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PHYSICS B.Sc Part-I (H) & Sub. Paper-II Gr-B

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PHASE TRANSITION

First order Phase transition and claussius' clapeyron equation

The change of phase which takes place at constant temp and pressure & in which heat either absorbed or evolved during change of phase are called 1st order phase transition.

In this transition, entropy & density changes and Gibb's function G remains constat.

Let us consider an enclosure containing liquid and its saturated vapour then at at isothermal and isobaric change

$$g_1 = g_2$$

Let the temp is increased by dT, for equilibrium

$$g_1 + dg_1 = g_2 + dg_2$$

$$\Rightarrow dg_1 = dg_2$$

If the condition of saturation is satisfied.

$$\left(\frac{\partial g_1}{\partial T}\right)_{sat} = \left(\frac{\partial g_2}{\partial T}\right)_{sat} \quad \text{—— (A)}$$

If the Pressure also changes from P to P+dP

$$dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP.$$

$$\text{or, } \left(\frac{\partial g_1}{\partial T}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right) \quad \text{——— (A) (B)}$$

But for Unit mass.

$g = f\,S.$

$$dg = V\,dP - S\,dT$$

$$\text{or, } \left(\frac{\partial g}{\partial T}\right)_P = -S \quad \& \quad \left(\frac{\partial g}{\partial P}\right)_T = V$$

From equⁿ (A) (B)

$$\left(\frac{\partial g_1}{\partial T}\right)_{sat} = -S_1 + V_1 \left(\frac{\partial P}{\partial T}\right)_{sat} \quad \text{——— (B)}$$

$$\text{Similarly, } \left(\frac{\partial g_2}{\partial T}\right)_{sat} = -S_2 + V_2 \left(\frac{\partial P}{\partial T}\right)_{sat}$$

From equⁿ (A)

$$-S_1 + V_1\left(\frac{\partial P}{\partial T}\right)_{sat} = -S_2 + V_2\left(\frac{\partial P}{\partial T}\right)_{sat}$$

$$\text{or, } \frac{\partial P}{\partial T} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{dQ}{T\,(V_2 - V_1)}$$

$$\text{or, } \boxed{\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)}}$$

Latent heat

This is classius clapeyoon equation

SECOND ORDER PHASE TRASITION AND Ehrenfest's Equation

Second order Phase transition can be defined as the phenomenon that takes place with no change in entropy and volume at constant temp and pressure. The second order phase transition are (i) Transition of liquid helium I to helium II at λ point (ii) Transition of a ferromagnetic material to a paramagnetic material at curie point (iii) Transition of superconductor into ordinary conductor in the absence of magnetic field.

For a phase transition

$$g_1 = g_2 \text{ or } g_1 - g_2 = 0$$

or, $$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = S_2 - S_1 = 0$$

& $$\left(\frac{\partial g_2}{\partial P}\right)_T + \left(\frac{\partial g_1}{\partial P}\right)_T = V_2 - V_1 = 0$$ — (A)

Now $$C_p = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial}{\partial T}\left\{\frac{\partial g}{\partial T}\right\}_P\right) = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_P$$ — (B)

the Isothermal compressibility (K) is given by,

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_P = -\frac{1}{V}\frac{\partial}{\partial P}\left(\frac{\partial g}{\partial P}\right)_T$$

or, $$\boxed{K.V. = -\frac{\partial^2 g}{\partial P^2}}$$ — (C)

The volume coefficient of expansion.

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P \Rightarrow \alpha V = \frac{\partial^2 g}{\partial T \cdot \partial P}$$ — (D)

From equ^n B.

$$\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P = \frac{C_{p_1} - C_{p_2}}{T}$$ — (E)

From equ^n(C) $$\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P^2}\right)_T = V[K_1 - K_2]$$ — (F)

From equ^n(D) $$\frac{\partial^2 g_2}{\partial T \cdot \partial P} - \frac{\partial^2 g_1}{\partial T \partial P} = V(\alpha_2 - \alpha_1)$$

For Second order Phase transition

$$dS_1 = dS_2$$

But $$dS = \left(\frac{dS}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \frac{C_p}{T} dT - \left(\frac{dV}{\partial T}\right)_P dP$$

$$= \left(\frac{C_p}{T}\right) dT - \alpha V \, dP$$

$\because dS_1 = dS_2$

$$\Rightarrow \left(\frac{C_{p_1}}{T}\right) dT - \alpha_1 V dP = \frac{C_{p_2}}{T} dT - \alpha_2 V dP$$

$$\frac{C_{p_1} - C_{p_2}}{T} = V \frac{(\alpha_1 - \alpha_2)\, dP}{\partial T}$$

or, $$\boxed{\frac{dP}{dT} = \frac{C_{p_1} - C_{p_2}}{V(\alpha_1 - \alpha_2)}} \quad \text{(X)}$$

Again $V = f(T, P)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\because \quad \Rightarrow \cancel{\frac{\partial^2 g}{\partial P \partial T} dT} = \frac{\partial^2 g}{\partial P \partial T} dT + \frac{\partial^2 g}{\partial P^2} dP$$

$\because dV_1 = dV_2$

$$\therefore \frac{\partial^2 g_1}{\partial P \partial T} dT + \frac{\partial^2 g_1}{\partial P^2} dP = \frac{\partial^2 g_2}{\partial P \partial T} dT + \frac{\partial^2 g_2}{\partial P^2} dP$$

$$\left[\frac{\partial^2 g_1}{\partial P^2} - \frac{\partial^2 g_2}{\partial P^2}\right] dP = \left[\frac{\partial^2 g_2}{\partial P \partial T} - \frac{\partial^2 g_1}{\partial P \partial T}\right] dT$$

$$\cancel{V}(K_2 - K_1)\, dP = \cancel{V}(\alpha_2 - \alpha_1)\, dT$$

$$\boxed{\frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{K_2 - K_1}} \quad \text{(Y)}$$

The eqn X & Y are called Ehrenfest's equations