GASEOUS STATE

Introduction :

Matter as we know broadly exists in three states.

There are always two opposite tendencies between particles of matter which determine the state of matter

- Inter molecular attractive forces.
- The molecular motion / random motion.



In this chapter the properties and behaviours of the gases will be analysed and discussed in detail. These properties are measured with the help of the gas laws as proposed Boyle, Charles, Gay lussac etc

There are in total eleven elements in the periodic table which exist as gases under normal conditions.



Fig. : Eleven elements that exist as gases

Following are the few physical properties of gaseous state :

- (i) The volume and shape of gases is not fixed. These assume the volume and shape of the container.
- (ii) The thermal energy of gases >> molecular attraction.
- (iii) Gases have infinite expansibility and high compressibility.
- (iv) Gases exert pressure equally in all directions
- (v) Gases have much lower density than the solids and liquids due to negligible intermolecular forces.
- (vi) Gas mix evenly with other gases or their mixtures are homogeneous in composition.

Boyle's law and measurement of pressure :

Statement :

For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

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

hence PV = const

this constant will be dependent on the amount of the gas and temperature of the gas.



Applications of Boyles Law. For the two points 'A' and 'B' $P_1V_1 = K \& P_2V_2 = K$ hence it follows that $P_1V_1 = P_2V_2$.

Physical significance of Boyle's law: As discussed before, on increasing pressure, the density of the air increases at constant temperature. This indicates that gases are compressible. Same effect can be seen in the daily life. Air is denser at the sea level and as the altitude increases air pressure decreases, which means air now becomes less denser. So, less oxygen molecules occupy the same volume. Therefore oxygen in air becomes insufficient for normal breathing, out of the result altitude sickness occurs with symptoms like headache, uneasiness. That is why mountaineers have to carry oxygen cylinders with them in case of emergencey to restore normal breathing.

Volume	Pressure	Temperature
Volume of the gas is the Volume of the container	Pressure = N/m ² = Pa \rightarrow S.I. unit C.G.S unit = dyne-cm ²	Kelvin scale \rightarrow Boiling point = 373 K ice point = 273 K
S.I. unit $\rightarrow m^3$	Convert 1N/m ² into dyne/cm ²	Farenheit scale \rightarrow B.P. = 212° F ice point = 32° F
C.G.S. unit →cm³	$\frac{1}{1} \frac{N}{m^2} = \frac{10^5}{10^4} \frac{dyne}{cm^2}$	Celcius scale \rightarrow B.P. = 100°C
1 ℓ = 10 ⁻³ m ³	1N/m ² = 10 dyne/cm ²	ice point = 0°C
$1 \ \ell = 10^3 \ cm^9$		$\frac{C-0}{100-0} = \frac{K-273}{373-273} = \frac{F-32}{212-32}$
$1 dm^3 = 1 \ \ell = 10^{-3} \ m^3$	1 atm = 1.013 × 10 ⁵ N/m ²	
$1 \text{ml} = 10^{-3} \ell = 1 \text{cm}^3 = 1 \text{cc}$	1 bar = 1 × 10 ⁵ N/m ²	$= \frac{R - R(0)}{R(100) - R(0)}$
	1 atm = 760 mm of Hg = 760 torr.	where R = Temp. on unknown scale.

<u>Units</u>

Atmospheric pressure :

The pressure exerted by atomosphere on earth's surface at sea level is called 1 atm.

1 atm = 1.013 bar

1 atm = $1.013 \times 10^5 \text{ N/m}^2 = 1.013 \text{ bar} = 760 \text{ torr}$

Solved Examples -

Ex.1 103 mL of carbon dioxide were collected at 27°C and 763 mm pressure. What will be its volume if the pressure is changed to 721 mm at the same temperature ?

Sol. Given

Conditions

V₁ = 103 mL

P₁ = 763 mm

Final Conditions $V_2 = ? mL$ $P_2 = 721 mm$

By applying Boyle's Law since temperature is constant,

 $P_2 \times V_2 = P_1 \times V_1$

Substituting the corresponding values, we have

$$721 \times V_2 = 763 \times 103 \quad \Rightarrow \quad V_2 = \frac{763 \times 103}{721} = 109 \text{ mL}$$

... Volume of carbon dioxide = 109 mL

Charles law :

For a fixed amount of gas at constant pressure volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.



