{2} \sqrt{\frac{M}{28}} \Rightarrow M = 207.15$

Since atomic mass of Xe = 131, the gas cannot contain more than one Xe atom per molecule. Hence, the molecular formula of unknown gas could be XeF_n .

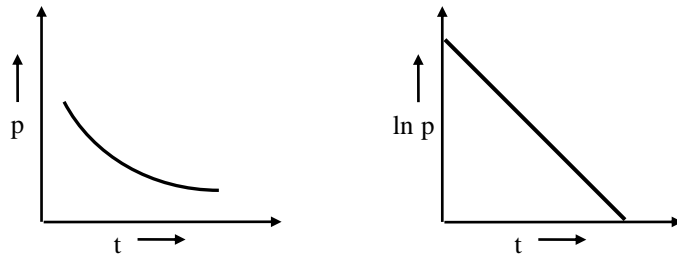
$$\Rightarrow 207.15 = 131 + 19n \Rightarrow n = 4 \text{ and gas is } XeF_4.$$

- **Instantaneous rate of diffusion**

Instantaneous rate of decrease of partial pressure ($-\frac{dp}{dt}$) to be directly proportional to instantaneous gas pressure and inversely proportional to square root of molar mass, instantaneous pressure at any time can be solved as $-\frac{dp}{dt} = \frac{Kp}{\sqrt{M}}$ where K is constant of proportionality,

$$\Rightarrow \int_{p_1}^{p_2} -\frac{dp}{p} = \frac{K}{\sqrt{M}} \int_0^t dt \Rightarrow \ln \left(\frac{p_1}{p_2} \right) = \frac{Kt}{\sqrt{M}} \quad \text{or} \quad p_2 = p_1 \exp \left(-\frac{Kt}{\sqrt{M}} \right)$$

Hence, partial pressure decreases exponentially with time as



Example13: Pressure of nitrogen gas falls from 4000 mm to 2000 mm in 30 min, when allowed to effuse through a pinhole in the cylinder. If the same cylinder is filled with an equimolar mixture of N_2 and He gas at 4000 mm of Hg, what would be the molar ratio of gases (N_2 / He) in the cylinder after 1.0 hour? Assume rate of decrease of pressure as linear function of gas pressure.

Solution: Since, initially equal moles of gases are present, initial partial pressure of both N_2 and He is 2000 mm of Hg. Also

$$-\frac{dP}{dt} = \frac{KP}{\sqrt{M}} \Rightarrow \ln \left(\frac{p_1}{p_2} \right) = \frac{K_1 t}{\sqrt{M}}$$

For $N_2(g)$: $\ln \left(\frac{4000}{2000} \right) = \frac{30K}{\sqrt{28}} \quad \dots (i)$

In mixture: For N_2 :

$$\ln \left(\frac{2000}{p_{(N_2)}} \right) = \frac{60 K}{\sqrt{28}} \quad \dots (ii)$$

For He: $\ln \left(\frac{2000}{p_{(He)}} \right) = \frac{60 K}{\sqrt{4}} \quad \dots (iii)$

Solving Eqs. (i), (ii) and (iii), $p_{N_2} = 500$ mm : $p_{He} = 51$ mm of Hg

Molar ratio after 1.0 hour (N_2 : He) = $p_{(N_2)} : p_{(He)} = 500 : 51$

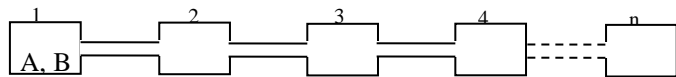
- **Diffusion in case of dissociation or association of gas**

Example 14: Rate of effusion of ethane gas is 1.9 times, the rate of effusion of a partially decomposed Cl_2O_7 (g) mixture. Determine the degree of dissociation of Cl_2O_7 (g).

Solution: $\frac{r_{(\text{C}_2\text{H}_6)}}{r_{\text{mix}}} = \sqrt{\frac{M_{\text{mix}}}{30}} = 1.9 \quad \Rightarrow \quad M_{\text{mix}} = 108.3 = \frac{M(\text{Cl}_2\text{O}_7)}{1 + 3.5 \alpha} = \frac{183}{1 + 3.5 \alpha} \Rightarrow \alpha = 0.197$

- ***Separation of gases using diffusion***

When a gaseous mixture containing lighter and heavier components is allowed to pass through several diffusion chambers connected in series, there occur enrichment of lighter component in each successive step. By carrying out diffusion of a gaseous mixture for a specific number of steps in succession, a specified enrichment of lighter component can be achieved as follows:



$$\Rightarrow \left(\frac{r_A}{r_B} \right)_{n-1} = \left(\frac{n_A}{n_B} \right)_1 \left(\frac{M_B}{M_A} \right)^{\frac{n-1}{2}} = \left(\frac{n_A}{n_B} \right)_n$$

This Equation indicates that after $(n - 1)^{\text{th}}$ step of diffusion a specific enrichment $(n_A/n_B)_n$ can be achieved in the n^{th} chamber.

