Real Gas

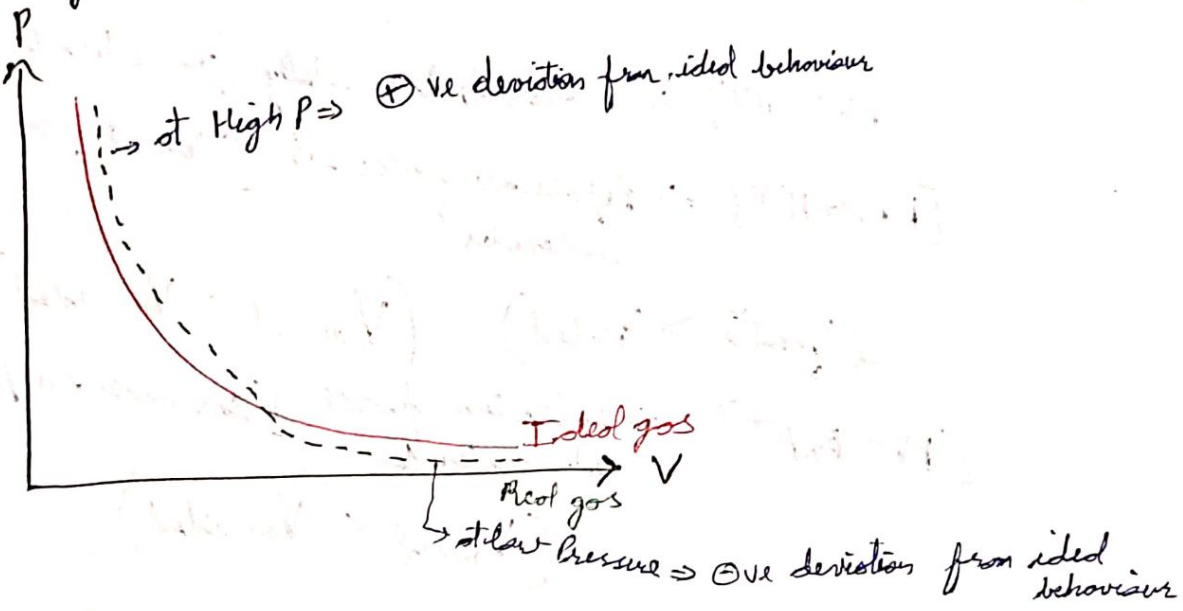
→ A real gas is that gas which do not obey ideal gas equation.

$PV = nRT$ (Ideal gas)

$PV \neq nRT$ (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 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 same temp & Pressure.

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

$$Z = \frac{V_{m,\,Real}}{V_{m\ Ideal}}$$ at const P & T (1)

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

$$Z = \frac{PM}{dRT} \quad (2)$$

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

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

($Z>1$) $[PV > nRT]$ ⇒ Repulsive force betw molecules [less compressible]

~~$(V_{m\ real} > V_{m\ ideal})$~~ $(V_{m\ real} > V_{m\ ideal})$

($Z<1$) $[PV < nRT]$ ⇒ Attraction force betw molecules [more compressible]

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

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.

$$Z = \frac{V_{m\,R}}{V_{m\,I}} = \frac{x - \frac{x}{100} \times 20}{x} = \frac{4x}{5x} = \frac{4}{5} = 0.8$$

$Z = 0.8$
Attraction

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

a) $V_m = 22.4\,l$ ✓b) $V_m < 22.4\,l$ c) $V_m > 22.4\,l$

d) none.

$PV < nRT$

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

$V < 22.4$

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

~~$0.9 = \frac{nRT}{P} = n_x(t)$~~

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

$0.9 \times 24.63\, d = 32$

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

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

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

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

Vander Waal's Gas Equation for Real Gas

Cause of Deviation :

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

→ To compensate the error, caused about two assumptions, following two correction were introduced.