Relation : T = t + 273

- Since volume is proportional to absolute temperature. The volume of a gas should be theoretically zero at absolute zero temperature.
- Infact no substance exists as gas at a temperature near absolute zero, though the straight line plots can be extrapolated to zero volume. Absolute zero can never be attained practically though it can be approch only.
- By considering –273.15°C as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

Isobars : The curves of volume temperature graph at different fixed pressures are called isobars. **Physical significance of Charle's Law :** Hot air balloon technology is based on Charles Law. On increase in temperature air expands. So, density of air decreases. The hot air in the balloon is less dense and lighter than the atmospheric air. Therefore the balloons filled with hot air rise up for meteorological observations.

Ex.2 If the temp. of a particular amount of gas is increased from 27°C to 57°C, find final volume of the gas, if initial volume = 1 It and assume pressure is constant.

Sol. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ \Rightarrow $\frac{1}{(273+27)} = \frac{V_2}{(273+57)}$ So $V_2 = 1.1$ lt.

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

Sol. $T_1 = 300 \text{ K}$

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

Hence applying charles law :

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

Now, this volume ' ΔV ' which escapes trans the container get cooled

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

Solve the two equations and get the value of ΔV an a t.

Determine Δv & calculate t that will be the answer.

Gay-lussac's law :

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

P
$$\alpha$$
 T
 $\frac{P}{T}$ = constant \rightarrow dependent on amount and volume of gas
 $\frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow$ temp on absolute scale

originally, the law was developed on the centigrade scale, where it was found that pressure is a linear function of temperature $P = P_0 + bt$ where 'b' is a constant and P_0 is pressure at zero degree centigrade.



Isochores : The lines showing the pressure temperature behaviour plotted at fixed volumes are called isochores.

Physical Significance of Gay Lussac's Law : It is seen that the pressure of the inflated tyres of automobiles is constant but in summers on a hot sunny day when the temperature is high, then the pressure inside the tyres increases, and they may burst. Similarly in winters, on a cold morning, when the temperature is low, then the pressure inside the tyres decreases considerably.

Ex.4 The temperature of a certain mass of a gas is doubled. If the initially the gas is at 1 atm pressure. Find the % increase in pressure ?

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

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

- **Ex.5** The temperature of a certain mass of a gas was increased from 27°C to 37°C at constant volume. What will be the pressure of the gas.
- **Sol.** $\frac{P_1}{T_1} = \frac{P_2}{T_2}$; $\frac{P}{300} = \frac{P_2}{310}$; $P_2 = \frac{31}{30}$ P

Avogadro's Hypothesis :

For similar values of pressure & temperature equal number of molecules of different gases will occupy equal volume.

 $N_1 \longrightarrow V$ (volume of N_1 molecules at P & T of one gas)

 $N_1 \longrightarrow V$ (volume of N_1 molecules at P & T of second gas)

Molar volume or volume occupied by one mole of each and every gas under similar conditions will be equal.

One mole of any gas or a combination of gases occupies 22.413996 L of volume at STP.

The previous standarad is still often used, and applies to all chemistry data more than decade old, in this definition Standard Temperature and Pressure STP denotes the same temperature of 0°C (273.15K), but a slightly higher pressure of 1 atm (101.325 kPa).

Standard Ambient Temperature and Pressure (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 k and 1 bar (i.e. exactly 10⁵ Pa) At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol⁻¹

Equation of State :

Combining all the gas relations in a single expression which discribes relationship between pressure, volume and temperature, of a given mass of gas we get an expression known as equation of state.

$$\frac{PV}{T} = \text{constant (dependent on moles of the gas n).}$$
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Ideal gas Equation :

PV = nRT

This is the ideal gas equation as it is obeyed by the hypothetical gases called ideal gases under all conditions of temperature and pressure.

