B.Sc. II
group-A (G.S.)

Relation between Vanderwaals constants (a and b) and Critical constants (T_c, P_c and V_c)

Sol^n: we knows,
vander waal's equation for the real gas is

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

on simplifying the equation

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

Multiply with V^2 both side

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

Divide by P,

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

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

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

At critical temp., pressure and volume

$T = T_c$; $P = P_c$ and $V = V_c$

Substituting the value T and P in equation (i)

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

Also

$V = V_c$

$\therefore$ $V - V_c = 0$ and $(V - V_c)^3 = 0$

Simplifying this equation

$$V^3 - 3V_cV^2 + 3VV_c^2 - V_c^3 = 0 \quad \text{---(iii)}$$

Hence the coefficients of similar power of V must be equal in both the equation (ii) and (iii)

$$3V_c = \left[b + \frac{RT_c}{P_c} \right] \quad \text{---- (iv)}$$

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

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

Dividing equation (vi) with equation (v)

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

$$\therefore \quad V_c = 3b \quad \text{--- (vii)}$$

Substituting the value of V_c in equation (v)

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

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

Putting values of P_c and V_c in equation (iv)

$$3 \times 3b = \left[b + \frac{RT_c}{a/27b^2} \right]$$

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

$$\therefore RT_c \frac{27b^2}{a} = 8b$$

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

This is Formula of Critical Temperature