PHASE TRANSITIONS

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$$dG = V\,dP - S\,dT \quad -(1)$$

$$dT = 0$$

$$dP = 0$$

$$dG = 0$$

$$\Rightarrow G = \text{Const}$$

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

EQUILIBRIUM BETWEEN PHASES AND THE PHASE TRANSITIONS

$$G = m_1 g_1 + m_2 g_2 \quad \text{--- (2)}$$

δm_1 & δm_2

but $\delta m_1 + \delta m_2 = 0$

$$\Rightarrow \delta m_1 = -\delta m_2$$

In this infinitesimal phase change

$$\delta G = 0$$

$$(2) \Rightarrow \delta G = \delta m_1 g_1 + \delta m_2 g_2$$

$$0 = \delta m_1 (g_1 - g_2)$$

$$\Rightarrow \boxed{g_1 = g_2} \quad \text{--- (3)}$$

$$g_1 + dg_1 = g_2 + dg_2 \quad -(1)$$

$$\Rightarrow dg_1 = dg_2 \quad -(2)$$

g being a f^n of T & P

$$dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP \quad -(3)$$

$$dg_2 = \left(\frac{\partial g_2}{\partial T}\right)_P dT + \left(\frac{\partial g_2}{\partial P}\right)_T dP \quad -(4)$$

Equating eq^n (3) & (4)

$P + dP$

$T + dT$

$g \rightarrow P\ T$

$1 \rightarrow g_1 + dg_1$

$2 \rightarrow g_2 + dg_2$

FIRST ORDER PHASE TRANSITIONS: CLAUSIUS-CLAPEYRON EQUATION

$$\left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP = \left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_2}{\partial P}\right)_T dP$$

$$\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$$

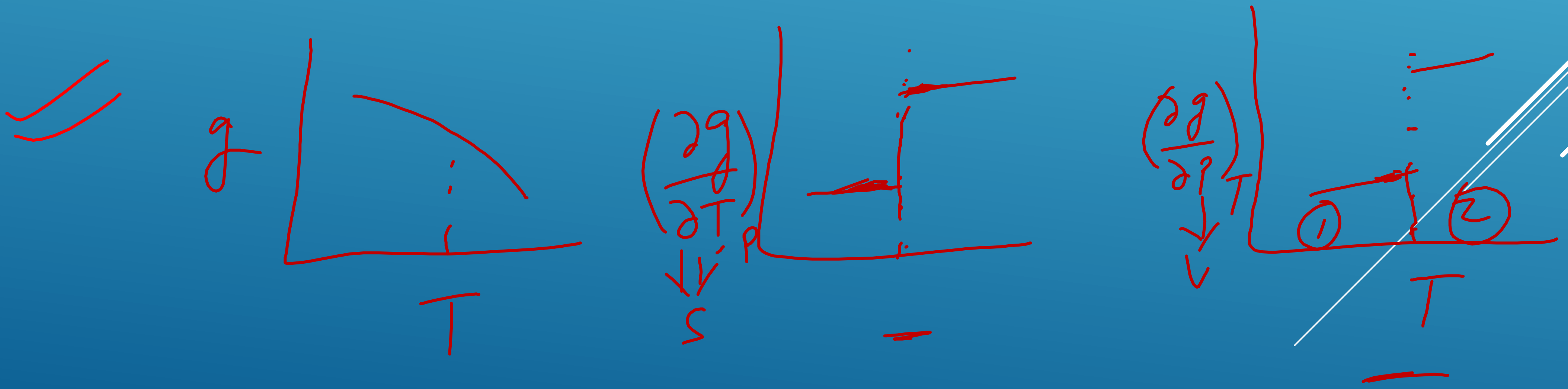
$$-S_1 \qquad V_1 \qquad -S_2 \qquad V_2$$

$$\Rightarrow -S_1\, dT + V_1\, dP = -S_2\, dT + V_2\, dP$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \quad -(5)$$