However there is no gas that is perfectly ideal. But the gases may show nearly ideal behaviour under the conditions of low pressure and high temperature and are called real gases.

$$\frac{PV}{nT} = constant$$
 [universal constant]
= R (ideal gas constant or universal gas constant)

experimentally R = 8.314 J/Kmole \approx 25/3 = 1.987 cal/mole ≈ 2 = 0.08 Latm/mole $\approx 1/12$ Density and molar Mass of a Gaseous Substance : Ideal gas equation is PV = nRT....(i) On rearranging the above equation, we get(ii) $\overline{V}^{=}\overline{RT}$ Putting the value of 'n' from equation (iii) in equation (ii), we get m(iv) MV RT Replacing $\frac{m}{v}$ in eq. (iv) with d (density) $\frac{d}{M} = \frac{P}{RT}$ Rarranging the above equation, we get $M = \frac{dRT}{R}$

Sol.

Ex.6 At 27°C and one atmosphere pressure, a gas volume V. What will be its volume at 177°C and a pressure of 1.5 atmosphere ?

Given conditions	Final conditions
$V_1 = V$	V ₂ = ?
$P_1 = 1 \text{ atm}$	$P_{2} = 1.5 \text{ atm}$
T ₁ = 273 + 27 = 300 K	T ₂ = 273 + 177 = 450 K
Applying gas equation, we have	
$\frac{1 \times V}{300} = \frac{1.5 \times V_2}{450}$	
$\therefore \qquad V_2 = \frac{1 \times V \times 450}{300 \times 1.5} = V$	\therefore Volume of the gas = V

- **Ex.7** The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing as ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure if the temperature remains same.
- **Sol.** After the opening of the stop cock the pressure of the each bulb will remain same.



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

 \therefore Pressure after the opening of the stop cock

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

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 :

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

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.

$$P_{Total} = P_1 + P_2 + P_3 = \frac{(n_1 + n_2 + n_3)RT}{V}$$

 $\frac{P_1}{P_T} = \frac{n_1}{n_T} = x_1$ (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)

Application

(i) Jet aeroplane flying at high altitude need pressurization of cabins so as to make partial pressure of oxygen sufficient for breathing, as the air pressure decreases with increase in altitude.

(ii) Calculation of the pressure of dry gas collected over water : When the gas is collected over water it is moist because of the water vapours. Saturated water vapour exert its own partial pressure called from the pressure of moist gas (P_{moist} gas or P_{total})

 $P_{drygas} = P_{total} - Aqueous tension$

Ex.8 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.

$$P_{N_2} = \left(\frac{n_{N_2}}{n_T}\right) \times P_T = \frac{55}{100} \times 760 = 418 \text{ torr.}$$
$$P_{O_2} = \left(\frac{n_{O_2}}{n_T}\right) \times P_T = \frac{25}{100} \times 760 = 190 \text{ torr.}$$
$$P_{CO_2} = (760 - 418 - 190) = 152 \text{ torr.}$$

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 =
$$\frac{\text{density of gas at T&P}}{\text{density of H}_2 \text{ under same P & T}}$$

 $P = \frac{m}{V} \cdot \frac{RT}{M} \implies P = \rho \frac{RT}{M} \implies \rho = \frac{PM}{RT}$
Vapour density = $\frac{PM_{gas}RT}{RT PM_{H_2}} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2}$
 $M_{gas} = 2 \times \text{vapour density}$

Average molecular mass of gaseous mixture :

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

_ Total mass of mixture

 $M_{mix} = \frac{1}{\text{Total no. of moles in mixture}}$

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.

$$M_{min} = \frac{n_1 + n_2 + n_3 + n_3}{n_1 + n_2 + n_3}$$

- **Ex.9** Calculate the mean molar mass of a mixture of gases having 7 g of Nitrogen, 22 g of CO₂ and 5.6 litres of CO at STP.
- Sol. Moles of N₂ = 7/28 = 1/4 Moles of CO₂ = 22/44 = 1/2 Moles of CO = 5.6 / 22.4 = 1/4 mean molar mass = M_{min} = $\frac{n_1 - M_1 + n_2 - M_2 + n_3 - M_3}{n_1 + n_2 + n_3} = (7 + 7 + 22) / 1 = 36$

Graham's Law of Diffusion/Effusion :

Diffusion :

Net spontaneous flow of gaseous molecule from region of high concentration (higher partial pressure) to region of lower concentration (lower partial pressure).

when removed 3 atm O₂ × Ň₂ × Š ặtm,

$$\stackrel{}{=}$$

flow will be from both sides, N₂ will try to equalise its partial

pressure in both the vessels, and so will O₂.