Example 15: A sample of Ne is originally 10% by mole in Ne^{20} isotope and remaining are Ne^{22} isotope. In how many steps of effusion, 25% enrichment of Ne^{20} can be achieved?

Solution: Initially $\left(\frac{\text{Ne}^{20}}{\text{Ne}^{22}} \right) = \frac{10}{90} = \frac{1}{9}$

Desired ratio : $\left(\frac{\text{Ne}^{20}}{\text{Ne}^{22}} \right) = \frac{25}{75} = \frac{1}{3}$

Applying equation : $\frac{1}{9} \left(\frac{22}{20} \right)^{\frac{n-1}{2}} = \frac{1}{3} \Rightarrow \frac{n-1}{2} \log \left(\frac{22}{20} \right) = \log 3 \Rightarrow n = 24$

2.8 Eudiometry

Eudiometry or “gas analysis”

The various reagents used for absorbing different gases are

$O_3 \longrightarrow$ turpentine oil

$O_2 \longrightarrow$ alkaline pyrogallol

$NO \longrightarrow$ $FeSO_4$ solution

$Cl_2, CO_2, SO_2 \longrightarrow$ alkali solution ($NaOH, KOH, Ca(OH)_2, HOCH_2CH_2NH_2$, etc.)

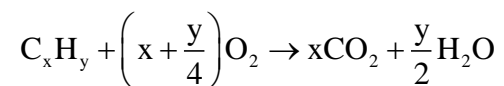
$NH_3 \rightarrow$ Water

$H_2O \rightarrow CuSO_4, CaCl_2$

$CO \rightarrow$ Ammonical Cu_2Cl_2

Example 16: A gaseous hydrocarbon requires 6 times its own volume of O₂ for complete oxidation and produces 4 times its volume of CO₂. What is its formula?

Solution: The balanced equation for combustion



$$1 \text{ vol. } \left(x + \frac{y}{4}\right) \text{ vol. } \therefore x + \frac{y}{4} = 6, \quad \text{or } 4x + y = 24 \dots \dots \dots (1)$$

Again $x = 4$ since evolved CO₂ is 4 times that of hydrocarbon

$\therefore 16 + y = 24$ or $y = 8 \therefore$ formula of hydrocarbon C₄H₈

3. KINETIC THEORY OF GASES

3.1 Postulates of KTG

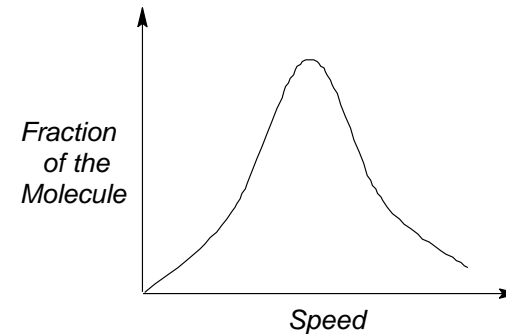
- The volume occupied by the molecules is negligible in comparison to the total volume occupied by the gas (i.e. volume of the container).
- There is no force of attraction or repulsion amongst the molecules, i.e. they are moving independent of one another.
- At any instant, a given molecule can have kinetic energy ranging from a small value to a very large value, but the average kinetic energy remains constant for a given temperature, i.e. the average kinetic energy is proportional to the absolute temperature of the gas.

3.2 Velocity Distribution of Gas molecules

Distribution of molecular speed over a possible range was first investigated by Maxwell using the theory of probability. Results were expressed as the Maxwell law for distribution of molecular speed as

$$dN_u = 4\pi N \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\frac{mu^2}{2RT}} u^2 du$$

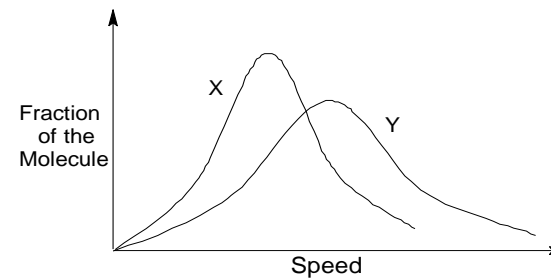
$$= 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mu^2}{2kT}} u^2 du$$



A plot of fraction of molecules in the speed range u and $u + du$, $\frac{1}{N} \left(\frac{dN_u}{du} \right)$ vs u is described in the graph.

The peaks in the curve correspond to a speed, which is possessed by maximum fraction of molecules, called “most probable speed”.

