Class ⇒ B.Sc.(Hons.) Part-II
Subject ⇒ Chemistry
Chapter ⇒ Thermodynamics
Topic ⇒ Work function and Free energy.

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WORK FUNCTION
OR
Helmholtz free energy
OR
Helmholtz function

A thermodynamic quantity which is used in the study of thermodynamics is called work function or Helmholtz free energy or Helmholtz function.

This is denoted by A and is defined by the equation.

$$A = U - TS \quad \text{——— (1)}$$

Where U = Internal energy of the system
T = Temperature.
S = Entropy

Since, U, T and S are the functions of the state of the system only and do not depend upon its previous history, therefore, A also must be a state function.

In order to understand the physical significance of the work function, consider an isothermal change taking place at temperature T, then

$$A_1 = U_1 - TS_1 \quad \text{for the Initial state} \quad \text{——— (2)}$$

and $$A_2 = U_2 - TS_2 \quad \text{for the final state} \quad \text{——— (3)}$$

Where A_1, U_1 and S_1 are respectively the values of

work function, Internal energy and entropy of the system in the initial state and A_2, U_2 and S_2 are the corresponding values in the final state.

∴ Change in the function A accompanying the process is given by

$$A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1)$$

or $$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1)$$

$$\therefore \Delta A = \Delta U - T\Delta S \quad \text{——— (4)}$$

According to the definition of entropy

$$\Delta S = \frac{q_{rev.}}{T} \quad \text{——— (5)}$$

According to the first law of Thermodynamics as applied to an isothermal reversible process, we have,

$$\Delta U = q_{rev.} - w_{max} \quad \text{——— (6)}$$

Substituting the values of ΔS and ΔU from equation (5) and (6) in equation (4), we get

$$\Delta A = (q_{rev.} - w_{max}) - T.\frac{q_{rev.}}{T}$$

$$\therefore \Delta A = w_{max}$$

Thus for a process occurring at constant temperature, the decrease in the work function A is equal to the maximum work done by the system.

It is for this reason that this thermodynamic quantity has been termed as work function.

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FREE ENERGY
OR
Gibb's free energy
OR
Gibbs function

Free energy is a thermodynamic quantity. This is usually denoted by G and is defined the equation.

$$G = H - TS \quad \text{——— (1)}$$

Where H, T and S are the heat content, temperature and entropy of the system respectively.

Since H, T and S are the function of the state only, therefore G is also function of the state of the system only. Hence for the isothermal process occurring at Temperature T, we can write

$$G_1 = H_1 - TS_1 \text{ for the initial state} \quad \text{——— (2)}$$

$$G_2 = H_2 - TS_2 \text{ for the final state} \quad \text{——— (3)}$$

or $G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$

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

$$\therefore \Delta G = \Delta H - T\Delta S \quad \text{——— (4)}$$

Where ΔG = Change in Gibbs free energy of the system.

ΔH = Enthalpy change of the system.

ΔS = Entropy change of the system.

The physical significance of Gibbs free energy may be understood as follows

At constant temperature (T),

$$\Delta S = \frac{q_{rev.}}{T}$$

i.e. $T\Delta S = q_{rev.}$ ——— (5)

At constant pressure (P),

$$\Delta H = \Delta U + P\Delta V \quad \text{——— (6)}$$

Substituting the values of $T\Delta S$ and ΔH from eqn.

5 and 6 in equation 4 we get,

$$\Delta G = (\Delta U + P\Delta V) - q_{rev.}$$

or $$\Delta G = (\Delta U - q_{rev.}) + P\Delta V \quad \text{——— (7)}$$

Now, according to the first law of Thermodynamics

$$\Delta U = q_{rev.} - W_{max}$$ (work done by a system carries negative sign)

or $$\Delta U - q_{rev.} = -W_{max}$$

Substituting this value in equation 7 we get

$$\Delta G = -W_{max} + P\Delta V$$

$$\Delta G = W_{max} - P\Delta V$$

But $P\Delta V$ is the work of expansion done by the system corresponding to the increase in volume ΔV.

Hence, $(W_{max} - P\Delta V)$ gives the maximum work other than the work of expansion. This is called the maximum useful work available from the process.

We conclude that for a process occurring at constant temperature and constant pressure, the decrease in Gibb's free energy is equal to the maximum useful work obtainable from the process i.e.

The total work minus the pressure volume work or work of expansion.

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