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Class ⇒ B.Sc (Hons.) Part - II
Subject ⇒ Chemistry
Chapter ⇒ Second Law of Thermodynamics
Topic ⇒ Gibbs-Helmholtz Equation

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Gibbs-Helmholtz Equation

Gibbs and Helmholtz derived two equations and are known as Gibbs-Helmholtz Equation.

One equation can be expressed in terms of changes in free energy and enthalpy while the other can be expressed in terms of changes in internal energy and work function.

The Gibbs free energy (G) is given by the eqn.

$$G = H - TS \quad \text{——— (1)}$$

For an isothermal process,

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

and

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

subtracting eqn. (2) from eqn. (3), we get

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

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

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

Where ΔG is the change in free energy of the system.

ΔH is the change in enthalpy of the system and ΔS is the entropy change of the system.

Putting $H = U + PV$ in eqn. (1) we get

$$G = U + PV - TS \quad \text{——— (5)}$$

Differentiating this eqn. completely, we get

$$dG = dU + PdV + VdP - TdS - SdT \quad \text{——— (6)}$$

But $ds = \frac{\delta q_{rev}}{T} = \frac{du + Pdv}{T}$ (from 1st law of thermodynamics)

or, $Tds = du + Pdv$

Substituting this value in eqn. ⑥, we get

$$dG = VdP - SdT$$

If pressure is kept constant,

$dP = 0$, so that the above eqn reduces to

$$(dG)_P = -(SdT)_P$$

or, $$\left(\frac{\partial G_1}{\partial T}\right)_P = -S \quad \text{——— ⑦}$$

∴ For the initial state,

$$\left(\frac{\partial G_1}{\partial T}\right)_P = -S_1 \quad \text{——— ⑧}$$

∴ for the final state,

$$\left(\frac{\partial G_2}{\partial T}\right)_P = -S_2 \quad \text{——— ⑨}$$

Subtracting equation ⑧ from ⑨, we get

$$\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -S_2 - (-S_1)$$

$$= -S_2 + S_1 = -(S_2 - S_1)$$

$$= -\Delta S$$

or it may be written as

$$\left[\frac{\partial (G_2 - G_1)}{\partial T}\right]_P = -\Delta S$$

$$\left[\frac{\partial (\Delta G)}{\partial T}\right]_P = -\Delta S$$

Substituting this value of $-\Delta S$ in equation ④, we get

$$\Delta G = \Delta H + T\left[\frac{\partial (\Delta G)}{\partial T}\right]_P$$

This equation is called Gibbs - Helmholtz equation in terms of free energy and enthalpy change

at constant pressure applicable to all processes.

This equation is used for calculating the enthalpy change ΔH for a process or a reaction provided the values of free energy changes at two different temperatures are known.

An analogous equation involving work function A can be obtained using the equation

$$A = U - TS$$

For a reaction at constant volume, the corresponding equation will be

$$\Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V$$

This equation is called Gibbs-Helmholtz equation in terms of internal energy and work function at constant volume.

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