Thermodynamic Potential or Gibbs Function :-

The Gibbs function G of a system is given by

$$G = U - TS + PV$$

Let us consider a system that can do other forms of work in addition to P.dV work, e.g. a voltaic cell. In the case of a voltaic cell, the electrical work is $-E.dI$. Similarly for a magnetic material, the magnetic work is $-M dH$. In general the work will be given by P.dV plus a sum of terms each being the product of intensive variable (such as P, E or M) and the differential of an extensive variable (such as dV, dI and dH). In the case of a voltaic cell, the intensive variable is E and differential of extensive variable of dI.

Suppose in general, in addition to P.dV the intensive variables is Y and differential of extensive variable is dx. The work done for any reversible process

$$\delta W = P.dV + Y.dx$$

$$W = \int_{V_1}^{V_2} P.dV + \int_{x_1}^{x_2} Y.dx$$

take $\int_{x_1}^{x_2} Y.dx = A$

Let us consider a process where the system works at constant pressure P_0 and the change in volume $(V_2 - V_1)$

$$\therefore \int_{V_1}^{V_2} P.dV = P_0 (V_2 - V_1)$$

$$\therefore W = P_0 (V_2 - V_1) + A \quad \text{— (i)}$$

For a system that exchanges the heat with a reservoir temperature,

$$W \leq (U_1 - U_2) - T_0 (S_1 - S_2) \quad \text{— (ii)}$$

$P_0(V_2 - V_1) + A \leq (U_1 - U_2) - T_0(S_1 - S_2)$

$$A \leq (U_1 - U_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2) \quad \text{--- (iii)}$$

Let us consider a specific process, where the initial and the final states of the system and surroundings are at the same tempr. (T_0) and pressure (P_0).

$$T_0 = T \quad \text{and} \quad P_0 = P$$

From eqn (iii),

$$A_{P,T} \leq (U_1 - U_2)_{P,T} - T(S_1 - S_2)_{P,T} + P(V_1 - V_2)_{P,T} \quad \text{--- (iv)}$$

But for the Gibbs function $G = U - TS + PV$ — (v)

Therefore, for two equilibrium states at the same pressure and tempr.

$$(G_1 - G_2)_{P,T} = (U_1 - U_2)_{P,T} - T(S_1 - S_2)_{P,T} + P(V_1 - V_2)_{P,T} \quad \text{--- (vi)}$$

From eqn (iv) and (vi)

$$A_{P,T} \leq (G_1 - G_2)_{P,T} \quad \text{--- (vii)}$$

Thus, the difference between Gibbs function of a system between two equilibrium states sets the maximum limit to the work in addition to P.dV work provided the initial and the final states are at the same pressure and temperature and the system exchanges heat with a single heat reservoir. The work done will be maximum when the process is reversible. The process in this case will be isothermal - isobaric. If the process is irreversible, work done will be less than maximum.