

**B.Sc Part-I (H) & Sub. Paper-II Gr-B**  
**PHYSICS**  
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**Thermodynamical Potential (Function)**

Thermodynamical Function :- The state of thermodynamic system of constant may be specified in terms of  $P, V, U, T$  and  $S$  between which two thermodynamical relation exist

$$dQ = du + PdV$$

and  $dQ = Tds$

For complete description of the behaviour of such system, some other relation are required. These relation are simplified when certain function of above variable are introduced.

- There are four thermodynamical function
- (a) Internal energy (U)      (b) Gibbs function (G)
  - (c) Enthalpy (H)            (d) Helmholtz function (F)

① Internal energy (U) :- The internal energy  $U$  of a system is a thermodynamical variable. Let a system undergoes an infinitesimal reversible change from one equilibrium state to another. The change in internal energy is given by

$$\begin{aligned} du &= dQ - PdV \\ &= Tds - PdV \end{aligned}$$

Now  $\left(\frac{\partial u}{\partial s}\right)_V = T$  and  $\left(\frac{\partial u}{\partial V}\right)_S = -P$

Now  $du$  is perfect differential so that

$$\begin{aligned} \frac{\partial}{\partial V} \left(\frac{\partial u}{\partial s}\right) &= \frac{\partial}{\partial s} \left(\frac{\partial u}{\partial V}\right) \\ \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S &= \left(\frac{\partial P}{\partial s}\right)_V \checkmark \end{aligned}$$

② Helmholtz function (F) :- The Thermodynamic Potential ~~at~~ at constant volume i.e Helmholtz function is defined by the equation,

$$F = U - TS$$

Since U, T and S are perfect differentials. The change in Helmholtz free energy

$$dF = du - Tds - sdt$$

$$\text{or } dF = \underline{Tds - PdV} - Tds - sdt$$

$$= -PdV - sdt$$

At constant Volume,  $dV = 0$

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

$$\therefore U = F + TS$$

$$U = F - T \frac{\partial F}{\partial T}$$

This is K/a Gibb's Helmholtz equation

③ Enthalpy (H) :- The enthalpy (H) of thermodynamic function is defined as

$$H = U + PV$$

When the system undergoes an infinitesimal process from one equilibrium state to another equilibrium state then the change in enthalpy:

$$dH = du + PdV + VdP$$

$$dH = dQ + VdP$$

For isobaric change  $dP = 0$

$$\therefore dH = dQ$$

If  $H_i$  and  $H_f$  are the initial and final enthalpy then  $(H_f - H_i) = dQ$ .

Hence the change in enthalpy during isobaric process is equal to heat transferred.

4) Gibbs function (G): - This is also k/a Gibbs free energy or thermodynamical potential at constant Pressure. It is defined as

$$G = H - TS$$

$$G = U + PV - TS$$

$$\Rightarrow dG = du + PdV + VdP - Tds - SdT$$

$$\text{or, } dG = VdP - SdT$$

In reversible process, the Gibbs function G

If the process is irreversible, at constant Pressure  $dG = 0$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

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

### PHASE TRANSITION

#### First order Phase transition and clausius clapeyron equation

The change of phase which takes place at constant temp and pressure & in which heat either absorbed or evolved during change of phase are called 1st order phase transition

In this transition, entropy & density changes and Gibbs function G remains constant

Let us consider an enclosure containing liquid and its saturated vapour then at isothermal and isobaric change

Let the temp is increased by  $dT$ , for equilibrium  $g_1 = g_2$   
 $g_1 + dg_1 = g_2 + dg_2$

$$\Rightarrow dg_1 = dg_2$$

If the condition of saturation is satisfied.

$$\left(\frac{\partial g_1}{\partial T}\right)_{\text{sat}} = \left(\frac{\partial g_2}{\partial T}\right)_{\text{sat}} \quad \text{--- (A)}$$