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Deg II Chem. Hons, Paper - III

Topic :- Thermodynamics

Clapeyron - clausius equation :-

This equation is applicable whenever any given substance is present in two Phases in equilibrium with each other. For example, in the melting of a solid, the two Phases in equilibrium are the solid and the liquid ($S \rightleftarrows L$) and in the evaporation of a liquid, the two Phases in equilibrium are the liquid and the vapour ($L \rightleftarrows V$)

Similarly, in the case of allotropic transformations at the transition Point, the two Phases in equilibrium are the two allotropic form of the substance eg $S_R \overset{95.6^{\circ}C}{\rightleftarrows} S_M$)

The equation may be deduced from the free energy considerations :- suppose a system contains one component which exists in two Phases A and B. Let the temperature and Pressure be T & P respectively.

Let the free energy per mole of the substance in the two phases be G_A and G_B since the system is in equilibrium there is no free energy change.

ie $G_A = G_B$ ——— (1)

If the temperature of the system is now raised to $T+dt$, the pressure will rise as well. Let the new pressure be $P+dp$. The free energy per mole will also increase to $G_A + dG_A$ in the phase A and to $G_B + dG_B$ in Phase B. However, since the two phases are still in equilibrium

$$G_A + dG_A = G_B + dG_B \quad —(2)$$

$$\therefore dG_A = dG_B.$$

Since the various equilibrium to be considered under the clapeyron equation the work done is only due to volume change the equation

$dG = Vdp - SdT$ is applicable

$dG_A = V_A dp - S_A dT$ for Phase A

$dG_B = V_B dp - S_B dT$ for Phase B

Where V_A and V_B are the molar volumes and S_A and S_B are the molar entropies

of the Component in the two Phase A and B respectively.

$$V_A dp - S_A dT = V_B dp - S_B dT$$

or $$dp (V_B - V_A) = dT (S_B - S_A)$$

or $$\frac{dp}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{V_B - V_A}$$

Where ΔS = Increase of entropy when the System changes from state A to state B.

If q is the heat absorbed per mole of the substance during the phase transformation at the temperature T then $$\Delta S = \frac{q}{T}$$

Hence $$\frac{dp}{dT} = \frac{q}{T(V_B - V_A)}$$

This is the clapeyron - clausius equation. V_A and V_B are the molar volume of substance in the two phases A and B respectively. $V_B - V_A$ represents the change in volume when 1 mole of the substance changes from Phase A to Phase B.