# Thermodynamics

**(Module -4)**

**B.Sc. III Year**

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# CONTENTS…

- Variation of heat of a reaction with temperature
- Kirchoffs equation

# KIRCHHOFF'S EQUATION

Variation of Heat off a reaction or Enthalpy of formation with temperature is given by Kirchhoff's equation

# KIRCHHOFF'S EQUATION

The amount of heat evolved or absorbed in a process, varies with temperature. The exact relationship showing the variation of the heat of reaction with temperature was given by Kirchhoff in 1858

# KIRCHHOFF'S EQUATION

Statement: The change in the heat of a reaction at constant pressure for every degree change of temperature is equal to the change in the heat capacity at constant pressure.

# KIRCHHOFF'S EQUATION

Mathematically it is expressed as follows,

$$\frac{\Delta H2 - \Delta H1}{T2 - T1} = \Delta Cp$$

# KIRCHHOFF'S EQUATION

It can be derived easily with the help of the first law of thermodynamics.

Consider the simple process,

$$A_{(reactants)} \text{----------}\rightarrow B_{(products)}$$

# KIRCHHOFF'S EQUATION

Now, suppose $H_A$ & $H_B$ are the heat contents or enthalpies of the reactants and products respectively. Then the heat of reaction accompanying the process will be given by,

$$\Delta H = H_B - H_A$$

# KIRCHHOFF'S EQUATION

Differentiating the equation with respect to temperature at constant pressure, we get

$$\left[\frac{\mathrm{d}(\Delta H)}{\mathrm{dT}}\right] = \left[\frac{\mathrm{dH_B}}{\mathrm{dT}}\right] - \left[\frac{\mathrm{d(HA)}}{\mathrm{dT}}\right]$$

# KIRCHHOFF'S EQUATION

According to the definition of heat capacity at constant pressure,

$$C_p = \left[\frac{dH}{dT}\right]$$

$$\left[\frac{d(\Delta H)}{dT}\right] = (C_p)_B - (C_p)_A$$

# KIRCHHOFF'S EQUATION

Where, $(C_p)_B$, $(C_p)_A$ are the mean molar heat capacities of the products and reactants respectively at the given pressure.

Then,

$$\frac{d(\Delta H)}{dT} = \Delta C_p$$

$$d\,(\Delta H) = \Delta C_p \,.\, dT$$

# KIRCHHOFF'S EQUATION

This is only for a small temperature difference, dT. The equation for large temperature difference (say $T_1$ and $T_2$) can be obtained by integrating the above equation between the limits.

$$\int_{H1}^{H2} d(\Delta \mathrm{H}) = \int_{T1}^{T2} \Delta \mathrm{C_p} \,.\, \mathrm{dT}$$

$$\Delta \mathrm{H}_2 - \Delta \mathrm{H}_1 = \Delta \mathrm{C_p}\ (\mathrm{T}_2 - \mathrm{T}_1)$$

# KIRCHHOFF'S EQUATION

Then, finally we get the famous Kirchoffs equation as,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

The change in the heat of reaction at constant pressure for every degree change of temperature is equal to the change in the heat capacity at constant pressure.

# THANK YOU……