- Some conclusive points for distribution of molecular speeds are :

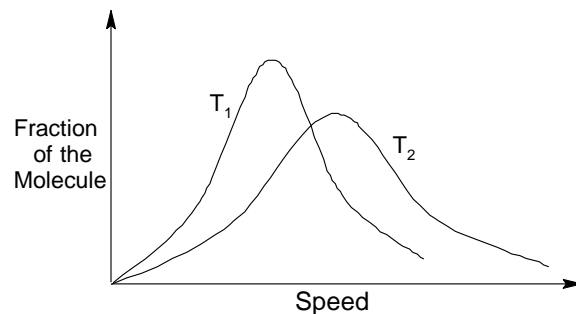


For a given number of mole and temperature but different gas

$(T_2 > T_1)$

The total area under the curve in
of total

Figure is a measure
number of molecules in collection



For a given gas and number of mole but different temperature

$(M_X > M_Y):$

$$\text{Average velocity} = \frac{n_1 u_1 + n_2 u_2 + n_3 u_3 + \dots + n_n u_n}{n}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$U_{rms} = \sqrt{\frac{n_1 u_1^2 + n_2 u_2^2 + n_3 u_3^2 + \dots + n_n u_n^2}{n}}$$

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

$$V_{mp} = \sqrt{\frac{2RT}{M}}$$

$$\text{Furthermore } U_{mp} : U_{av} : U_{rms} :: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$$

$$\text{Also } U_{av} = U_{rms} \times 0.9213$$

- For calculating V_{rms} , V_{mp} , or V_{av} by above relations the value of M should be used in kg/mole and R should be taken as 8.314 J/K mole to get velocity in m/s.

Example 17: Derive an expression relating to increase in U_{rms} of a gas for a relatively small temperature rise and calculate increase in u_{rms} for a sample of Ne(g) as the temperature is increased from 100 K to 101 K?

Solution: $u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \frac{du_{\text{rms}}}{dT} = \sqrt{\frac{3R}{M}} \frac{1}{2\sqrt{T}} = \frac{3R}{2M} \times \frac{1}{\sqrt{\frac{3RT}{M}}} = \frac{3R}{2Mu_{\text{rms}}}$

$$\Rightarrow du_{\text{rms}} = \frac{3R}{2Mu_{\text{rms}}} dT \Rightarrow \Delta u_{\text{rms}} = \frac{3R}{2Mu_{\text{rms}}} \Delta T$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 100}{20 \times 10^{-3}}} = 353 \text{ ms}^{-1}$$

$$\Delta u_{\text{rms}} = \frac{3 \times 8.134}{2 \times 20 \times 10^{-3} \times 353} \times (101 - 100) = 1.766 \text{ ms}^{-1}$$

3.3 Kinetic interpretation of Pressure

$$p = \frac{mN}{V} \left(\frac{1}{3} \overline{u^2} \right) \quad \text{or} \quad pV = \frac{1}{3} mN \overline{u^2}$$

From Maxwell distribution we already know $\overline{u^2} = \frac{3RT}{M}$

$$\text{So} \quad pV = \frac{1}{3} mN \times \frac{3RT}{M} = nM \times \frac{RT}{M} = nRT \quad \Rightarrow \quad pV = nRT$$

- Average Translational kinetic energy per molecule $= \frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} Kt$
- Average Translational Kinetic energy per mole $= N_A \times \frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} RT$
- $k(\text{Boltzmann constant}) = R/N_A = 1.38 \times 10^{-23} \text{ JK}^{-1}$

Example 18: Calculate the pressure exerted by 10^{25} gas molecules each of mass 10^{-22} g in a container of volume 1.0 dm^3 . The root mean square speed is 10^5 cm s^{-1} .

Solution: $pV = \frac{1}{3} mN\bar{u}^2 \Rightarrow p = \frac{1}{3} \times 10^{-25} \text{ kg} \times 10^{25} \times (10^3 \text{ ms}^{-1})^2 \times \frac{1}{10^{-3} \text{ m}^3} \Rightarrow \frac{1}{3} \times 10^9 \text{ Pa}$

Example 19: A two litre bulb contains 3×10^{23} gas molecules and exert 10^6 Pa pressure. Calculate translational energy per molecule and total translational energy.

Solution: $pV = nRT \Rightarrow T = \frac{pV}{nR} = \frac{10^6 \times 2 \times 10^{-3} \times 6.022 \times 10^{23}}{3 \times 10^{23} \times 8.314} = 483 \text{ K}$

$$\Rightarrow E_{\text{trans}} = \frac{3}{2} k_b T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 483 = 10^{-20} \text{ J / molecule}$$

$$E_{\text{trans}} (\text{Total}) = \frac{3}{2} k_b TN = 3000.25 \text{ J}$$

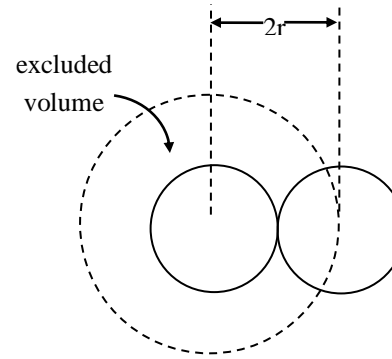
4. REAL GASES

The ideal gas laws are derived from the kinetic theory of gases which is based on the following two important assumptions:

- (i) The volume occupied by the molecules is negligible in comparison to the total volume of the gas.
- (ii) The molecules exert no forces of attraction upon one another.

It is because neither of these assumptions can be regarded as applicable to real gases that the real gases show departure from the ideal behaviour.

