

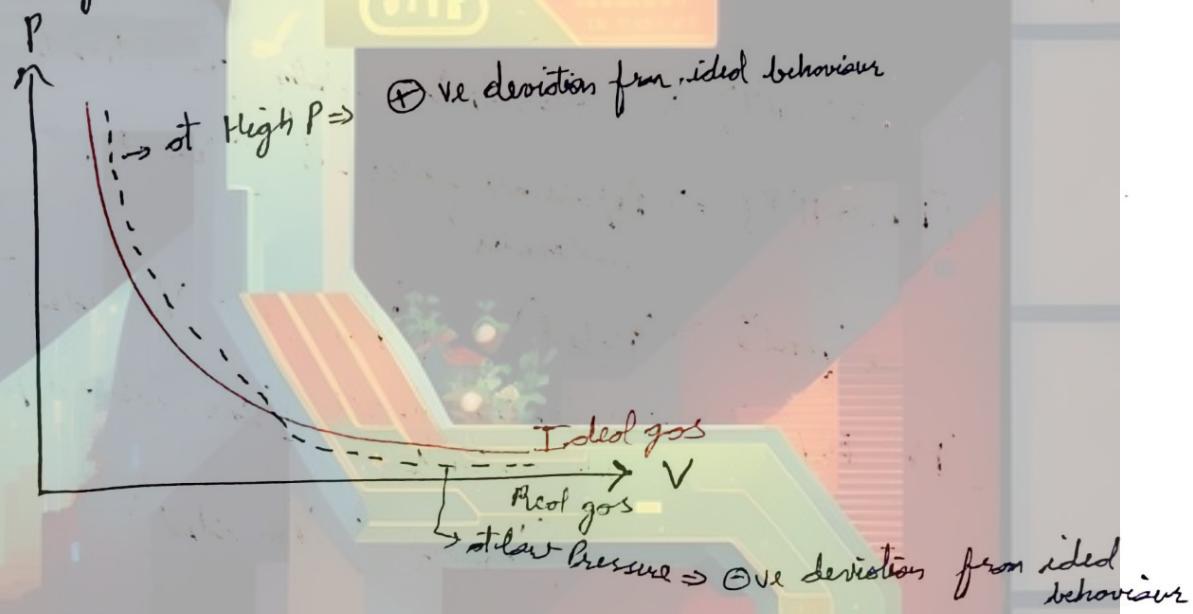
Real Gas

→ A real gas is that gas which do not obey ideal gas equation.

$$PV = nRT \text{ (Ideal gas)}$$

$$PV \neq nRT \text{ (Real-gas)}$$

- All the gases are real gases the concept of ideal gas is hypothetical.
- Under condition of very low pressure & High temperature A real gas tends to be behave like an ideal gas.



Compressibility Factor (z) - The compressibility factor gives a measure of deviation of Real gas from Ideal behaviour.

→ Compressibility Factor (z) is defined as ratio molar volume of real gas at given Temperature & Pressure to the molar volume of Ideal gas at some temp & pressure.

$$\text{molar volume} = \frac{V}{(V_m)}$$

$$Z = \frac{V_{m, \text{real}}}{V_{m, \text{ideal}}} \quad \text{at const } P, T$$

①

$$Z = \frac{V}{\left(\frac{nRT}{P}\right)} \Rightarrow \frac{PV}{nRT} = \frac{PV}{\frac{m}{M}RT} = \frac{PM}{V} = \frac{PM}{RT}$$

$$Z = \frac{PM}{RT} \quad \text{②}$$

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

($Z=1$) $[PV = nRT] \Rightarrow$ Gas behaves ideally (no interaction)

($Z > 1$) $[PV > nRT] \Rightarrow$ Repulsive force b/w [less compressible] molecules

$$\left(\cancel{V_{m, \text{real}} > V_{m, \text{ideal}}} \right) \quad (V_{m, \text{real}} > V_{m, \text{ideal}})$$