P _{N2} = 2.5 atm	P _{N2} = 2.5 atm
P _{o₂} = 1.5 atm	P _{o₂} = 1.5 atm

Graham's Law :

"Under similar condition of temperature and 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
$$r \propto \frac{1}{\sqrt{d}} d = \text{density of gas}$$

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{V.D_2}{V.D_1}} \qquad \text{V.D is vapour density}$$

$$r = \text{volume flow rate} = \frac{dV_{\text{out}}}{dt}$$

$$r = \text{mole flow rate} = \frac{dn_{\text{out}}}{dt}$$

r = distance travelled by gaseous molecule per unit time = $\frac{dx}{dt}$

• 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 $\propto ~\frac{P}{\sqrt{TM}}~A~~;~P-Pressure,~A-area~of~hole,~T-Temp.$, 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.

$$\mathbf{r} \propto \mathbf{P}$$

 $\mathbf{r} \propto \frac{1}{\sqrt{M}} ; \frac{\mathbf{r}_1}{\mathbf{r}_2} = \frac{\mathbf{P}_1}{\mathbf{P}_2} \sqrt{\frac{\mathbf{M}_2}{\mathbf{M}_1}}$

Ex.10 In a tube of length 5 m having 2 identical holes at the opposite ends. $H_2 \& O_2$ are made to effuses into the tube from opposite ends under identical conditions. Find the point where gases will meet for the first time.

$$H_{2} \xrightarrow{f_{1}} G_{2}$$
Sol. $\frac{r_{1}}{r_{2}} = \frac{ax}{dt} \times \frac{dt}{dx} = \sqrt{\frac{m_{2}}{m_{1}}} = \frac{dx_{1}}{dx_{2}} = \sqrt{\frac{32}{2}}$

$$\frac{dx_{1}}{dx_{2}} = 4 \qquad \Rightarrow \qquad \frac{distance travelled by H_{2}}{distance travelled by O_{2}} = 4$$

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

$$5x = 20 \qquad \Rightarrow \qquad x = 4m \text{ from } H_{2} \text{ side}$$

- **Ex.11** The pressure in a vessel that contained pure oxygen dropped from 2000 torr to 1500 torr in 40 min as 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 ?
- **Ans.** M = 128 g/mol

Sol. Change in pessure = 2000-1500 = 500 torr; time-taken = 40 min

rate₁ = $\frac{500}{40}$ torr/min; similarly rate₂ = $\frac{500}{80}$ torr/min $\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M}{32}}$ $\frac{\frac{500}{40}}{\frac{500}{80}} = \sqrt{\frac{M}{32}}$ M = 128 g/mol

Kinetic Theory of Gases :

Postulates / assumptions of KTG :

- A gas consists of tiny spherical particles called molecules of the gas which are identical in shape & size (mass)
- 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 <u>~</u> 0.
- Gaseous molecules are always in random motion and collide with other gaseous molecule & with walls of the container.
- Pressure of the gas is due to these molecular collisions with walls of the container
- These collisions are elastic in nature
- Molecular attraction forces are negligible. Infact, for an ideal gas attraction or repulsion forces are equal to zero.
- Newton's laws of motion are applicable on the motion of the gaseous molecule.
- Effect of gravity is negligible on molecular motion.
- The average K.E. of gaseous molecules is proportional to absolute temp of the gas.

$$\frac{1}{2}$$
 M ($\overline{u^2}$) α T (bar is for average)

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

The average kinetic is given by

$$\overline{E}_{\kappa} = \frac{1}{2}mc^2$$

where c is given by

$$c = \sqrt{\frac{\left(n_{1}v_{1}^{2} + n_{2}v_{2}^{2} + n_{3}v_{3}^{2} + \dots \right)}{\left(n_{1} + n_{2} + n_{3} + \dots \right)}}$$

This 'c' is known as root-mean-square speed. As the name implies, to calculate c, first take the square of the individual speeds, then their mean and finally the square root of the mean.

