Gaseous States of matter

(1) Using Van der Waals eqn, determine the value for the critical constant of a gas.

Soln.: From van der Waals eqn we have

$$(p + a/v^2)(v - b) = RT \quad \text{for 1 mol gas}$$

$$\Rightarrow pv + a/v - pb - \frac{ab}{v^2} = RT$$

$$\Rightarrow pv^3 + av - pbv^2 - ab = RTv^2$$

$$\Rightarrow pv^3 + av - pbv^2 - ab - RTv^2 = 0$$

Dividing by p and arranging in decreasing power of v, we have

$$v^3 - (RT/p + b)v^2 + \frac{av}{p} - \frac{ab}{p} = 0 \rightarrow (1)$$

This is a cubic eqn of v which have a three soln i.e. all are real or one real and two imaginary values.

Under critical condition we have

$$v = V_c$$

$$\Rightarrow V - V_c = 0$$

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$$\Rightarrow (V-V_c)^3 = 0$$

$$\Rightarrow V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \rightarrow (2)$$

This eq^n should be identical with the vander waals eq^n (1). When $T = T_c$ & $P = P_c$, we get from eq^n (1)

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

Comparing the coefficient of eq^n (2) & (3) we get

$$3V_c = b + \frac{RT_c}{P_c} \longrightarrow (4)$$

$$3V_c^2 = a/P_c \longrightarrow (5)$$

and $V_c^3 = ab/P_c \longrightarrow (6)$

Now (6) ÷ (5) $\Rightarrow V_c/b = 3$

$$\Rightarrow \boxed{V_c = 3b} \longrightarrow (7)$$

P.T.O.

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From eq^n (5) $\Rightarrow$ $a = 3V_c^2 \times P_c$

$$\Rightarrow \boxed{P_c = \frac{a}{3V_c^2} = \frac{a}{27b^2}} \rightarrow (8)$$

Putting value of (7) & (8) in eq^n (4) we get

$$\Rightarrow 9b = b + \frac{RT_c}{a/27b^2}$$

$$\Rightarrow \boxed{T_c = \frac{8a}{27Rb}} \longrightarrow (9)$$

<u>Law of corresponding states and its significance</u>

Sol: From Van der waals eq^n we get

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

If the values of P, V and T are expressed as fraction of corresponding values (P_c, V_c and T_c) we have -

$$P/P_c = \pi, \Rightarrow P = \pi P_c$$

P.T.O.