($Z < 1$) $[PV < nRT] \Rightarrow$ Attraction force [more compressible] b/w molecules

$$(V_{m, \text{real}} < V_{m, \text{ideal}})$$

Q1. Under similar Condition of Pressure & Temperature, The molar volume of Real gas is 20% less than molar volume of ideal gas. i) find Z ii) predict type of dominating force.

$$Z = \frac{V_{m, \text{real}}}{V_{m, \text{ideal}}} = \frac{x - \frac{2c}{100} \times 20}{x} = \frac{4x}{5x} = \frac{4}{5} = 0.8$$

$$Z = 0.8 \\ \text{Attraction}$$

Q2. In a gas attractive force dominates at 0°C , 1 atm
It volume will be -

- a) $V_m = 22.4 \text{ l}$ b) $V_m < 22.4 \text{ l}$ c) $V_m > 22.4 \text{ l}$
d) none.

$$PV = nRT$$

$$1 \times V < 1 \times R \times 273$$

$$V < 22.4$$

Q3. At 300 K, 1 atm, 2 for O_2 is 0.9 find mass required to fill 1 l container.

$$\frac{0.9 \times nRT}{P} = n_x (1)$$

$$0.9 = \frac{PM}{dRT} = \frac{1 \times 32}{d \times 0.0821 \times 300}$$

$$0.9 \times 24.63 \text{ rd} = 32$$

$$d = \frac{32}{0.9 \times 24.63}$$

$$\text{mass} = \frac{32}{0.9 \times 24.63} \text{ kg}$$

$$\text{mass} = \frac{32}{22.167}$$

$$\boxed{\text{mass} = 1.44 \text{ kg}}$$

1) Van der Waal's Gas Equation for Real Gases

Cause of Deviation :-

1. → Inter molecular forces are considerable in real gases and therefore can not be neglected.
2. → Size of molecule is also not negligible.

Q. -

→ To compensate the errors, caused about the assumptions, following two corrections were introduced.

① Volume Correction

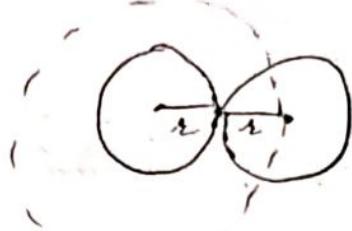
$$V_{\text{gas}} = V_{\text{Container}} - V_{\text{molecules}}$$

Volume of gaseous molecule → Different from V_{gas} .

$$PV = nRT$$

↳ free volume → volume available in the container for its free movement.

$$\text{freevol} = V_{\text{Container}} - (\text{Volume of gas molecules})_{\text{experiments}}$$



$$\text{Volume occupied by 2 particles} = \frac{4}{3} \pi (2r)^3 \\ = 8 \left(\frac{4}{3} \pi r^3 \right)$$

$$\therefore 1 \text{ particle} = 4 \left(\frac{4}{3} \pi r^3 \right)$$

$$\therefore 1 \text{ mole Particles} = \boxed{4 \left(\frac{4}{3} \pi r^3 \right) N_A = b}$$

\rightarrow Van der Waals constant

Note :- ① b = excluded volume per mol

② b = Van der Waals constant

③ excluded volume per molecule is 4 times to actual volume of molecule.

$$V_{\text{free}} = V_{\text{contains}} - nb$$

$\rightarrow n \rightarrow \text{moles}$

$b \rightarrow$ Van der Waals constant

$nb \rightarrow$ Volume of n mol gas molecules

Important Characteristics of Van der Waals constant (b)

1. \rightarrow Unit $\frac{l}{\text{mol}} \propto \frac{\text{cm}^3}{\text{mol}} \propto \frac{\text{m}^3}{\text{mol}} \propto \frac{\text{dm}^3}{\text{mol}}$

2. \rightarrow Value of ' b ' is unique to each gas & is Temperature independent.