It can be shown that c is related to temperature by

$$c = \sqrt{\frac{3RT}{M}}$$

The average kinetic energy depends only on absolute temperature and is related to absolute temperature by the expression

$$\overline{\mathsf{E}}_{\mathsf{K}} = \frac{3\mathsf{R}\mathsf{T}}{2\mathsf{N}_{\mathsf{A}}} = \frac{3}{2}\mathsf{k}\mathsf{T}$$

where K = Boltzmann constant = $1.38 \times 10^{-23} \text{ J K}^{-1}$

• Root mean square speed (U_{rms})

$$U_{\text{rms}} = \sqrt{U^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{mN_A}}$$

Where m-mass of one molecule

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

$$U_{ms} = \sqrt{\frac{3RT}{M}}$$
 M = molar mass

Average speed (U_{av})

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

K is Boltzmann constant

• Most probable speed (U_{mp}) :

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

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



Solved Examples –

Ex.12 In a container of capacity 1 litre there are 10²³ molecules each of mass 10⁻²² g. If root mean square speed is 10⁵ cm/sec then calculate pressure of the gas.

Sol.
$$PV = \frac{1}{3} \text{ mN } U_{\text{ms}}^2$$

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

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.
- 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 .
- The peak corresponds to most probable speed.
- At higher temperature, fraction of molecules having speed less than a particular value decreases.
- For Gases with different molar masses will have following graph at a given temperature.



Real Gases :

Actually the concept of ideal gas is hypothetical as there is no gas which practically is ideal. So, the non-ideal gases are the real gases which are the actually existing gases which obey gas equation approximately only under two conditions.

(i) Low pressure

(ii) High temperature

- Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- Real gases deviates from ideal behaviour because
- Real gaseous molecules have a finite volume.
 {since on liquefication real gases occupies a finite volume}
- 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}

To test that whether the relation PV = nRT is valid for real gasses, graphical representation of Boyle's Law was examined for various gases like CO, CH_4 He and H_2 etc.

(i) Pressure (P) volume (v) versus pressure (P) plot :



Fig. : Plot of PV vs P for real gases and ideal gas

We already know that for ideal gases PV vs P plot is a straight line parallel to x-axis at all pressures at constant temperature and product PV is constant.

(ii) Pressure (P) versus Volume (V) Plot : It is apparent from the graph that real gases show a different curve from the curve of ideal gases

However the real gas behaviour approach ideal gas behaviour at low pressure. This justifies the point that real gases behave like ideal gases at low pressure.

However at very high pressure the volume of real gases is more which is calculated experimentally than that of the theoretically calculated volume from Boyle's law (for ideal gases).

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



Variation of Z with pressure at constant temperature :



Concelusions made from the graph :

(i) Z = 1: Compressibility factor is equal to unity for ideal gases at all temperature and pressure values. **Reason :** For ideal gases, gas equation is PV = nRT. As PV is equal to nRT, so their ratio is unity.

(ii) $Z \approx 1$: Compressibility factor is almost equal to unity at low pressure.

Reason : At low pressure, the interactions between the molecules is negligible, therefore there is no appreciable effect on the volume. So, Z = 1

(iii) Z > 1: Compressibility factor is greater than unity (positive deviation) at high pressure.

Reason : At high pressure, the gas molecules come very close to each other, so the forces of repulsion start operating between them. For ideal gases, as the pressure increases, volume decreases $\begin{pmatrix} & 1 \\ & 1 \end{pmatrix}$

proportionally $\left(P \propto \frac{1}{V}\right)$ so the product PV remains constant. But this is not the case with real gases. In

them with increase in pressure (high pressure) the forces of repulsion does not allow the volume to decrease proportionally. Instead volume starts increassing. There by, as both pressure and volume are increased. So, the product PV also increase with increasing pressure (PV > 1).

(iv) Compressibility factor is less than unity (negative deviation) When pressure is intermediate.

Reason : When the pressure is intermediate, then the gas molecules are at a sufficient distance to avoid repulsion. Instead, forces of attraction operate. Because of this, the molecules attract each other and they come closer., So the volume decreases more than expected or decrease in volume is not proportional to the increase in pressure.

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



Pressure alone does not decide the behaviour of gases. Temperature is also an important factor which plays role.

Boyle Temperature or Boyle point : It is the temperature at which real gases obey ideal gas laws over an appreciable range of pressure.

$$T_{B} = \frac{a}{Rb}$$

Boyle temperature depends on the nature of the gas.

Effect of Temperature on the compressibility Factor :

(i) Above the Boyle temperature : Real gas show positive deviation (Z > 1) from ideality. This is because with increase in temperature, the molecules move far from each other. So, volume increases thereby the forces of attraction between the molecules become feeble.