① Volume Correction

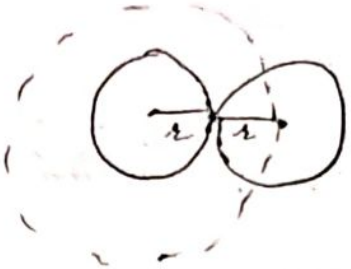
$V_{gas} = V_{container} = V_{observed}$

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

$PV = nRT$

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

$free\ vol = V_{container} - (\underbrace{\text{Volume of gase molecules}}_{\text{experimental}})$



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

$= 8\left(\frac{4}{3}\pi r^3\right)$

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

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

↳ Vanderwall constant

Note :- ① b = excluded volume per mol
② b = Vanderwal Constant
③ excluded volume per molecule is 4 times to actual volume of molecule.

$$\boxed{V_{free} = V_{container} - nb}$$

$n \rightarrow$ moles
$b \rightarrow$ Vanderwall constant
$nb \rightarrow$ Volume of n mol gas molecules

Important Characteristics of Vanderwalls constant (b)

1. → Unit $\frac{l}{mol}$ or $\frac{cm^3}{mol}$ or $\frac{m^3}{mol}$ or $\frac{dm^3}{mol}$

2. → Value of 'b' is <u>unique to each gas</u> & is Temperature independent.

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

$b(H_2) < b(N_2) < b(CO_2) < b(C_4H_{10})$

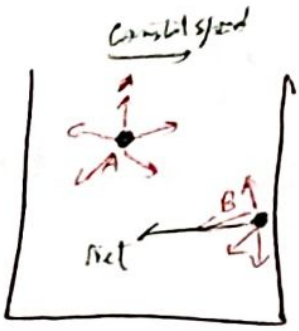
$\boxed{\text{Size} \uparrow \; ; \; r \uparrow \; ; \; b \uparrow}$

4. → 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 ided gas under similar conditions.



$PV = nRT$

↳ Pressure exerted by gas particle when no force of attraction

$P = P_{gas} + P_{correction}$

→ 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) $P_{correction} \propto N^*$

(2) $P_{correction} \propto Z_1$

By Combing

$P_{correction} \propto N^* Z_1$

$\propto \left(\frac{n}{V}\right)\left(\frac{n}{V}\right)$

$$P_{correction} = \frac{an^2}{V^2}$$ a ⇒ wonderwall constant

Vanderwall Equation for real gas

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

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

Imp properties of Vanderwall constant 'a'

1. → $\frac{atm\ l^2}{mol^2}$

2. → A value of 'a' has unique value for each gas & temperature independent.

3. → The value of 'a' gives a measure of attractive forces that are present between gas particles.

attraction ↑ ; a ↑

4. → A attraction forces depends on polar & non-polar nature of gas, size of gas particles, molecular weight.

5. → As the size of particles increases, the value of 'a' also increases.

Size ↑ ; Surface area ↑ ; mol wt ↑ ;

a ↑

a(H_2) a(N_2) a(CO_2) a(H_2O)

a(H_2) < a(N_2) < a(CO_2) < a(H_2O)

↳ H-bond

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

Vanderwall's equation under different conditions

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

Case I At low pressure condition

P → low Volume → High

V_m → High

$V_m - b \simeq V_m$

neglect

~~$V_m - a$~~

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

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

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

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

$Z < 1$

↳ −ve deviation

Attraction force dominate

$a \uparrow$; $Z \downarrow$

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

$y = c + mx$

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

Case 2 Very High Pressure Condition

$P \uparrow\uparrow$ (very High) $V \downarrow$ (Low)

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

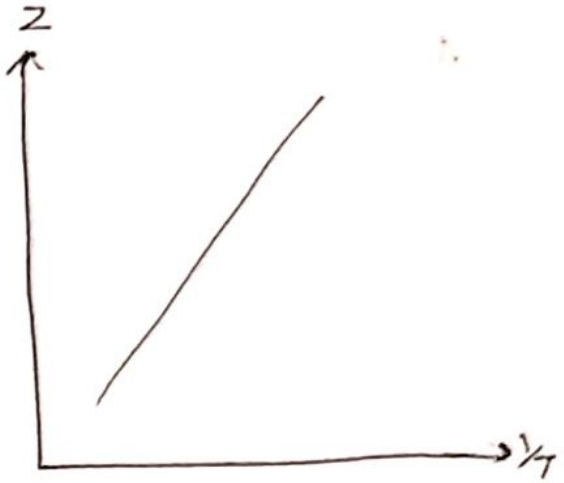
(very High) (High) (very High)

$\frac{a}{V_m^2} \rightarrow$ neglect

$P(V_m - b) = RT$

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

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



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

$Z > 1 \Rightarrow$ repulsion Force dominate

(+) ve deviation

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

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

Case 3 For H_2 & He gas only.

