B.Sc Part - II ; Paper - III (A)

Phase rule : ⟹ $F = C - P + 2$ (F is the no. of variables)

~~Consider~~ Let a heterogeneous system in equilibrium of C components in which P phases are present. Since state of the system will depend upon the ~~number of phases~~ temp and pressure, these two variables are always there. The concentration variables of each components depends upon the no. of phase.

Since if the concentration of (C-1) components are known then concentration of last component is automatically fixed hence (C-1) component term are needed to expressed the composition of the system. For P phases, the total no. of concentration variables is $P(C-1)$

Therefore total variables of the system is equal to $[P(C-1) + 2]$.

From thermodynamic consideration if the phases are in equilibrium then partial molal free energy of every component in different phases is the same since ~~when~~ P phases are present hence (P-1) equations are available for each component and for C component, the total no. of equations are $C(P-1)$. These eqn cannot be varry and hence degree of freedom f = Total no. of variable - no. of equation

$$F = [P(C-1) + 2] - [C(P-1)]$$

$$= PC - P + 2 - PC + C = C - P + 2$$

This is called the phase rule

Q. Explain why in phase diagram of water system the solid - vapour & liquid - vapour lines have (+)ve slopes while the solid - liquid has a (-)ve slope.

Ans. The clapeyron equation decides the sign of slops of the lines represented by the two phase equilibria. The slope of the lines for solid - liquid & liquid - vapour equilibria is always (+)ve as entropy change (ΔS) & volume change (ΔV) both are (+)ve for such equilibria. But the sign of $\frac{dP}{dT}$ for solid . liquid equilibria depends on their relative densities or volumes.

By clapeyron equation

$$\frac{dP}{dT} = \frac{S_V - S_S}{T(V_V - V_S)} = \frac{+ve}{+ve} = +ve \quad \text{(for solid - vapour)}$$

$$\frac{dP}{dT} = \frac{S_V - S_L}{T(V_V - V_L)} = \frac{+ve}{+ve} = +ve \quad \text{(for liquid - vapour)}$$

$$\frac{dP}{dT} = \frac{S_L - S_S}{T(V_L - V_S)} = \frac{+ve}{-ve} = (-)ve \quad \text{(for (ice) solid + liquid)}$$

~~$(V_L - V_S)$ is $(-)ve$ as V_S~~

Since $V_S > V_L$ for water system

Therefore $V_L - V_S = (-)ve$