3. \rightarrow The value of ' b ' gives measure of size of gas particle

$$b(\text{H}_2) \ll b(\text{N}_2) < b(\text{CO}_2) \leq b(\text{C}_2\text{H}_6)$$

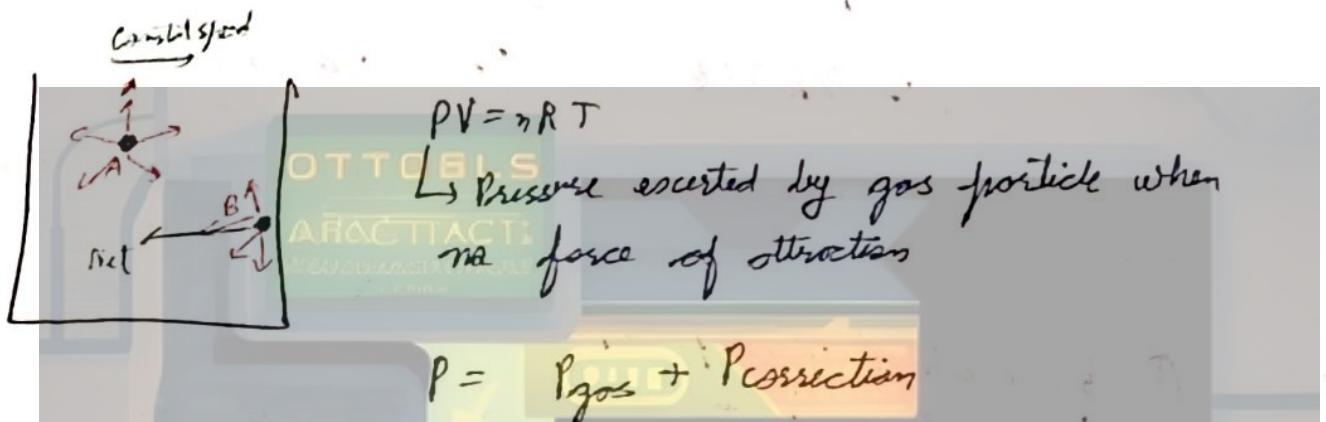
$\boxed{\text{Size} \uparrow ; \therefore \downarrow ; b \uparrow}$

4. \rightarrow The value of ' b ' also gives a measure of repulsion forces acting between gaseous particles.

$\boxed{\text{repulsion force} \uparrow ; b \uparrow}$

② Pressure Correction

→ Vanderwall assumed that in a real gas sample only force of attraction dominates hence, the pressure of gas will be less than the pressure of ideal gas under similar conditions.



- For molecule A net force of attraction is zero so, it moves with a constant speed. But if we consider another molecule B, which is about to collide to wall of container, it experience a net force of retardation due to which, speed of gas particle decreases hence, It exerted less pressure than it could have if there were no force of attraction
- According to vanderwall 'P' correction term depends on following:-

- ① Pcorrection of N^*
- ② Pcorrection of Z ,

By writing

Correction of $N^* Z$,

$$\propto \left(\frac{1}{v}\right) \left(\frac{1}{N}\right)$$

$$P_{\text{correction}} = \frac{n^2}{V^2}$$

\Rightarrow van der waals constant

Vanderwaal Equation for real gas

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

Real gas eq.

OTTOBELS

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

Imp. properties of Vanderwaal const. 'a'

1. $\rightarrow \frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}$
2. \rightarrow A value of 'a' has unique value for each gas & temperature independent.
3. \rightarrow The value of 'a' gives a measure of attractive forces that are present between gas particles.
4. \rightarrow Attraction forces depends on polar & non-polar nature of gas, size of gas particles, molecular weight.
5. \rightarrow As the size of particles increases, The value of 'a' also increases.

attraction \uparrow ; $a \uparrow$

~~Size~~ \uparrow ; Surface area \uparrow ; mol wt \uparrow ;

$a \uparrow$

$$\alpha(H_2) < \alpha(N_2) < \alpha(CO_2) < \alpha(H_2O)$$

$$\alpha(H_2) < \alpha(N_2) < \alpha(CO_2) < \alpha(H_2O)$$

\hookrightarrow H-bond

→ The gases having higher value of 'a' can be liquified easily.