→ He & H_2 gases, value of a is very low.

both are non-polar and molar mass also very less.

$a \rightarrow 0$

$P(V_m - b) = RT$

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

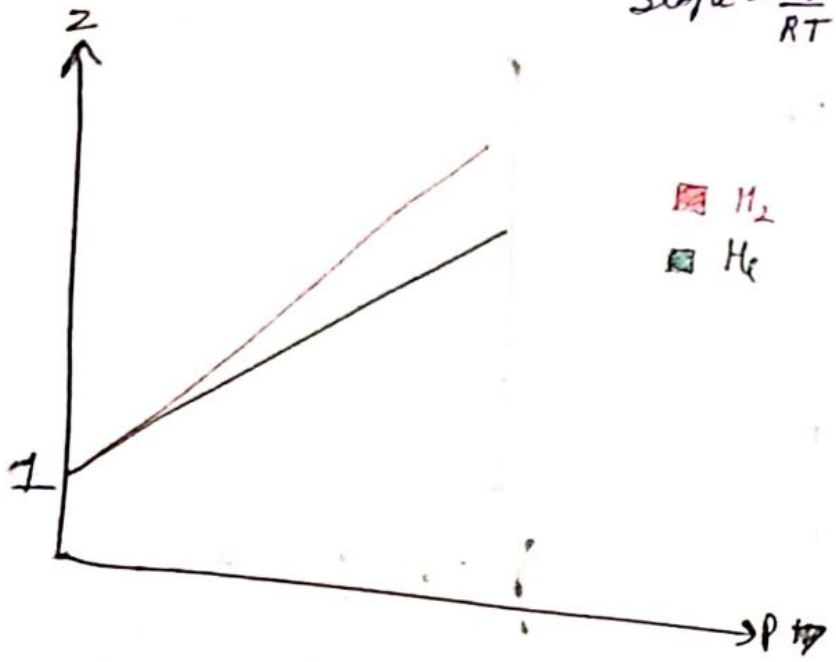
always (+) ve deviation

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

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

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

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



Q.5. 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 behave ~~real~~ really ($a = 3.6$ ~~atm~~ $\frac{atm\,l^2}{mol^2}$ $\quad b = 0.5\,\frac{l}{mol}$)

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

$P = \frac{0.5 \times 0.0821 \times 300}{0.5}$

~~$P = 24.63$ atm~~

$P = 24.63$ atm i)

ii) $\left(P + \frac{3.6}{1}\right) = \frac{RT}{1 - 0.5}$

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

$P = 49.26 - 3.6$

$P = 45.66$ atm ii)

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

given:- $a = 4 \frac{atm\ l^2}{mol^2}$ $b = 0.8\ l/mol$ $MM = \frac{40\ g}{mol}$

$$2.5 = \frac{PM}{RT}$$

$$2.5 = \frac{\left(P + \frac{a}{V_m^2}\right) \times 40}{24.63}$$

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

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

$n \to 1$ (assume)

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

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

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

$$V = 16$$

$$\left(P + \frac{4}{256}\right)(16 - 0.8) = 24.63$$

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

$$P = \frac{2463}{1520} - \frac{1}{64}$$

$$\boxed{P = 1.6}$$

Q7. Calculate compressibility factor for a vanderwaal's gas which occupy 20 lit/mol at 127°C [a = 2.8 b = negligible]

$$Z = 1 - \frac{A}{ATV_m}$$

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

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

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

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

$$\boxed{0.9887}$$

Q8. The Compressibility factor of a Vanderwall gas = 0.8 at 300 K
1.2 atm. find Vanderwall's constant (a). neglect volume occupied
by volume.