(ii) Below the Boyle temperature : Below the Boyle temperature 'Z' value first decreases and reaches a minimum value with increase in pressure because of forces of attraction which start operating between the molecules. Later, on further increase in pressure force of repulsion operate. So, now value of Z increases continuously

Conclusions

Gases show ideal behaviour at

- (i) High temperature
- (ii) Low pressure

Conclusions :

- Z = 1 for ideal gas
- Z > 1 at all pressures for He/H $_2$
- 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 :

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

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.



Excluded volume (not available for free momement)

excluded volume per mole of gas (b) = N_A 4 $\left\{\frac{4}{3}\pi r^3\right\}$ = 4 x N_A 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 :



Molecule in middle of container

Real gas

Due to these attraction, speed during collision will be reduced Momentum will be less Force applied will be less Pressure will be less. $P_{ideal} = P + \{correction term\}$ net correction term $\propto \left(\frac{n}{v}\right) \left(\frac{n}{v}\right) = \frac{an^2}{v^2}$

'a' is constant of proportionality and this is dependent on force of attraction Stronger the force of attraction greater will be 'a' (Constant)

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

Vander waal's equation is

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

Verification of Vander Waal's Equations

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

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

 V_m = volume of 1 mole of gas

• AT LOW PRESSURE (at separate temp.)

At low pressure V_m will be high.

Hence b can be neglected in comparision to V_m . but $\frac{a}{V_m^2}$ can't be neglected as pressure is low

Thus equation would be

$$\begin{pmatrix} \mathsf{P} + \frac{\mathsf{a}}{\mathsf{V}_m^2} \end{pmatrix} \mathsf{V}_m = \mathsf{RT} \qquad \Rightarrow \qquad \mathsf{PV}_m + \frac{\mathsf{a}}{\mathsf{V}_m} = \mathsf{RT}$$

$$\frac{\mathsf{PV}_m}{\mathsf{RT}} + \frac{\mathsf{a}}{\mathsf{V}_m\mathsf{RT}} = 1 \qquad \Rightarrow \qquad \mathsf{Z} = 1 - \frac{\mathsf{a}}{\mathsf{V}_m\mathsf{RT}} \qquad \qquad \mathsf{Z} < 1$$

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

AT HIGH PRESSURE (moderate temp.)

 $V_{\rm m}$ will be low

so b can't be neglected in comparision to V_m

but $\frac{a}{V^2}$ 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_m will be very large

hence 'b' can be neglected and $\frac{a}{V_m^2}$ can also be neglected as $V_{_m}$ is very large

 $PV_m = RT$ (ideal gas condition)



For H₂ or He a ∼ 0 because molecules are smaller in size or vander wall forces will be very weak, these are non polar so no dipole-dipole interactions are present in the actions.
 P(V − b) = RT

so
$$Z = 1 + \frac{Pb}{RT}$$





Critical constant of a gas :

When pressure increases at constant temp volume of gas decreases

$$P = P_{1} = \frac{T_{4}}{T_{c}} = \frac{T_{4}}{T_{c}}$$

 $AB \rightarrow gas$ 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

 \mathbf{T}_{c} or critical temp : Temperature above which a gas can not be liquified

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

 P_c or critical pressure : Minimum pressure which must be applied at critical temp to convert the gas into liquid.

$$\mathsf{P}_{\mathsf{C}} = \frac{\mathsf{a}}{\mathsf{27b}^2}$$

 V_c or critical volume : Volume occupied by one mole of gas at T_c & P_c

$$V_c = 3b$$

H₂O

polar

– Solved Examples –

Ex.13 Arrange following in decreasing 'a' factor (H₂O, CO₂, Ar)

Sol.

> CO₂ > Ar

• For non polar molecules : Greater the size or surface area, greater will be vander waals' forces, so greater will be 'a' constant.

Ex.14 Arrange following gases according to 'a' (He, Ar, Ne, Kr).

Sol. a_{Kr}

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

- More 'a' factor means high boiling point.
- O liquification pressure (LP) : Is the pressure required to convert gas into liquid. for easy liquefaction a↑ and LP↓
 When Z < 1, V_m < V_{m ideal} ⇒ easily liquifiable

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

Ex.15 Arrange the following according to liquification pressure (n-pentane ; iso-pentane , neo pentane).

