Class ⇒ B.Sc. Part I Subsidiary
Subject ⇒ Chemistry
Chapter ⇒ Thermochemistry
Topic ⇒ Kirchhoff's Equation

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Kirchhoff's Equation

Kirchhoff's equation gives the relationship between variation in heat of reaction with temperature.

Statement ⇒ The change in the heat of reaction at constant pressure for every degree change of temp. is equal to the change in the heat capacity at constant pressure, accompanying the reaction.

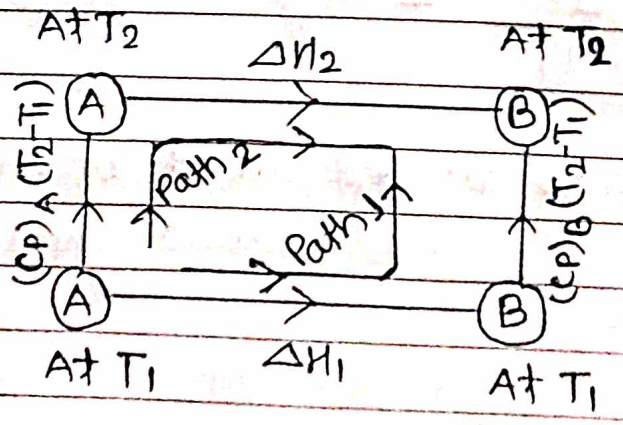
Let us consider the general reaction

$$A \longrightarrow B$$

Suppose the heat of reaction (heat evolved) at temperature $T_1 = \Delta H_1$ and

The heat of reaction (heat evolved) at temperature $T_2 = \Delta H_2$

Starting from A at temperature T_1 we can reach B at temperature T_2 by two different paths.



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Path-1

We perform the reaction at temperature T_1 to obtain B at the same temperature and then heat this up to the temperature T_2. Then,

Heat evolved in the first stage $= \Delta H_1$

Heat absorbed in the second stage $= (C_p)_B (T_2 - T_1)$

Where, $(C_p)_B$ = Average molar heat capacity of the products.

$\therefore$ Net heat evolved $= \Delta H_1 - (C_p)_B (T_2 - T_1)$

Path-2

We first heat up the reactants to the temperature T_2 and then perform the reaction to give the products at the same temperature. Then if $(C_p)_A$ is the average molar heat capacity of the reactant A.

Heat absorbed in the first stage $= (C_p)_A (T_2 - T_1)$

Heat evolved in the second stage $= \Delta H_2$

$\therefore$ Net heat evolved $= \Delta H_2 - (C_p)_A (T_2 - T_1)$

Since the initial and the final states are the same in both the above cases, therefore, by law of conservation of energy, we must have

Net heat evolved by Path 1 = Net heat evolved by path 2

i.e.

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

or,
$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p \quad \text{——— (1)}$$

When the reaction is carried out at constant volume $\Rightarrow$

We have the thermodynamic relation

$$\Delta H = \Delta E + P\Delta V$$

Under conditions of constant volume, $\Delta V = 0$

$$\therefore \Delta H = \Delta E$$

Hence equation (1) takes the form

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_V$$

Where $\Delta C_V = (C_V)_B - (C_V)_A$ is the change in the heat capacity at constant volume accompanying the reaction. $(C_V)_A$ and $(C_V)_B$ are the mean molar heat capacities at constant volume of the reactants and products. ΔE_1 and ΔE_2 are the internal energy changes (i.e. heat of reaction at constant volume) when the reaction is carried out at temperatures T_1 and T_2 respectively.

Thus Kirchhoff's eqn. may also be expressed as follows –

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

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