4.1 Van der waal Equation



• Volume Correction

$V = V_{\text{container}} - nb$ as shown in Fig

Thus excluded volume per pair of molecules $\frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$

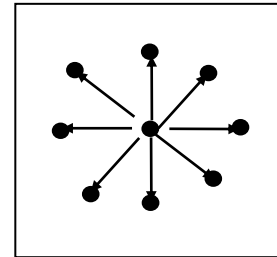
Excluded volume per molecule $= \frac{1}{2}\left[8\left(\frac{4}{3}\pi r^3\right)\right] = 4\left(\frac{4}{3}\pi r^3\right) = 4 \text{ (volume occupied by a molecule)}$

Since b represents excluded volume per mole of the gas, it is obvious that

$$b = N_A \left[4 \left(\frac{4}{3} \pi r^3 \right) \right]$$

• Pressure Correction

$$p_i = p_r + \text{correction term}$$



This correction term depends upon two factors:

(i) the number of molecules per unit volume of the container is given as

$$N' = \frac{nN_A}{V} \quad \text{or} \quad N' \propto \frac{n}{V}$$

(ii) the number of molecules striking the side of vessel in a unit time also depends upon the number of molecules present in unit volume of the container, and hence in the

present case: $N' \propto \frac{n}{V}$

Taking both these factors together, we have

$$\text{Correction term} \propto \left(\frac{n}{V}\right) \left(\frac{n}{V}\right) \quad \text{or} \quad \text{Correction term} \propto \frac{n^2}{V^2} \Rightarrow \text{correction term} = a \frac{n^2}{V^2}$$

Where a is the proportionality constant and is a measure of the forces of attraction between the molecules.

$$\text{Thus} \quad p_i = p_r + a \frac{n^2}{V^2}$$

When these expressions are substituted in the ideal gas equation $p_i V_i = nRT$, we get

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

This equation is applicable to real gases and is known as the **Van der Waals** equation.

- **The constants a & b: Van der Waals constant for attraction (a) and excluded volume (b) are characteristic for a given gas. Some salient features of a & b are:**

- i) For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of excluded volume (b).
- ii) The gas having higher value of 'a' can be liquefied easily and therefore H_2 & He are not liquefied easily.
- iii) The units of $a = \text{litre}^2 \text{ atm mole}^{-2}$ & that of $b = \text{litre mole}^{-1}$
- iv) The numerical values of a & b are in the order of 10^{-1} to 10^{-2} & 10^{-2} to 10^{-4} respectively.

v) Volume correction factor, depends on molecular size and larger molecule will have larger b .

For example, size of He, CH₄, CF₄, C₄H₁₀ are in order of He < CH₄ < CF₄ < C₄H₁₀ and same will be the order of b .

vi) Pressure correction factor ($\frac{n^2a}{V^2}$) depends on intermolecular force of attraction. Hence, larger the intermolecular force of attraction larger the value of 'a', for same n and V . For example, intermolecular force of attraction among the molecules H₂, CO₂, NH₃ are in order of

H₂ < CO₂ < NH₃ (H-bonding) thus same is the order of a .

4.2 Compressibility Factor

$$Z = \frac{V_m}{V_{m,ideal}} = \frac{p}{RT} V_m$$

For an ideal gas $Z=1$ and is independent of pressure and temperature.

For a real gas, $Z = (T, p)$, is a function of both temperature and pressure.

i) At low pressures: 'V' is large and 'b' is negligible in comparison with V. The Vander Waals equation reduces to:

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

$$PV = RT - \frac{a}{V} \text{ or } PV < RT$$

This accounts for the dip in PV vs P isotherm at low pressures.

ii) At fairly high pressures $\frac{a}{V^2}$ may be neglected in comparison with P. The Vander