Sol.

Sol.

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

liquification pressure = LP $LP_{n-pentane} < LP_{pentane} < LP_{pentane}$

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

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

- **Ex.16** Two vander waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions ?
- **Sol.** If two gases have same value of b but different values of a, then the gas having a larger value of a will occupy lesser volume. This is because the gas with a larger value of a will have larger force of attraction and hence lesser distance between its molecules.
- **Ex.17** Critical temperature of oxygen and nitrogen gas is 154.3 K and 126.0 K respectively. Which of these gases has higher magnitude of intermolecular forces between them ?
- **Sol.** Higher is the critical temperature, more easily the gas can be liquefied. Further, more are the intermolecular forces of attraction more is the liquefaction. Therefore oxygen gas with higher critical temperature has high intermolecular forces of attraction than nitrogen gas with low critical temperature.

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

A gas is initially at 1 atm pressure. To compress it to 1/4 th of initial volume, what will be the pressure required ?

$$P_{1} = 1 \text{ atm} \qquad V_{1} = V$$

$$P_{2} = ? \qquad V_{2} = \frac{V}{4}$$

$$P_{1}V_{1} = P_{1}V_{2} \qquad \text{at const. T & n}$$

$$P_{2} = \frac{P_{1}V_{1}}{V_{2}} = \frac{1 \text{ atm} \times V}{\frac{V}{4}} = 4 \text{ atm Ans.}$$

CHEMISTRY FOR NEET

2. A vessel contains $H_2 \& O_2$ in the molar ratio of 8 : 1 respectively. This mixture of gases is allowed to diffuse through a hole, find composition of the mixture coming out of the hole.

Sol. Here,
$$n_{H_2} : n_{O_2} = 8 : 1$$
 & $\frac{r_{H_2}}{r_{O_2}} = \frac{n_{H_2}}{n_{O_2}} \sqrt{\frac{M_{O_2}}{M_{H_2}}}$
 $\Rightarrow \frac{r_{H_2}}{r_{O_2}} = \frac{8}{1} \times \sqrt{\frac{32}{2}} = \frac{32}{1}$
 $\Rightarrow \frac{(no. of moles of H_2 coming out)/\Delta t}{(no. of moles of O_2 coming out)/\Delta t} = \frac{32}{1}$
Required composition of $H_2 : O_2$ coming out = 32 : 1 Ans.
3. Under critical states of a gas for one mole of a gas, compressibility factor is

(1)
$$\frac{3}{8}$$
 (2) $\frac{8}{3}$ (3) 1 (4) $\frac{1}{4}$

Sol. For 1 mole of gas $Z = \frac{P_c V_c}{RT_c}$ (Under critical condition)

But,
$$P_c = \frac{a}{27b^2}$$
, $V_c = 3b$, $T_c = \frac{8a}{27Rb}$
 $Z = \left(\frac{a}{27b^2}\right) \times \frac{3b}{R} \times \frac{27Rb}{8a} = \frac{3}{8}$ Ans. (1)

- 4. A weather balloon filled with hydrogen at 1 atm and 300 K has volume equal to 12000 litres. On ascending it reaches a place where temperature is 250 K and pressure is 0.5 atm. The volume of the balloon is :
- (1) 24000 litres (2) 20000 litres (3) 10000 litres (4) 12000 litres Sol. Using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $\frac{1 \text{ atm } \times 12000 \text{ L}}{300 \text{ K}} = \frac{0.5 \text{ atm } \times V_2}{250 \text{ K}}$ $\therefore \quad V_2 = 20,000 \text{ L}$ Hence Ans. (2)
- 5. 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. (1) Density (2) Pressure (3) KE per mol (4) RMS speed

(1) Density
(2) Pressure
(3)
Sol. Given that
$$T_A M_A = T_B M_A \implies \frac{T_A}{M_A} = \frac{T_B}{M_B}$$

But, r.m.s. = $\sqrt{\frac{3RT}{M}}$
r.m.s_A = $\sqrt{\frac{3RT_A}{M_A}}$ & r.m.s_B = $\sqrt{\frac{3RT_B}{M_B}}$
r.m.s_A = r.m.s_B Ans. (4)