B.Sc Part I (Physics Hons)
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Question:- Establish Gibbs - Helmholtz equation and indicate its important.?

Ans:- **Gibbs - Helmholtz Equation:-**

The internal energy of U of a system is the energy which it possesses due to its molecular constitution and motion. In general it is the sum of the K.E of the molecules due to their motion and P.E of the molecules due to their mutual attraction.

The free energy of a system has been defined Helmholtz free energy or "Thermodynamic Potential" at constant volume is given by

$$F = U - TS \quad \text{---------- (1)}$$

Here T is the temperature and S is entropy of the system. Let us suppose that the system undergoes at infenetesimal reversible ~~engine~~ change. The change in F will be given as

$$dF = dU - (Tds + SdT)$$

But $dU = dQ - dW$ and $dQ = Tds$ (from 2nd law)

$$\Rightarrow dU = Tds - dW$$

$$\therefore dF = Tds - dW - Tds + SdT$$

$$= -dW - SdT$$

But $dW = PdV$ ---------- (2)

$$\therefore dF = PdV - SdT$$

Writing the partial differential of F at constant volume ($dV = 0$)

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

from equation (1) we have

$$F = U - T\left\{-\left(\frac{\partial F}{\partial T}\right)_V\right\}$$

$$= U + T\left(\frac{\partial F}{\partial T}\right)_V$$

$$\therefore U = F - T\left(\frac{\partial F}{\partial T}\right)_V \quad \text{---------- (3)}$$

This is the required Gibbs - Helmholtz equation.

Importance:-

This equation does not involve the entropy S whose calculation is often difficult. It can easily

be applied to study the thermodynamic of isothermal changes in a chemical system.

Let us suppose that the chemical system changes isothermaly at temp. T from stat ① to state ②. Than from Gibbs-Helmholtz eq^n

$$U_2 - U_1 = F_2 - F_1 \text{ or } -T\frac{\partial}{\partial T}(F_2 - F_1)V$$

$$\text{or } \Delta U = \Delta F - T\left[\frac{\partial}{\partial T}\Delta F\right]_V \quad - - - - - \quad (4)$$

In the case of isothermal change $dT = 0$, from eq^n (2)

$$dF = -dW \text{ or } dW = -dF$$

which is the work obtained from the system during a reversible change, and from the Ist law of thermodynamics $-\Delta U = U_r$, which is the heat of reaction at constant volume.

$$\therefore -U_r = -W - T\left[\frac{\partial}{\partial T}(-W)\right]$$

$$\text{or } W - U_r = T\frac{dW}{dT}$$

We can calculate the variation of W with temperature, i.e we can calculate the temp. at which the required amount of work would be obtained from the system.