$$S_2 - S_1 = \frac{\delta Q}{T} = \frac{L}{T}$$

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



$$g_1 = g_2 \Rightarrow g_1 - g_2 = 0 \quad - (1)$$

$$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = s_2 - s_1 = 0 \quad - (2)$$

$$\& \quad \left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = v_2 - v_1 = 0 \quad - (3)$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_P$$

$$\left(\frac{\partial Q}{\partial T}\right)_P$$

SECOND ORDER PHASE TRANSITIONS: EHRENFEST'S EQUATIONS

$$\left(\frac{C_p}{T}\right) = \left(\frac{\partial s}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[-\left(\frac{\partial g}{\partial T}\right)_p\right]_p = -\left(\frac{\partial^2 g}{\partial T^2}\right)_p \quad \text{— (4)}$$

Isothermal compressibility

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{— (5)}$$

$$\Rightarrow KV = -\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_T$$

$$KV = -\left(\frac{\partial^2 g}{\partial P^2}\right)_T \quad \text{— (6)}$$

Isobaric volume expansivity

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{— (7)}$$

↘ coeff of expansion

$$\Rightarrow \alpha V = \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_P$$

$$\Rightarrow \alpha V = \left(\frac{\partial^2 g}{\partial T \partial P}\right) \quad - (8)$$

$$\frac{C_{P_1}}{T} = -\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P \quad - (9)$$

$$\frac{C_{P_2}}{T} = -\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P \quad - (10)$$

$$\Rightarrow \left(\frac{\partial^2 g_2}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P = \frac{C_{P_1} - C_{P_2}}{T} \quad - (11)$$

$$\left(\frac{\partial^2 g_2}{\partial p^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial p^2}\right)_T = v(K_1 - K_2) \quad \text{— (12)}$$

&

$$\left(\frac{\partial^2 g_2}{\partial T \partial P}\right) - \left(\frac{\partial^2 g_1}{\partial T \partial P}\right) = v(\alpha_2 - \alpha_1) \quad \text{— (13)}$$

$$s_1 = S_2$$

$$\Rightarrow \quad s_1 + ds_1 = S_2 + dS_2$$

$$\Rightarrow \underline{\underline{dS_1}} = \underline{\underline{dS_2}} \quad \text{— (14)}$$

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

$$= \left(\frac{C_P}{T}\right) dT - \underline{\underline{\left(\frac{\partial V}{\partial T}\right)_P}} dP$$

$$dS = \left(\frac{C_P}{T}\right) dT - V\alpha\, dP \quad - (15)$$

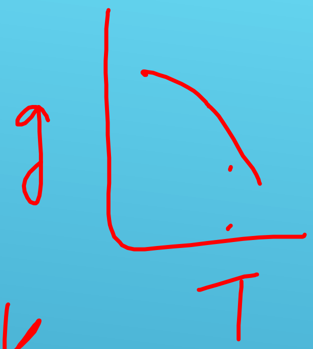
$$dS_1 = \left(\frac{C_{P_1}}{T}\right) dT - V\alpha_1\, dP \quad - (16)$$

$$dS_2 = \left(\frac{C_{P_2}}{T}\right) dT - V\alpha_2\, dP \quad - (17)$$

$$\left(\frac{C_{P_1}}{T}\right) dT - V\alpha_1\, dP = \left(\frac{C_{P_2}}{T}\right) dT - V\alpha_2\, dP$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{C_{P_2} - C_{P_1}}{TV(\alpha_2 - \alpha_1)}} \quad - (18)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$



$$\left(\frac{\partial V}{\partial P}\right)_T = -VK$$

$$dV = V\alpha\, dT - VK\, dP$$

$$\Rightarrow V\alpha_1\, dT - VK_1\, dP = V\alpha_2\, dT - VK_2\, dP$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{K_2 - K_1}} \quad \text{—} (19)$$

Eq^n (18) & (19) are Ehrenfest's Eq^n for second order phase transition

THANKYOU