Vanderwaal's equation under different conditions

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

Case I

At low pressure condition

Attraction

$P \rightarrow \text{low}$ Volume \rightarrow High

$V_m \rightarrow \text{High}$

$$V_m - b \approx V_m$$

neglect

$\cancel{V_m - b}$

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

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{RTV_m} = 1$$

$$Z = 1 - \frac{a}{RTV_m}$$

\hookrightarrow \ominus ve deviation

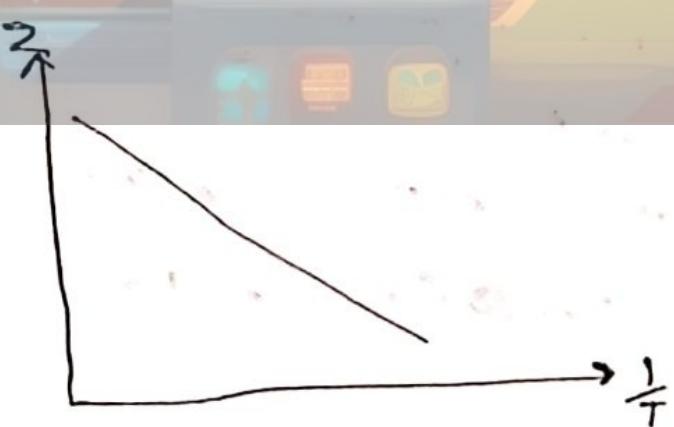
$$Z < 1$$

Attraction force dominate
 $a \uparrow, Z \downarrow$

$$Z = 1 - \frac{a}{V_m R} \left(\frac{P}{T} \right)$$

$$y = c + mx$$

$$\text{Slope} = -\frac{a}{V_m R} = \tan \theta$$



Case 2 Very High Pressure Condition

$\Delta P \uparrow \uparrow$
very high

$V \downarrow$
High
Low

$$\left(P + \frac{A}{V_m^2} \right) \approx P$$

very high high very high

$$\frac{A}{V_m^2} \rightarrow \text{neglect}$$

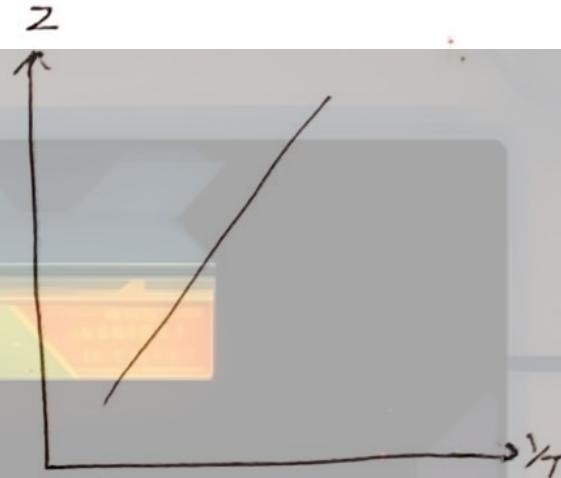
$$P(V_m - b) = RT$$

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

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

$$\frac{P V_m}{RT} = \frac{V_m}{V_m - b}$$

$$Z = \frac{V_m}{V_m - b}$$



$$\text{Slope} = \frac{Pb}{R} = \tan \theta$$

$Z > 1 \Rightarrow \text{repulsion Force dominate}$
④ \forall elevation

Case 3 For H₂ & He gas only.

\rightarrow He & H₂ gases, value of a is very low.

