

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

Thermodynamical Function :- The state of thermodynamics 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

$$du = dQ - PdV$$

$$= Tds - PdV$$

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

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$$

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

$$g_1 = g_2$$

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

$$\Rightarrow dg_1 = dg_2$$

If the condition of saturation is satisfied.

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