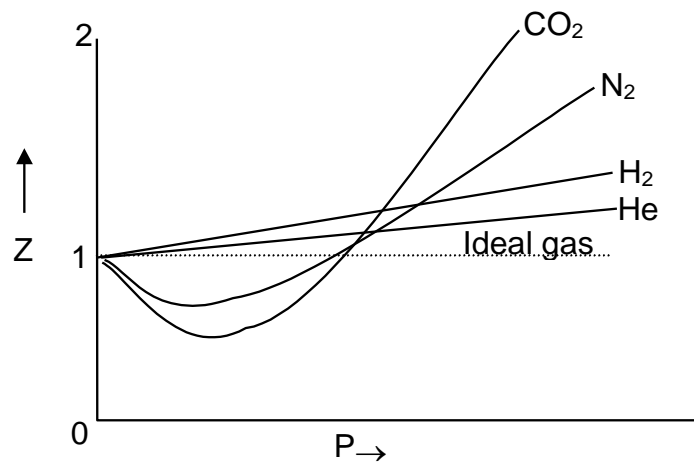
Waals equation becomes

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

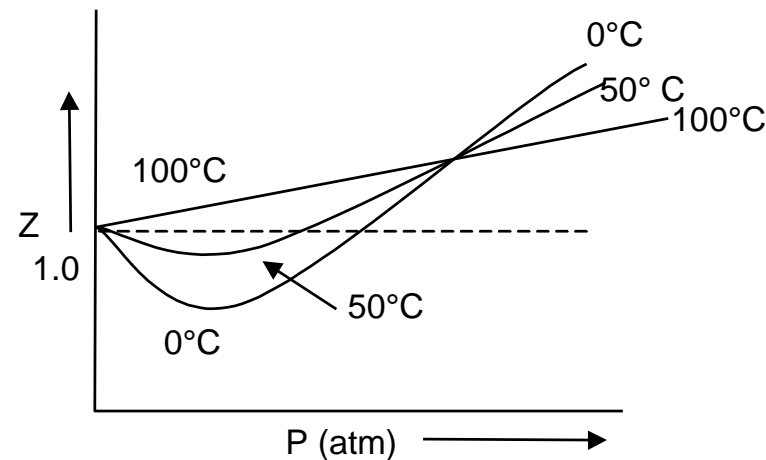
$$PV - Pb = RT$$

iii) At very low pressures: V becomes so large that both b and $\frac{a}{V^2}$ become negligible and the Vander Waals equation reduces to $PV = RT$. This shows why gases approach ideal behaviour at very low pressures.

- iv) Hydrogen and Helium: These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So $\frac{a}{V^2}$ is negligible even at ordinary temperatures. Thus $PV > RT$.



(Deviation of gases from ideal temperature is behaviour with pressure.)



The plot of Z vs P for N₂ gas at different shown here.

Example20: The density of steam at 100°C and 1.0 atm pressure is 0.5974 kg m⁻³.
Determine compressibility factor for steam in the given condition.

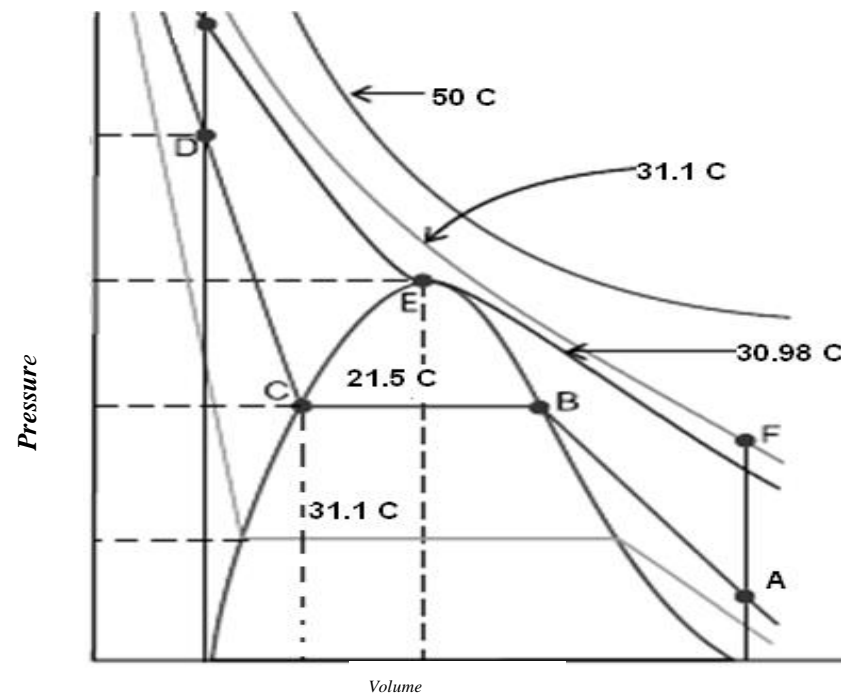
Solution Since $Z = V_{m,\text{real}}/V_{m,\text{ideal}} = \rho_{\text{ideal}}/\rho_{\text{real}}$

$$Z = \frac{pM}{\rho RT} = \frac{1 \times 18}{0.5974 \times 0.082 \times 373} = 0.985$$

4.3 Liquefaction of Gases

First complete data on pressure - volume -temperature relations of a substance in both gaseous and liquid state was obtained by **Thomas Andrews** on carbon dioxide.

At 30.98 °C carbon dioxide remains gas upto 73 atm pressures. The temperature 30.98 °C is called **critical temperature** (T_c) of carbon dioxide.



At critical point horizontal portion of the isotherm merges into one point.

$$\text{So at point E} \quad \left(\frac{\partial P}{\partial V} \right)_{T_c} = 0 \text{ and } \left(\frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0$$

.

$$\left(\frac{\partial p}{\partial V} \right)_T = 0 \text{ and the condition that this slope has a maximum value of } \frac{\partial}{\partial V} \left\{ \left(\frac{\partial p}{\partial V} \right)_T \right\}_T = 0$$

$$V_c = 3b, \quad T_c = \frac{8a}{27Rb}$$

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{R(8a/27Rb)}{(3b - b)} - \frac{a}{(3b)^2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

4.4 Virial equation

All real gas equations of state can be expressed approximately in one common form, called the Virial equation of state which has the following form for 1 mole of a gas.