Both are non-polar and molar mass values very less.

$$a \rightarrow 0$$

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

$$Z = \frac{V_m}{V_m - b}$$

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

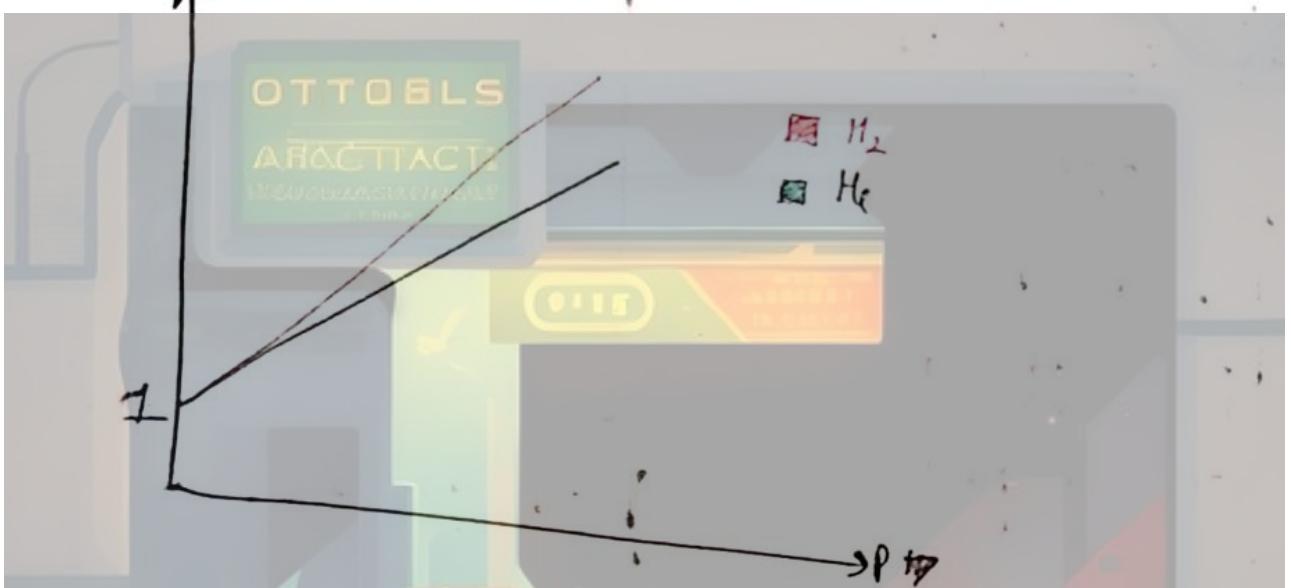
always ④ \forall elevation

Q4. Plot Z vs P for the H_2 & He gas on same graph.
 $b(H_2) > b(He)$. find slopes.

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

$$y = 1 + \frac{b}{R} \left(\frac{1}{T} \right) P x$$

$$\text{slope} = \frac{b}{RT}$$



Q5. 22 g CO_2 is taken in a container of 500 ml capacity at 27°C temp calculate Pressure exerted by gas

- i) When it behaves ideally
- ii) When it behaves ~~not~~ really ($a = 3.6 \frac{\text{atm}^2}{\text{mol}^2}$ $b = 0.5 \frac{\text{l}}{\text{mol}}$)

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

$$P = \frac{0.5 \times 0.2463}{0.5}$$

$$P = 24.63 \text{ atm}$$

$$P = 24.63 \text{ atm } i)$$

$$(P + \frac{3.6}{0.5}) = \frac{RT}{0.5 - 0.5}$$

$$P = \frac{24.63}{0.5} - 3.6$$

$$P = 49.26 - 3.6$$

$$P = 45.66 \text{ atm } ii)$$

Q6. At what pressure, The density of a underground gas will be 2.5 g/l at 27°C

$$\text{given: } a = 4 \frac{\text{atm}^2}{\text{mol}^2} \quad b = 0.8 \frac{\text{l}}{\text{mol}} \quad M_M = \frac{40 \text{ g}}{\text{mol}}$$

$$2.5 = \frac{P M}{R T}$$

$$2.5 = \left(P + \frac{4}{V_m^2} \right) \times 40$$

$$\left[\left(P + \frac{4}{V_m^2} \right) \left(V_m - 0.8 \right) = 24.63 \right] = 24.63$$

$$\Rightarrow \left(P + \frac{4}{V_m^2} \right) \left(\frac{V}{n} - 0.8 \right) = 24.63 \quad \left| \left(P + \frac{4}{256} \right) (16 - 0.8) = 24.63 \right.$$

