

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 of 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

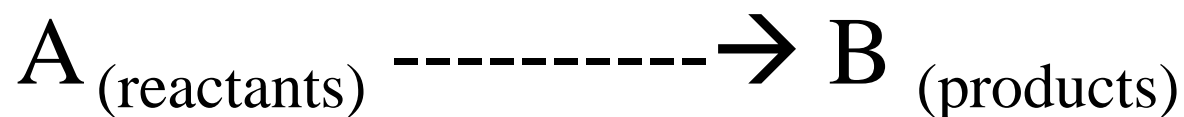
Mathematically it is expressed as follows,

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

KIRCHHOFF'S EQUATION

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

Consider the simple process,



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

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

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,

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

$$d(\Delta H) = \Delta C_p \cdot dT$$

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.

$$\int_{H_1}^{H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

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.....

