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Deg - I (H) - Gaseous State
Topics - Reduced Equation of State & Law of Corresponding State

Reduced Equation of State

If the pressure, volume & Temp of a gas are expressed in terms of the critical pressure, critical volume & critical Temp respectively, then it can expressed as

$$P = \pi P_c,\quad V = \phi V_c \;\&\; T = \theta T_c \quad \text{--- (1)}$$

Then

$$\pi = \frac{P}{P_c},\quad \phi = \frac{V}{V_c} \;\&\; \theta = \frac{T}{T_c}$$

The quantities, π = reduced pressure
ϕ = reduced volume
θ = reduced Temp

Putting the values of P, V & T from equation (1) in the Vanderwaal Equation of State

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

we get

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Again Putting the values of P_c, V_c & T_c in terms of Vanderwaal constant

$V_c = 3b$, $P_c = \frac{a}{27b^2}$, $T_c = \frac{8a}{27Rb}$

Vander waal Equation becomes.

$$\left(\pi \frac{a}{27b^2} + \frac{a}{\phi^2 9b^2}\right)(\phi \cdot 3b - b) = R\theta \frac{8a}{27Rb}$$

$$\frac{a}{27b^2}\left(\pi + \frac{3}{\phi^2}\right) b(3\phi - 1) = \theta \cdot \frac{8a}{27b}$$

Thus, $\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$ — (2)

The above equation is called reduced equation of state which relates reduced pressr (π), reduced volume (ϕ) & reduced Tempr (θ) ~~in terms of~~ among themselves & it is free from vanderWaal constant a & b.

Law of Corresponding States:

Another important conclusion from the above eqn (2) is

"If two substance have the same reduced pressr & the same reduced Tempr, they must have the same reduced volume."

The above statement is called Law of Corresponding State. It indicates that all fluids when compared at the same reduced Tempr & reduced pressr have approximatly the same Compressibility factor $\left(Z = \frac{PV}{nRT}\right)$ and all deviate from ideal gas behaviour to about the same degree.

Boyle's Temperature :-

Def:- The tempr at which a real-gas behaves like an ideal gas over an appreciable pressr range is called Boyle's Tempr.

At this tempr. the Compressibility factor $\left[Z = \frac{PV\,(\text{Observed})}{PV\,(\text{ideal})}\right]$ value close to one.

Derivation of Boyle's Tempr.

It may be derived from the vander-waal's equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{— (3)}$$

By simplifying.

$$PV = RT - \frac{a}{V} + Pb + \frac{ab}{V^2} \quad \text{— (4)}$$

As both vanderwaal's Constant a & b are small and if the pressr is not so high. V is not so small, $\frac{ab}{V^2}$ can be neglected.

Thus $$PV = RT - \frac{a}{V} + Pb \quad \text{— (5)}$$

We know that $PV = RT$

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

So. $\frac{a}{V} = \frac{aP}{RT}$

Thus Putting the value of a/V in eq^n (5)

$$PV = RT - \frac{aP}{RT} + Pb$$

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

For ideal gas $PV = RT$

Thus $P\left(b - \frac{a}{RT}\right) = 0$

P has a finite value,

$$\left(b - \frac{a}{RT}\right) = 0$$

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

$$\therefore T = \frac{a}{Rb}$$

Thus $T_b = \frac{a}{Rb}$ T_b = Boyle's Temp^r

By knowing a & b. We Can Calculate Boyle's Temp^r