now → (assume)

$$\left(P + \frac{4}{V^2} \right) (V - 0.8) = 24.63$$

$$\frac{40}{V} = 2.5$$

$$V = \frac{40}{2.5}$$

$$V = 16$$

$$P + \frac{1}{64} = \frac{24.63}{15.2}$$

$$P = \frac{24.63}{1520} - \frac{1}{64}$$

$$\boxed{P = 1.6}$$

Q7. Calculate compressibility factor z for a underground's gas which occupies 20 lit/mol at 127°C ($a = 2.8$ $b = \text{negligible}$)

$$z = 1 - \frac{a}{RTV_m}$$

$$z = 1 - \frac{2.8}{24.63 \times 20}$$

$$z = 1 - \frac{1.4}{246.3}$$

$$\boxed{0.9887}$$

$$z = \frac{246.3 - 1.4}{246.3}$$

$$z = \frac{244.9}{246.3}$$

Q8. The Compressibility factor of a Van der Waals gas = 0.8 at 200 K
 1.02 dm³. find Van der Waals constant (α). neglect volume occupied by molecule.

$$0.8 = 1 - \frac{\alpha}{RTV_m}$$

$$\frac{\alpha}{RTV_m} = 0.2$$

$$\alpha = 24.63(0.2)V_m$$

$$\alpha = 4.926 V_m$$

$$\alpha = \frac{4.926 \times 19.65656}{1.2}$$

$$\alpha = \frac{24.63 \times 9.828}{3}$$

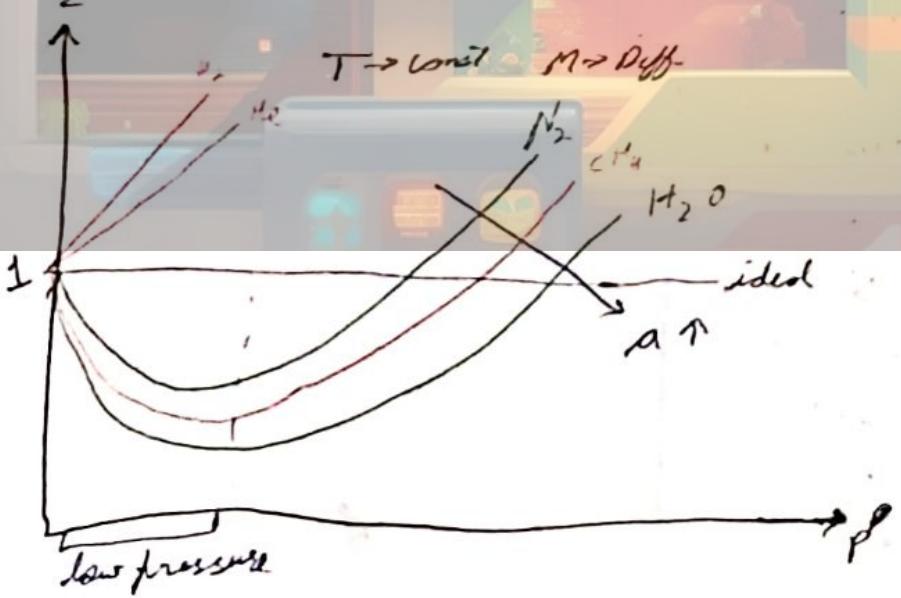
$$\alpha = 79. \text{Something}$$

$$\alpha = 80.687213$$

\Rightarrow Compressibility

\Rightarrow Z-P graph

case I



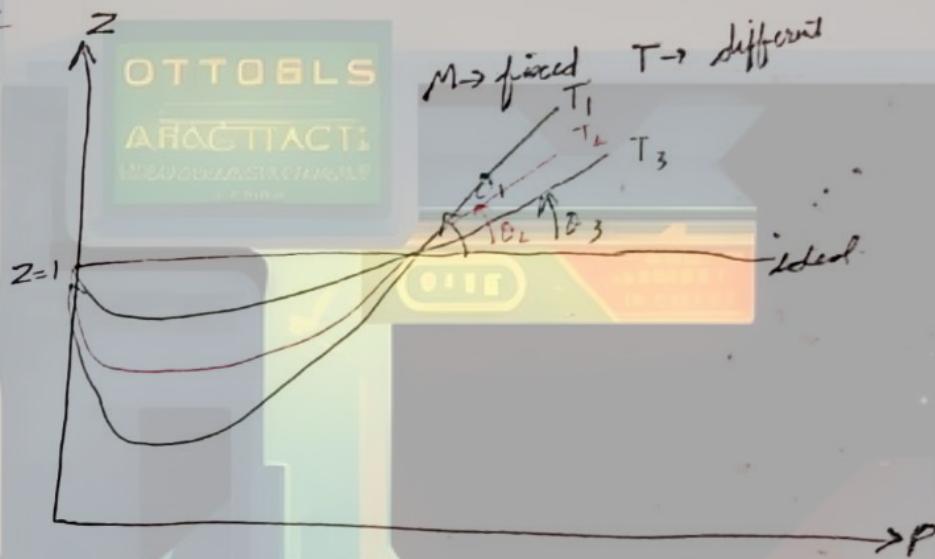
at low pressure

$$Z = 1 - \frac{a}{V_m RT}$$

near ; Over slope ↑

$$\alpha(N_2) < \alpha(18H_2) < \alpha(H_2O)$$

Case II



$$Z = 1 + \frac{b}{RT} P$$

$$\text{Slope} = \frac{b}{RT}$$

$$\Theta_1 > \Theta_2 > \Theta_3$$

$$\left(\frac{b}{RT_1}\right) > \left(\frac{b}{RT_2}\right) > \left(\frac{b}{RT_3}\right)$$

$b, R \rightarrow \text{constant}$

$$T_3 > T_2 > T_1$$

Note :-

→ For ~~Highest~~ highest deviation, High pressure & low temperature

$$Z \uparrow \quad P \uparrow \quad T \downarrow$$

Virial gas eqn

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