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

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

$$a = 24.63(0.2)V_m$$

$$a = 4.926 V_m$$

$$\left(P - \frac{a^2}{V_m^2}\right) V_m = 24.63$$

$$\left(P - \frac{4.926}{V_m}\right) V_m = 24.63$$

$$1.2 V_m - 4.926 = 24.63$$

$$V_m = \frac{19.656}{1.2}$$

$$a = \frac{4.926 \times 19.656}{1.2}$$

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

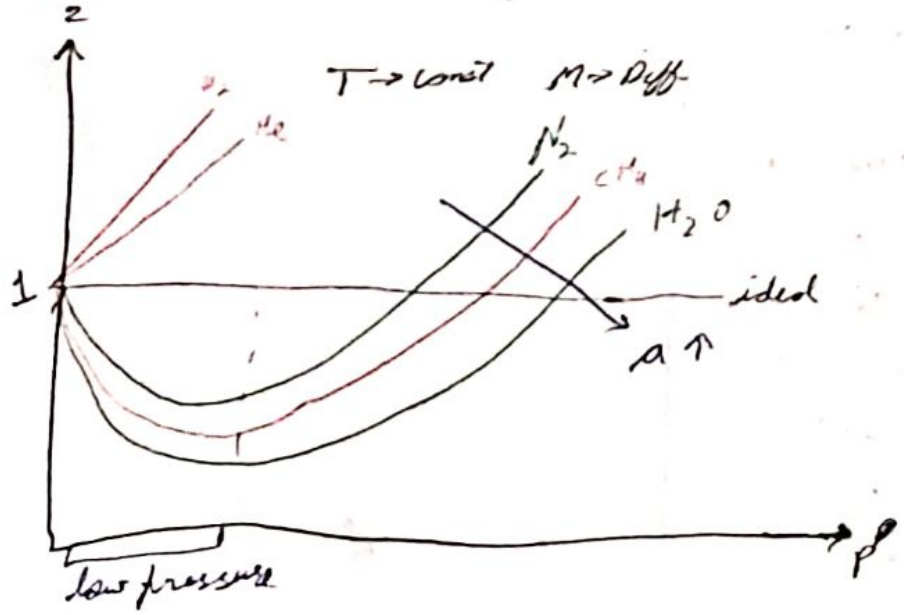
~~$a = 79.$ something~~

$$a = 80.687213$$

* Graphs

Z-P graph

Case I



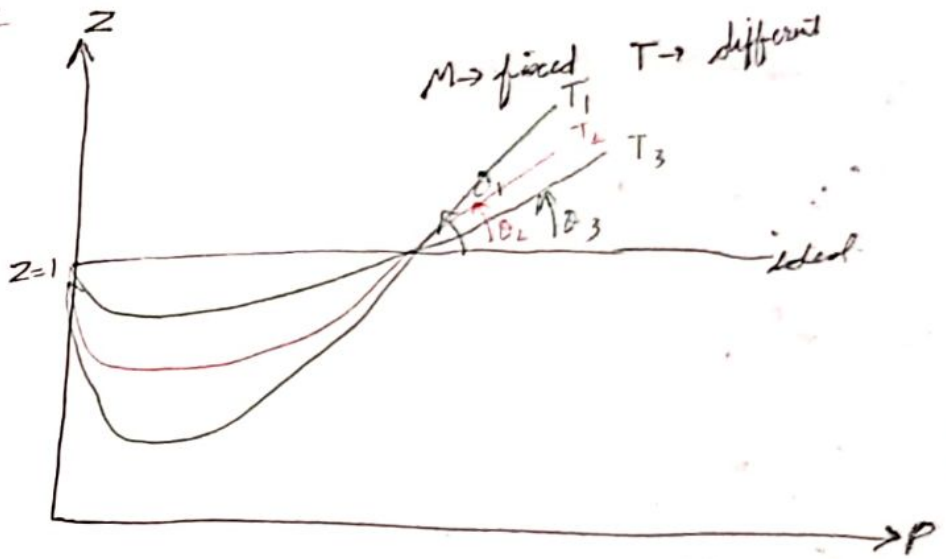
at low pressure

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

a ↑ ; -ve slope ↑

$a(N_2) < a(BH_4) < a(H_2O)$

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 → constant

$\boxed{T_3 > T_2 > T_1}$

Note :-

→ For ~~Most~~ Highest deviation, High Pressure & low temperature

Z ↑ P ↑ T ↓

Virial gas Eqn

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

A, B, C & D are Virial Coeff which are Temp dependent

Virial form of Vanderwaal gas Eqn

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

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

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

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

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

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

$$Z = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT} \qquad \left[(1-x)^{-1} = 1 + x + x^2 + x^3 + \cdots\right]$$

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

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

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

A (1st virial coeff) = 1

$B = b - \frac{a}{RT}$ — temp dependent

$C = b^2$

$D = b^3$

⋮

