

Deg II Chem. Hons, Paper - III

Topic :- Thermodynamics

Work & Free energy function (Rest)

Let us suppose that the values of three functions in equation (1) at constant temperature  $T$  be  $A_1$ ,  $E_1$  and  $S_1$  then

$$A_1 = E_1 - TS_1 \quad \text{--- (3)}$$

Let an appreciable change take place at the same temperature  $T$  so that the value of three functions become  $A_2$ ,  $E_2$  and  $S_2$  Then

$$A_2 = E_2 - TS_2 \quad \text{--- (4)}$$

Subtracting eq. (3) from eq. (4) we get

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

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

$\Delta A =$  Increase in the function  $A$ ,

$\Delta E =$  Corresponding increase in internal energy

$\Delta S =$  Increase in the entropy of the system.

~~Let~~

suppose the change under reference is brought about

reversibly at constant temperature  $T$  and that the heat absorbed is equal to  $q_r$ . Then, evidently, the increase of entropy is given by

$$\Delta S = \frac{q_r}{T}$$

$$\therefore \Delta A = \Delta E - T \cdot \frac{q_r}{T}$$

$$\therefore \Delta A = \Delta E - q_r \quad \text{--- (5)}$$

But from the 1st Law of Thermodynamics  $\Delta E = q_r - W$

$$\therefore -W = \Delta E - q_r \quad \text{--- (6)}$$

Comparing eq. (5) and (6) we get

$$\boxed{-\Delta A = W} \quad \checkmark \quad \text{--- (7)}$$

Since the process was carried out reversibly  $W_r$  represents the maximum work.

It is thus clear that decrease in the function  $A$  (ie  $-\Delta A$ ) gives the maximum work that can be obtained from the system during the given change.  $A$  is therefore, termed as "work function".

Free energy function :-

Considering equation (2)

$$G = H - TS$$

If  $G_1, H_1$  and  $S_1$  represent thermodynamic functions for the system in its initial state and  $G_2, H_2$  and  $S_2$  in the final state, temperature remaining constant at  $T$  we have

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\therefore \Delta G = \Delta H - T\Delta S \quad \text{--- (8)}$$

We know that at constant pressure

$$\Delta H = \Delta E + P\Delta V$$

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

$$\text{or } \Delta G = (\Delta E - T\Delta S) + P\Delta V$$

$$\Delta G = \Delta A + P\Delta V$$

Since  $\Delta A = -W$

$$\therefore \Delta G = -W + P\Delta V$$

$$\text{or } \boxed{-\Delta G = W - P\Delta V} \quad \checkmark \text{--- (9)}$$

Work other than that due to change in volume is called net work.

$$-\Delta G = \text{net work}$$

$$-\Delta G = \text{Decrease in free energy}$$

infer

The net work that it measures

may be electrical work or chemical work which is very useful in Physical Chemistry