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

where B, C, are temperature dependent constants known as second, third, etc., virial coefficients. These coefficients must be evaluated experimentally at each different temperature.

$$Z = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{V_m} + \left(\frac{b}{V_m} \right)^2 + \dots$$

Thus for the second virial coefficient, we have

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

Third virial coefficient $C = b^2$, and so on.

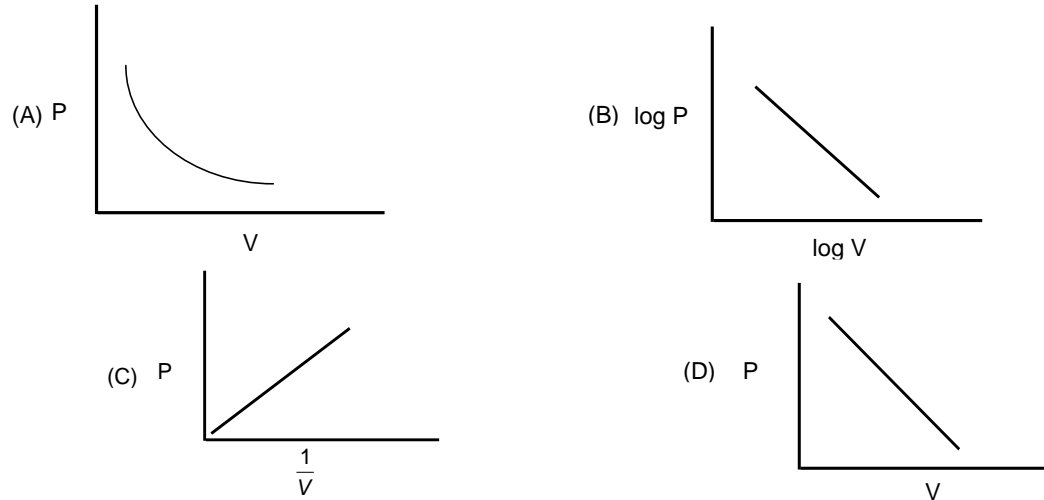
An alternate form of the virial equation of state involves the expression of Z in terms of a power series in p , i.e. $Z = 1 + A_1p + A_2p^2 + \dots$

- **BOYLE'S TEMPERATURE**

$$T = \frac{a}{Rb} = \text{Boyle's temperature (T}_B\text{)}$$

Boyle temperature is that temperature at which a real gas behaves like an ideal gas for a range of pressure.

QUE 1 Which of the following curve does not represent Boyle's law?



Solution: $P = \frac{C}{V}$ Where C is a constant. We can see that (c) is true as the graph of P vs $\frac{1}{V}$ would be a straight line.

(B) is true because $\log P = \log C - \log V$.

(A) is true because $\frac{dP}{dV} = \frac{-C}{V^2}$

which means that as V increases the slope decreases and is always negative \therefore (D)

QUE 2 Boyle's law may be expressed as

(A) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V}$ (B) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V^2}$ (C) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V}$ (D) none

Solution: from Boyle's law; $PV = \text{constant}$; $PdV + VdP = 0$; $\left(\frac{dP}{dV}\right)_T = -\frac{P}{V} = -\frac{K}{V^2}$

Thus $(PV = K) \therefore$ **(B)**

QUE 3 A commercial gas cylinder contains 75 L of He at 15 bar (Gauge pressure). Assuming ideal gas behavior for the isothermal expansion, how many 3.0 L balloons at 1.1 bar pressure can be filled by the gas in the cylinder?

(A) 338 (B) 430 (C) 403 (D) 304

Solution: Assuming atmospheric pressure to be one bar, initial pressure and final pressure of He gas present in cylinder will be:

$$p_i = 15 + 1 = 16 \text{ bar and } p_f = 1.1 \text{ bar}$$

$$\text{Volume of He gas when expanded isothermally to 1.1 bar} = \frac{16 \times 75}{1.1} = 1090.9 \text{ L}$$

Out of 1090.9L, 75 L of gas will remain in cylinder since this point pressure equilibrium will be established.

$$\Rightarrow \text{Numbers of balloons} = \frac{1090.9 - 75}{3} = 338$$

Thus (A)

QUE 4 A vessel has N_2 gas saturated with water vapor at a total pressure of 1 atm. The partial pressure of water vapour is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, at the same temperature the total pressure of this system in the new vessel is

- (A) 3.0 atm (B) 1 atm (C) 3.33 atm (D) 2.4 atm

Solution: $P'_{N_2} + P'_{H_2O} = 1 \text{ atm}$ $P'_{H_2O} = 0.3 \text{ atm}$ $P'_{N_2} = 0.7 \text{ atm}$