Case I extremely low pressure condition

$P \to 0 \quad V_m \to \infty$

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

$\boxed{Z = 1}$ behaves like ideal gas

Case II At low pressure

$P \to$ low $\quad V_m \to$ High (↑)

$V_m^2 \to$ very High (↑↑)

$Z = 1 + \left(\frac{b - \frac{a}{RT}}{V_m}\right) + \underbrace{\frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} \cdots}_{\text{neglect.}}$

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

$b - \frac{a}{RT} = 0$

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

$\boxed{T_b = \frac{a}{Rb}}$ boyle's temp

→ Gas behaves as ideal gas at its boyle's temp only at low pressure condition.

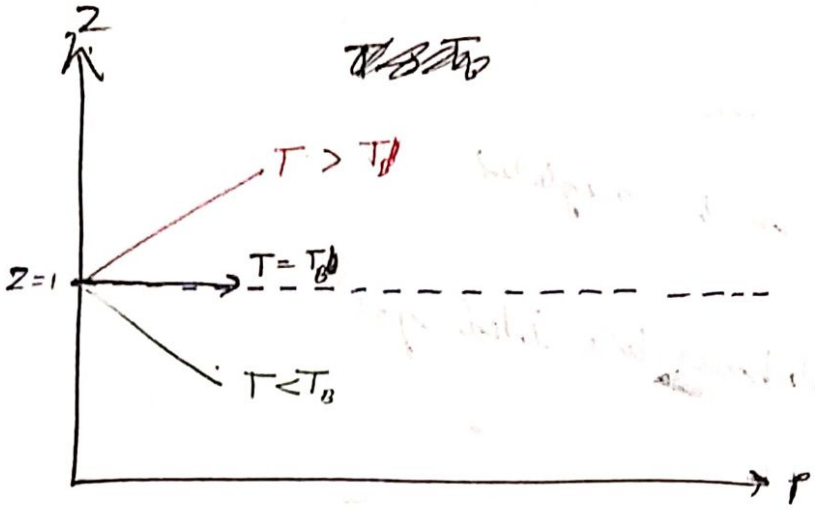
Boyle's Temp (T_b) → It is that temperature at which a real gas behaves like an ideal gas. in low pressure condition.

~~is at~~ low pressure condition

$T = T_b \Rightarrow Z = 1 \Rightarrow$ ideal behaviour

$T > T_b \Rightarrow Z > 1 \Rightarrow \oplus$ ve deviation (repulsion dominate)

$T < T_b \Rightarrow Z < 1 \Rightarrow \ominus$ ve deviation (attraction dominate)



Q9. Calculate the volume occupied by two mole of a vanderwaal gas at 5 atm, 800K. (given: $a = 4 \frac{atm\ l^2}{mol^2}$ $b = 0.0625 \frac{l}{mol}$ $R = 0.08 \frac{atm\ l}{mol\ K}$)

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

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

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

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

$$T_b = \frac{a}{Rb} = \frac{4}{0.08 \times 0.0625} = \frac{4}{5 \times 10^{-3}} = \frac{4000}{5} = 800\ K$$

Ideal Gas:-

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

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

$$\boxed{V = 25.6\ l} \qquad \boxed{V = 256.6\ l}$$