

Deg II Chem. Hons, Paper - III

Topic :- Thermodynamics

Gibbs - Helmholtz equation :-

Gibbs-Helmholtz equation is applicable to both Physical and Chemical change. This can be derived from the Second Law of Thermodynamics by using free energy equation

Let us suppose that G_1 represents the free energy of a system in its initial state at temperature T . Suppose that temperature rises to $T + dT$ where dT is infinitesimally small. Let the free energy at this new temperature is $G_1 + dG_1$

Now suppose that when the system is in its final state, its free energy is given by G_2 at T and $G_2 + dG_2$ at the temperature $T + dT$. If pressure is constant all along then

$$dG_1 = -S_1 dT \quad \text{--- (1)}$$

~~under~~ and $dG_2 = -S_2 dT \quad \text{--- (2)}$

S_1 and S_2 are the entropies of

of the system in the initial and final state of the system

subtracting eq. (1) from eq. (2) we get

$$d(G_2 - G_1) = -(S_2 - S_1) dT$$

$$\text{or } d(\Delta G) = -\Delta S dT$$

As the pressure is constant

$$\left[\frac{\partial(\Delta G)}{\partial T} \right]_P = -\Delta S \quad \text{--- (3)}$$

As we know that

$$-\Delta S = \frac{\Delta G - \Delta H}{T}$$

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

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

This equation is known as the

Gibbs-Helmholtz equation.

It is applicable to all processes

occurring at constant pressure

It has been used to calculate

the heat change, (ΔH) for a reaction

taking place at constant pressure

provided the values of free energy

change at two different temp. are known