(c) Critical Points for van der Walls Gases

The van der Waals equation of state for a gas is given by

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

where P, V and T represent the pressure, volume and temperature respectively, and a and b are constant parameters. At the critical point, all the roots of the above cubic equation are degenerate means all roots are equal.

Mathematically, the critical isotherm is the point of inflection.

On the basis of above definition, one can find the critical volume V_c, critical pressure P_c and critical temperature T_c for van der Waal gas.

For van der Waals equation,

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

$$P=\frac{RT}{V-b}-\frac{a}{V^2} \qquad \text{(i)}$$

$$\left(\frac{\partial P}{\partial V}\right)_T=0\text{, for extremum point}$$

$$\left(\frac{\partial P}{\partial V}\right)_T=-\frac{RT}{(V-b)^2}+\frac{2a}{V^2}=0 \text{ at } V=V_c,\ T=T_c \qquad \text{(ii)}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T=0\text{, for inflection point}$$

$$\frac{2RT}{(V-b)^3}-\frac{6a}{V^3}=0\text{, at } V=V_c,\ T=T_c \qquad \text{(iii)}$$

Solving (ii) and (iii), $V_c=3b$ and $T_c=\frac{8a}{27Rb}$

On putting the value of V_c and T_c, one can get $P_c=\frac{a}{27b^2}$

$\frac{RT_c}{P_c v_c}=\frac{8}{3}=c_c$, which is popularly known as **critical coefficient** for van der Waals gas.