A, B, C & D are Virial coeff which are T independent

Virial form of Van der waals gas eqn

OTTOOLS

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

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

$$P = \frac{RT}{(V_m - b)} - \frac{A}{V_m^2}$$

$$\frac{PV_m}{RT} = \frac{RT}{V_m - b} \times \frac{PV_m}{RT} - \frac{A}{V_m^2} \times \frac{V_m}{RT}$$

$$Z = \frac{PV_m}{V_m - b} - \frac{A}{V_m RT}$$

$$Z = \frac{1}{1 - \frac{b}{V_m}} - \frac{A}{V_m RT}$$

$$Z = \left(1 - \frac{b}{V_m} \right)^{-1} - \frac{A}{V_m RT} \quad [(1-x)^{-1} = 1 + x + x^2 + x^3 + \dots]$$

$$Z = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} \dots - \frac{A}{V_m RT}$$

$$Z = 1 + \left(b - \frac{A}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} \dots$$

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

$$A \text{ (1st virial coeff)} = 1$$

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

$$C = b^2$$

$$D = b^3$$

⋮

temp dependent

Case I extremely low pressure condition
 $P \rightarrow 0, V_m \rightarrow \infty$

$\frac{1}{V_m} \rightarrow 0, \frac{1}{V_m^2} \rightarrow \frac{1}{V_m^3} \rightarrow 0$ can be neglected

$Z = 1$ behaves like ideal gas

Case II At low pressures

$P \rightarrow \text{low } V_m \rightarrow \text{High } (\uparrow)$
 $V_m^2 \rightarrow \text{very High } (\uparrow \uparrow)$

$$Z = 1 + \left(\frac{b-a}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} \dots$$

neglect.

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

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

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

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

boyle's temp

→ Gases becomes ideal gas at its Boyle's temp only at low pressure condition.

