T.D.C part-I

T.D.C. part-I Paper-I (Gaseous state)

Van der waals equation and critical constants :→

For one mole of a gas Van der waals equation is -

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

or, $$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying both side by V^2/P, we get

$$V^3 - bV^2 + \frac{aV}{P} - \frac{ab}{P} - \frac{RTV^2}{P} = 0$$

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

This is a cubical equation in the variable V. This equation has 3 values of V for any single value of P and T. Either all the ~~3 values~~ three values of V may be real or any one may be real and the other two imaginary. At the critical point all the 3 values of V become identical. Since the temp. now is critical, this value of V represents the critical volume, V_c, of the gas. that is -

$$V = V_c$$

or $$V - V_c = 0$$

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

or, $$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad (i)$$

This equation must be identical with van and critical pressure (P_c), which may be written as —

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

Equating the coefficients of equation (I) and (II), we get

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

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

and

$$V_c^3 = \frac{ab}{P_c} \quad \text{—— (V)}$$

Dividing eqn (V) by (IV), we get

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

$$\boxed{V_c = 3b}$$

Inserting the value of V_c in eqn (IV), we get

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

$$\therefore \boxed{P_c = \frac{a}{27b^2}}$$

Inserting the values of V_c and P_c in equation (iii), we get

$$3 \times 3b = b + \frac{PT_c}{a/27b^2}$$

or $$9b - b = \frac{PT_c}{a} \times 27b^2$$

or $$8b = \frac{PT_c}{a} \times 27b^2$$

$$\therefore \boxed{T_c = \frac{8a}{27Pb}}$$

Thus,

$$\boxed{V_c = 3b}$$

$$\boxed{P_c = \frac{a}{27b^2}}$$

and $$\boxed{T_c = \frac{8a}{27Pb}}$$

Van der waal's constants "a" and "b" in terms of critical constants —

since, $V_c = 3b$.

$$\therefore \boxed{b = \frac{V_c}{3}}$$

since, $$P_c = \frac{a}{27b^2}$$

$$\therefore a = 27b^2 \times P_c$$
$$= P_c \times 3 \times 9b^2$$
$$= 3P_c \times (3b)^2$$
$$= 3P_c \times V_c^2$$

$$\therefore \boxed{a = 3P_c \cdot V_c^2}$$

Critical co-efficient $= \frac{RT_c}{P_c \cdot V_c}$.

An important consequence of van der waals equation is obtained by using the equation at critical point with value of "a" and "b" in terms of critical constants.

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

or, $$\left(P_c + \frac{3P_c \cdot \cancel{V_c^2}}{\cancel{V_c^2}}\right)\left(V_c - \frac{V_c}{3}\right) = RT_c$$

$$(\because a = 3P_cV_c^2 \text{ and } b =$$

or, $$4P_c \times \frac{2V_c}{3} = RT_c$$

or, $$\frac{RT_c}{P_cV_c} = \frac{8}{3} = 2.66 = \text{cons}$$

This characterizes van der waal's gas just as compressibility factor, $Z=$ characterises ideal gas.

Reduced equation of state

'OR'

Law of corresponding states :⟶

In order to transform van der waals equation in a form applicable to all gases, we define reduced pressure (π), reduced temp. (θ) and reduced volume (ϕ) as follows —

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

Thus,
$$P = \pi P_c \quad , \quad T = \theta T_c \quad \text{and} \quad V = \phi V_c$$

Substituting these values in van der w equation

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

we get

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

Substituting the values of P_c, V_c and T we get.

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

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

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