B.Sc. II (H). Paper - III A

Change in free energy with temperature and pressure

From definition of free energy

$$G = H - TS \quad \text{— (i)}$$

and from definition of enthalpy:

$$H = E + PV \quad \text{— (ii)}$$

From equation (i) and (ii)

$$G = E + PV - TS \quad \text{— (iii)}$$

differentiating this eq (iii)

$$dG = dE + Vdp + Pdv + Tds - SdT \quad \text{— (iv)}$$

From definition of entropy

$$dS = \frac{\delta q_{rev}}{T} \quad \text{— (v)}$$

and from first law of thermodynamics:

$$dq_{rev} = dE + Pdv \quad \text{— (vi)}$$

From (v) and (vi)

$$dS = \frac{dE + Pdv}{T}$$

or $TdS = dE + PdV$ — (vii)

putting value of eqn (vii) in eqn (iv)

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

or $dG = Vdp - SdT$ — (viii)

This is called total differential equation of free energy.

At constant temperature, $dT = 0$

equation (viii) will be.

$$\left(\frac{dG}{dp}\right)_T = V \quad \text{— (ix)}$$

i.e change of free energy with pressure at constant temperature is equal to volume of the system

and at constant pressure, $dp = 0$

equation (viii) will be

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