Now new pressure of N_2 in another vessel of volume $V/3$ at same temperature T is given by

$$\therefore P''_{N_2} \times \frac{V_1}{3} = 0.7V \quad P''_{N_2} = 2.1 \text{ atm}$$

since aqueous tension remains constant, and thus total pressure in new vessel

$$= P''_{N_2} + P'_{H_2O} = 2.1 + 0.3 = 2.4 \text{ atm} \therefore \text{(D)}$$

QUE 5 X ml of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is :

(A) 10 seconds : He

(B) 20 seconds : O_2

(C) 25 seconds : CO

(D) 35 seconds : CO_2

Solution: $\frac{r_{H_2}}{r_{He}} = \sqrt{\frac{4}{2}} = \sqrt{2}$ \therefore (A) is incorrect ; $\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{32}{2}} = 4$ (B) is correct

$\frac{r_{H_2}}{r_{CO}} = \sqrt{\frac{28}{2}} = \sqrt{14}$ (C) is incorrect ; $\frac{r_{H_2}}{r_{CO_2}} = \sqrt{\frac{2}{44}} = \sqrt{\frac{1}{22}}$ (D) is incorrect \therefore (B)

QUE 6 In what molar ratio He and CH₄ should be mixed so that when the mixture is allowed to effuse through a pinhole, initially both gases come out at equal rate?

- (A) 2:1 (B) 1:1
(C) 2:3 (D) 4:1

Solution: Since, rate of effusion $(r) = \frac{n}{\sqrt{M}}$ from a mixture.

$$\frac{r(\text{He})}{r(\text{CH}_4)} = \frac{n(\text{He})}{n(\text{CH}_4)} \sqrt{\frac{16}{4}} = 1.0 \quad \Rightarrow \quad n_{\text{CH}_4} : n_{\text{He}} = 2 : 1 \quad \therefore \text{(A)}$$

QUE 7 Dalton's law of partial pressure is not applicable to, at normal conditions

- (A) H_2 and N_2 mixture (B) H_2 and Cl_2 mixture
(C) H_2 and CO_2 mixture (D) H_2 and O_2 mixture

Solution: H_2 and Cl_2 reacts to form HCl ; Dalton's law of partial pressure is valid only for the gases which don't react at ordinary conditions \therefore (B)

QUE 8 For two gases A and B with molecular weights M_A and M_B , it is observed that at a certain temperature T_1 the mean velocity of A is equal to the root mean square velocity of B. thus the mean velocity of A can be made equal to the mean velocity of B if

- (A) A is at temperature T and B at T' , $T > T'$
- (B) A is lowered to a temperature T_2 , $T_2 < T$ while B is at T
- (C) Both A and B are raised to a higher temperature
- (D) Both A and B are placed at lower temperature

Solution: $(U_{AV})_A = \sqrt{\frac{8RT}{\pi M_A}}$ and $(U_{rms})_B = \sqrt{\frac{3RT}{M_B}} \quad \therefore \quad \frac{8}{3\pi} = \frac{M_A}{M_B}$

for A $(U_{AV}) = \sqrt{\frac{8RT_2}{\pi M_A}}$ for B $(U_{AV}) = \sqrt{\frac{8RT}{\pi M_B}}$

$$\frac{T_2}{T} = \frac{M_A}{M_B} = \frac{8}{3\pi}$$

$$\therefore T_2 = \frac{8}{3\pi} T \text{ or}$$

$$T_2 < T \quad \therefore \text{ (B)}$$

QUE 9 The K.E. of N molecule of O_2 is x Joules at -123°C . Another sample of O_2 at 27°C has a KE of $2x$ Joules. The latter sample contains.

- (A) N molecules of O_2 (B) $2N$ molecules of O_2
 (C) $N/2$ molecules of O_2 (D) $N/4$ molecule of O_2

Solution: Total KE = $\frac{3}{2}nRT$; $T = -123 + 273 = +150\text{ K}$; $\frac{3}{2} \times nR \times 150 = xJ$

$$\Rightarrow 225 \times 8.314 \times n = x$$

$$\text{At } 27^\circ\text{C} = 27 + 273 = 300\text{K}$$

$$\text{Total KE} = 2x \text{ Joule} = \frac{3}{2} \times n_1 \times 8.314 \times 300 \quad \Rightarrow n_1 = n \quad \therefore \text{(A)}$$

QUE 10 If for two gases of molecular weights M_A and M_B at temperature T_A and T_B , $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases.

- (A) density (B) pressure (C) KE per mol (D) V_{rms}

Solution: i) density of a gas $(\rho) = \frac{PM}{RT}$

Since $\frac{M_B}{T_B} = \frac{M_A}{T_A}$, \therefore at the same pressure $\rho_A = \rho_B$. But if pressure is different then $\rho_A \neq \rho_B$.

ii) Pressure of the gases would be equal if their densities are equal otherwise not.

iii) KE per mol $= \frac{3}{2}RT$

\therefore It will be different for the two gases.

iv) $V_{\text{rms}} = \sqrt{\frac{3RT}{M}}$, since $\frac{T_A}{M_A} = \frac{T_B}{M_B}$; V_{rms} of A = V_{rms} of B \therefore (D)

QUE 11 Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a Helium atom is

- (A) two times that of hydrogen molecule (B) same as that of a hydrogen molecule
(C) four times that of a hydrogen molecule (D) half that of a hydrogen molecule

Solution: The average kinetic energy of an atom is given as $\frac{3}{2} kT$.

