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for Hons. (II), Paper III, Grp: A, Lect: 10

Work function [A] → Work function is the difference of internal energy of object & the product of temperature & entropy. It is denoted by 'A'.

$$A = E - TS$$

where A = Work function. E = Internal energy.
T = temperature, & S = Entropy.

- It is an extensive property, means it depends on the mass of the system.
- It is state function, means PVT dependent but path independent.
- In Cyclic process, $\Delta E = 0$, $\Delta T = 0$, so, $\Delta S = 0$
  So $\Delta A = 0$.

We know $A = E - TS$ —— I

$dA = dE - Tds - SdT$ —— II

from 1st law of Thermodynamics

$dq = dE + W_{rev.}$ —— III

from entropy $\Delta S = \frac{dq}{T}$ or $dq = Tds$ — IV

from equation IV we put the value of dq in equation III we have

$Tds = dE + W_{rev.}$

or $dE = Tds - W_{rev.}$ —— ~~IV~~ V

Now we put the value of dE from eqn V to II we have

$$dA = T\cancel{dS} - w_{rev} - T\cancel{dS} - SdT$$

$$dA = -w_{rev} + SdT \qquad \text{———} \quad \underline{VI}$$

At constant temperature (Isothermal condition)

$dT = 0$

So Modified equation of $\underline{VI}$ in Isothermal condition: $dA = -w_{rev} + S\times 0$

$$\boxed{dA = -w_{rev.}}$$

$$\text{or } \boxed{-dA = w_{rev.}} \qquad \text{———} \quad \underline{VII}$$

By the above expression it is clear that the maximum reversible work done by the system can be given by the decreases in work function at constant temperature.

When the process or reaction is spontaneous the value of $\Delta A = -ve$.

Gibb's free energy (G): The useful energy available in a system is called Gibb's free energy. It is denoted by G.

$G = H - TS$

Means, free energy is the difference of enthalpy & the product of temperature & entropy.

$$G_1 = H_1 - TS_1$$
$$G_2 = H_2 - TS_2$$

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$
or $\boxed{\Delta G = \Delta H - T\Delta S}$

Relation between ΔG & spontaneity:-

i) $\Delta G = -ve$, It favours to spontaneous processes.
ii) $\Delta G = +ve$: It favours to non spontaneous processes
iii) $\Delta G = 0$ At Equilibrium.

Rel. between ΔG & Net work done:-

$$G = H - TS \qquad \text{—— I}$$
or $$G = E + PV - TS \qquad (\because H = E + PV)$$
$$dG = dE + Pdv + Vdp - Tds - SdT \qquad \text{—— ii}$$

We know from preveous relation of ΔA & W_{rev}.
$dE = Tds - W_{rev}$. When the value of dE is subjected in equation ii we have

$$dG = \cancel{T}ds - W_{rev} + Pdv + Vdp - \cancel{T}ds - SdT$$
$$dG = -W_{rev} + Pdv + Vdp - SdT \qquad \text{—— iii}$$

We know W_{rev} = Mechanical work + Non mechanical work.

$W_{rev} = Pdv + W_{net}$, the value of W_{rev} is subjected to equation III we have

$$dG = -P\cancel{d}v - w_{net} + Pdv + Vdp - SdT$$

$$dG = Vdp - SdT - w_{net} \quad \text{—— IV}$$

At Constant temperature (Isothermal) $dT = 0$.
and at Constant Pressure (Isobar) $dp = 0$.

$$\text{So} \quad \boxed{(dG)_{T,P} = -w_{net}} \quad \text{—— V}$$

Amount of maximum work done at Constant temperature and pressure over and above the mechanical work is equal to the decrease in free energy of the System.

<u>Variation of Free energy with pressure at Constant temperature</u> :→

By equation IV, $dG = Vdp - SdT - w_{net}$
If the System does only mechanical work $w_{net} = 0$

$$\text{then } dG = Vdp - SdT$$

At Constant temperature (Isothermal) $dT = 0$

$$(dG)_T = Vdp \quad \text{—— VI}$$

When the State of System changes from initial to final State, then total change in free energy $= \int_1^2 dG = \int_1^2 Vdp$ —— VII

For an ideal gas $PV = nRT$, or $P = \frac{nRT}{V}$ — VIII
When we put the value of P from equation VIII to VII we have :-

$$\Delta G = nRT \int_1^2 \frac{dP}{P}$$

$$\boxed{\Delta G = nRT \ln\frac{P_2}{P_1}} \longrightarrow \text{(ix)}$$

OR

$$\boxed{\Delta G = nRT \ln\frac{V_1}{V_2}} \text{ — (x)} \quad \left(\because P_1V_1 = P_2V_2 \text{ or } \frac{P_2}{P_1} = \frac{V_1}{V_2}\right)$$

The above expression is able to predict the value of change in free energy even in expansion or compression.

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