Class ⇒ B.Sc. Part I Subsidiary
Subject ⇒ Chemistry
Chapter ⇒ 2 (Group A) Thermochemistry
Topic ⇒ Hess's Law of ~~constant~~ heat summation

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Hess's Law of Constant heat Summation

Hess's law states that the amount of heat evolved or absorbed in a process, including a chemical change, is the same whether the process takes place in one or several steps.

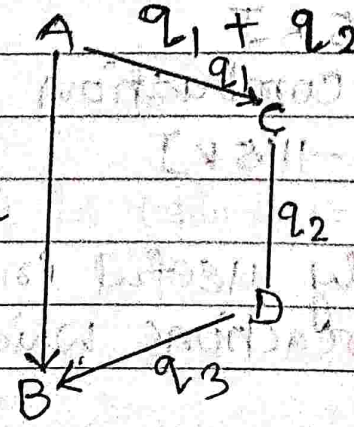
Suppose in a process, the system changes from ~~State~~ A to ~~state~~ B in one step and the heat exchanged in this change is q

Now suppose the system changes from ~~State~~ A to ~~state~~ state B in three steps involving a change from A to C, C to D and finally from D to B.

If q_1, q_2 and q_3 are the heats exchanged in the first, second and third step respectively.

Then according to Hess's Law,

$$q_1 + q_2 + q_3 = q$$



This generalisation means, in effect, that the enthalpy of reaction depends only on the initial reactants and final products and not at all on the intermediate products that may be formed

Applications of Hess's law

1. Calculation of enthalpy of reactions ⟹

Hess's law makes it possible to calculate enthalpies of many reactions which cannot be determined experimentally.

e.g. It is extremely difficult to measure the heat evolved when carbon burns in oxygen to form carbon monoxide.

$$C + \frac{1}{2}O_2 \longrightarrow CO \quad \Delta H = ?$$

Hess's law states that the heat evolved in the combustion of 1 mole of carbon is the same (393.5 KJ (ie $\Delta H = -393.5$ KJ) whether the reaction takes place in a single step as

$$C + O_2 \longrightarrow CO_2 \quad \Delta H = -393.5 \text{ KJ}$$

or, in two steps

$$C + \frac{1}{2}O_2 \longrightarrow CO \quad \Delta H = x \text{ KJ (let)}$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2 \quad \Delta H = y \text{ KJ (let)}$$

According to Hess's law

$$x + y = -393.5 \text{ KJ}$$

$$\text{or } x = -393.5 - y$$

$$= -393.5 - (-282.0) \quad \text{(measure } y \text{ value)}$$

$$= -111.5 \text{ KJ}$$

Thus ΔH for the combustion of carbon to give carbon monoxide is -111.5 KJ

2. Determination of enthalpy of slow reactions ⟹

Hess law is extremely useful in determining enthalpies of those reactions which take place

extremely slowly.

e.g.

(i) $S(rhombic) + O_2 \longrightarrow SO_2$ $\Delta H = -297.5\,kJ$

(ii) $S(monoclinic) + O_2 \longrightarrow SO_2$ $\Delta H = -300.0\,kJ$

Subtracting (i) from (ii) and transposing, we get,

$S(monoclinic) \longrightarrow S(rhombic)$ $\Delta H = -2.5\,kJ$

or, $S(rhombic) \longrightarrow S(monoclinic)$ $\Delta H = +2.5\,kJ$

Thus, transformation of one mole of rhombic sulphur into monoclinic sulphur is accompanied by absorption of 2.5 kJ of heat.