

## Gibbs Free Energy

It is the thermodynamic state function related to enthalpy & entropy.

$$G = H - TS$$

The free energy ( $G$ ) of system is a measure of available energy for doing useful work.

Energy available for useful work = Total energy available - New available form of energy

$$\Rightarrow \Delta G = \Delta H - \Delta(TS)$$
$$= \Delta H - \Delta T \cdot S - T \Delta S$$

At constant temperature, ( $\Delta T = 0$ )

$$\therefore \Delta G = \Delta H - T \Delta S$$

But,  $\boxed{\Delta H = \Delta E + P \Delta V}$   $\rightarrow$  Enthalpy formula (at const pressure)

$$\therefore \Delta G = \Delta E + P \Delta V - T \Delta S$$

$\swarrow$  internal energy       $\swarrow$  work done on/by system       $\swarrow$  newly available energy  
(At constant pressure & temperature)

General form :-  $\Delta G = \pm \Delta H \pm T \Delta S$

Here,  $+\Delta H \rightarrow$  endothermic  
 $-\Delta H \rightarrow$  exothermic

$+T \Delta S \rightarrow$  entropy decrease (System contraction)  
 $-T \Delta S \rightarrow$  entropy increase (System expansion)

$+P \Delta V \rightarrow$  System expansion  
 $-P \Delta V \rightarrow$  System contraction

Derivation (in terms of  $\Delta A = -W_{\max}$ )

$$G = H - TS$$
$$\Rightarrow \Delta G = \Delta H - T\Delta S \quad (\text{const temperature})$$

Here,  $\Delta S = \frac{q_{\text{rev}}}{T} \Rightarrow T\Delta S = q_{\text{rev}}$

and  $\Delta H = \Delta E + p\Delta V$  (const pressure)

$$\therefore \Delta G = \Delta E + p\Delta V - q_{\text{rev}}$$

But,  $\Delta A = \Delta E - T\Delta S$

$$\Rightarrow \Delta E = \Delta A + T\Delta S$$

$$\begin{aligned}\therefore \Delta G &= \Delta A + T\Delta S + p\Delta V - q_{\text{rev}} \\ &= \Delta A + \cancel{T\Delta S} + p\Delta V - \cancel{T\Delta S} \\ \Rightarrow \Delta G &= \Delta A + p\Delta V\end{aligned}$$

But,  $\Delta A = -W_{\max}$  (helmholtz eq<sup>n</sup>)

$$\therefore \Delta G = -W_{\max} + p\Delta V$$
$$\Rightarrow -\Delta G = W_{\max} - p\Delta V$$

$\therefore$  When  $\Delta G$  is -ve, Maximum work is done  
When  $\Delta G$  is +ve, Minimum work is done