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Deg. I (H) - Gaseous State
Topic - Relation b/w Critical Const. & Vanderwaal - Constant.

Critical - Constant (P_c, V_c & T_c) in terms of Vanderwaal - Constant (a & b).

Vanderwaal Equation of state for one mole of gas is expressed as

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

By multiplication it gives

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

multiplying by V^2, we get-

$$PV^3 + aV - PbV^2 - ab = RTV^2$$

Dividing all by P, it becomes

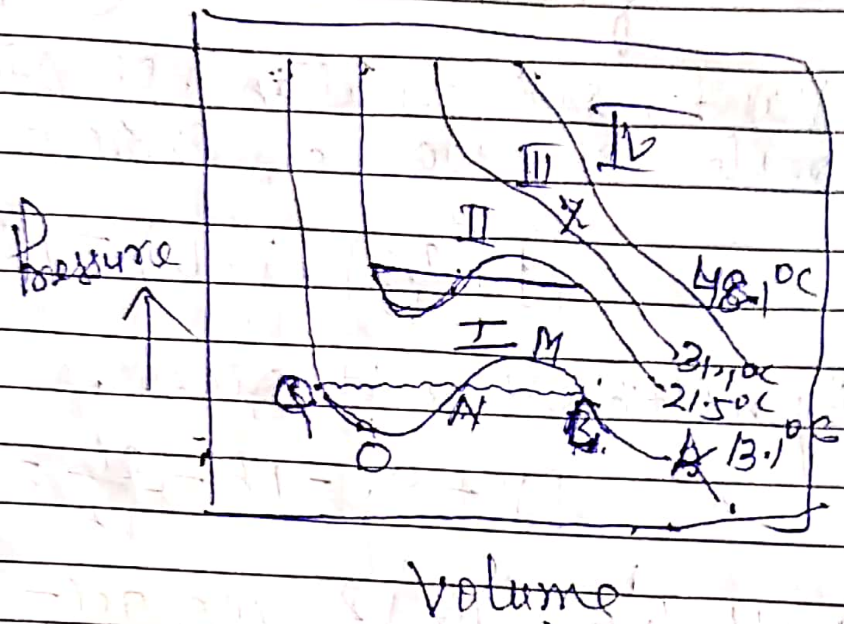
$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} = \frac{RTV^2}{P}$$

Rearranging in decreasing order of V, we get-

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

this is a cubic equation in the variable V & for any single set of the values of P and T, there should be three values of V. they all of which may be real one & other two are imaginary.

A plot of PV-Isotherm, then accordy to above cubic-equation. a curve similar to I is obtained.



It was observed that for certain pressure, there are three-values of V indicated on L, N & Q. As the tempr increase the isotherm moves up. At position II, the three values of V closes to each other. At stage-III, the three-value becomes identical as at point X. At stage-IV, there is only one real value of V corresponding to press (applied). The isother plotted in the above are based on theoretical calculation of V corresponding to different value of P obtained by using Vanderwaal-Equation. ~~The isotherm of CO2~~

The isotherm for CO_2 gas obtained by Andrews were close characteristics with these curve. the only difference that a wavelike portion LMN / CO & been replaced by horizontal line.

Carefully experiment observed that some portion corresponding to the curve LM & OQ can be realised in practice also. This represent super saturated vapour & super heated liquid respectively.

(At critical temp) (point) X the three values of V become identical. Such value of V represents critical volume (V_c)

Thus $V = V_c$

or $(V - V_c) = 0$

or $(V - V_c)^3 = 0$

By expanding the above eqn —

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad (1)$$

Van der waal equation is expressed earlier as

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \quad (2)$$

At the critical point, the term P & T may be replaced as P_c & T_c in eqn (2)

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \quad (3)$$

At critical point both equation (1) & (3) become identical.

By equating the co-efficient of terms of similiar powers of V. we get the following relation:

$$3V_c = b + \frac{RT_c}{P_c} \quad \text{--- (4)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{--- (5)}$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{--- (6)}$$

Dividing eqn (6) by eqn (5)

$$\frac{V_c^{\cancel{3}}}{3\cancel{V_c^2}} = \frac{\cancel{a}}{\cancel{P_c}} \times \frac{\cancel{P_c}}{\cancel{a}b}$$

Thus. $\boxed{V_c = 3b}$ --- (7)

Putting the value of V_c in eqn (5)

$$3 \times (3b)^2 = \frac{a}{P_c}$$

$$\therefore \boxed{P_c = \frac{a}{27b^2}} \quad \text{--- (8)}$$

Again Putting the value of P_c & V_c in eqn (4)

$$3 \times 3b = b + \frac{R \cdot T_c}{a} \times 27b^2$$

$$9b - b = \frac{R \cdot T_c}{a} \times 27b^2$$

$$8\cancel{b} = \frac{R \cdot T_c}{a} \times 27b^{\cancel{2}}$$

$$\therefore \boxed{T_c = \frac{8a}{27Rb}} \quad \text{--- (9)}$$