\therefore It does not depend on mass of the atom. \therefore (B)

QUE 12 The ratio between the rms velocity of H_2 at 50 K and that of O_2 at 800 K is
(A) 4 (B) 2 (C) 1 (D) 1/4 [IIT-JEE '96]

Solution: $V_{\text{rms}} (H_2 \text{ at } 50 \text{ K}) = \sqrt{\frac{3R \times 50}{2 \times 10^{-3}}}$; $V_{\text{rms}} (O_2 \text{ at } 800\text{K}) = \sqrt{\frac{3R \times 800}{32 \times 10^{-3}}}$

$$\frac{V_{\text{rms}} (H_2)}{V_{\text{rms}} (O_2)} = \frac{\sqrt{\frac{3R \times 50}{2 \times 10^{-3}}}}{\sqrt{\frac{3R \times 800}{32 \times 10^{-3}}}} = \frac{\sqrt{25 \times 10^3}}{\sqrt{25 \times 10^3}} = 1 \quad \therefore \text{(C)}$$

QUE 13 The temperature of an ideal gas is increased from 140 K to 560 K. If at 140 K the root mean square velocity of the gas molecule is V , at 560 K it becomes

- (A) $5V$ (B) $2V$ (C) $V/2$ (D) $V/4$

Solution: The V_{rms} at 140K is V

$$\therefore V = \sqrt{\frac{3R \times 140}{M}}$$

$$\text{At 540 K, } V' = \sqrt{\frac{3R \times 560}{M}} = \sqrt{\frac{3R \times 140 \times 4}{M}} = 2\sqrt{\frac{3R \times 140}{M}} = 2V$$

\therefore (B)

QUE 14 At 100°C and 1 atm, if the density of liquid water is 1.0 g/cc and that of water vapour is 0.0006 g/cc, then the volume occupied by water molecule in one litre of steam at that temperature is
(A) 6 cc (B) 60 cc (C) 0.6 cc (D) 0.06 cc

Solution: Mass of 1 lt water vapour = $V \times d = 1000 \times 0.0006 = 0.6\text{g}$
 \therefore volume of liquid water = $\frac{0.6}{1} = 0.6\text{cc} \therefore$ (C)

QUE 15 A gas can be liquefied by pressure alone when its temperature is
(A) higher than its critical temperature (B) lower than its critical temperature
(C) either of these (D) none

Solution: A gas can be liquefied only if its temperature is lower than its critical temperature
 \therefore (B)

QUE 16 The behavior of a real gas is usually depicted by plotting compressibility factor Z versus P at a constant temperature. At high temperature and high pressure, Z is usually more than one. This fact can be explained by van der Waals equation when

- (A) the constant 'a' is negligible and not 'b'
- (B) the constant 'b' is negligible and not 'a'
- (C) both constants 'a' & 'b' are negligible
- (D) both the constants 'a' & 'b' are not negligible.

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

At high pressures, 'b' cannot be ignored as the volume of the gas is very low. At high temperatures 'a' can be ignored

$$\therefore P(V - b) = RT \quad ; \quad PV - Pb = RT$$

$$PV = RT + Pb \quad ; \quad \frac{PV}{RT} = Z = 1 + \frac{Pb}{RT} \quad \therefore \text{(A)}$$

QUE 17 The compressibility factor for a given gas is 0.927 at 273 K and 100 atm.

Calculate the amount of gas required to fill a gas cylinder of 100 liter capacity under given conditions. (Molecular wt of gas is 30

(A) 16.4 Kg (B) 14.44 Kg (C) 4 Kg (D) 10.5 Kg

Solution Since for real gas $PV = Z nRT$

$$\Rightarrow 100 \times 100 = 0.927 \times w/30 \times 0.0821 \times 273$$

$$\Rightarrow W = 14.439 \text{ Kg} \therefore \text{(B)}$$

QUE 18 Using van der waal's equation, calculate the constant, 'a' (atm Ltr² mole⁻²) when two moles of a gas confined in a four litre flask exerts a pressure of 11 atm at a temperature of 300 K. The value of 'b' is 0.05 Litre mole⁻¹

- (A) 6.5 (B) 2.23 (C) 23.2 (D) .85

Solution Vander waal's gas equation is

$$(P + n^2a/V^2)(V-nb) = nRT$$

Since V =4 litre, P = 11 atm, T = 300K, b = 0.05 litre mol⁻¹, n = 2

$$\text{Thus } (11 + 2^2a/4^2)(4 - 2 \times 0.05) = 2 \times 0.082 \times 300$$

$$\Rightarrow a = 6.5 \text{ atm litre}^2 \text{ mol}^{-2} \therefore \text{(A)}$$