

BSc. II (H), Paper - IIIA

Gibbs-Helmholtz equation

From definition of Gibbs free energy (G)

$$G = H - TS \quad \text{--- (i)}$$

As G is a state function and process is at a isothermal hence

$$G_1 = H_1 - TS_1 \quad \text{initial state --- (ii)}$$

$$a) \quad G_2 = H_2 - TS_2 \quad \text{final state --- (iii)}$$

$$\text{or: } G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1) \\ = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \quad \text{--- (iv)}$$

Here ΔG is the change in free energy of the system

ΔH is change in Enthalpy of the system

ΔS is change in Entropy of the system

Now again from eqn (i)

$$G = E + PV - TS \quad \text{as } H = E + PV$$

Differentiating both side we get

$$dG = dE + PdV + VdP - TdS - SdT \quad \text{--- (v)}$$

But

$$dS = \frac{q_{rev}}{T} = \frac{dE + PdV}{T}$$

$$\text{or } TdS = dE + PdV \quad \text{--- (vi)}$$

putting value of eqn (vi) in eq (v)

$$dG = dE + PdV + VdP - dE - PdV - SdT$$

$$\text{or } dG = VdP - SdT \quad \text{--- (vii)}$$

$$\text{If } P = 0, VdP = 0$$

$$\text{then } \left(\frac{dG}{dP}\right)_P = -(SdT)_P$$

$$\text{or } \left(\frac{dG}{dT}\right)_P = -S$$

$$\text{For initial state } \left(\frac{\partial G_1}{\partial T}\right)_P = -S_1 \quad \text{--- (viii)}$$

$$\text{and Final state } \left(\frac{\partial G_2}{\partial T}\right)_P = -S_2 \quad \text{(ix)}$$

$$\text{or, } \left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -S_2 + S_1 = -(S_2 - S_1)$$

$$\text{or } \left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -\Delta S \quad \text{--- (x)}$$

$$\text{or } \left(\frac{\partial (G_2 - G_1)}{\partial T}\right)_P = -\Delta S$$

$$\text{or } \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \quad \text{--- (xi)}$$

putting value of $-\Delta S$ in (iv) we get

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T}\right)_P$$

This is most common form of Gibbs Helmholtz equation. --- X ---