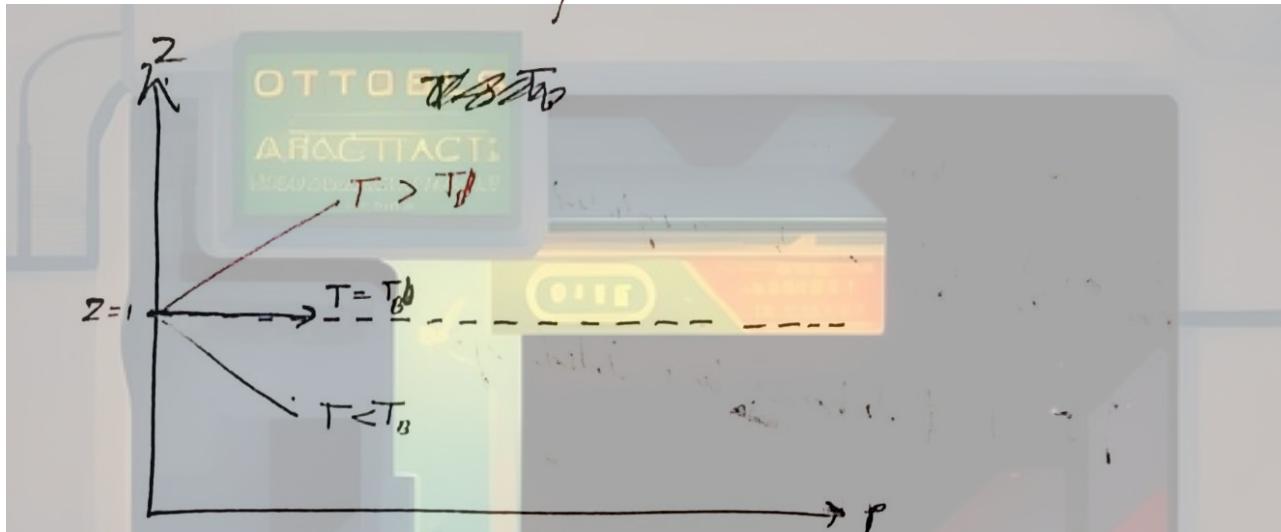
Boyle's Law Temp (T_b) \rightarrow It is that temperature at which a real gas behaves like an ideal gas, in low-pressure condition.

~~in low pressure condition,~~

$$T = T_b \Rightarrow z = 1 \Rightarrow \text{ideal behaviour}$$

$$T > T_b \Rightarrow z > 1 \Rightarrow \text{ve deviation (repulsion dominant)}$$

$$T < T_b \Rightarrow z < 1 \Rightarrow \text{ve deviation (attraction dominant)}$$



Q.9. Calculate the volume occupied by two mole of a van der waal's gas at 5 atm, 800 K. (given: $a = 4 \frac{\text{atm l}^2}{\text{mol}^2}$, $b = 0.0625 \frac{\text{l}}{\text{mol}}$, $R = 0.08 \frac{\text{dm l}}{\text{mol K}}$)

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

$$\left(5 + \frac{4}{V_m^2} \right) (V_m - 0.0625) = 0.08 \times 800$$

$$(5V_m^2 + 4)(V_m - 0.0625) = 64V_m^2$$

$$5V_m^3 + 20V_m^2 - 0.0625V_m^2 - 64V_m^2 + 4V_m - 0.2600 = 0$$

$$5V_m^3 + 20V_m^2 - 0.0625V_m^2 - 64V_m^2 + 4V_m - 0.2600 = 0$$

$$5V_m^3 - 20V_m^2 - 0.0625V_m^2 - 64V_m^2 + 4V_m - 0.2600 = 0$$

$$5V_m^3 - 84.0625V_m^2 + 4V_m - 0.2600 = 0$$

$$T_b = \frac{a}{Rb} = \frac{4}{0.08 \times 0.0625} = \frac{4}{0.005} = 800 \text{ K}$$

Idel Gas:-

$$5 \times V = 2 \times 0.08 \times 800$$

$$V = \frac{128}{5}$$

$$V = 25.6 \text{ l}$$

$$V = 25.6 \text{ l}$$