* Hess's law of Constant Heat Summation:-

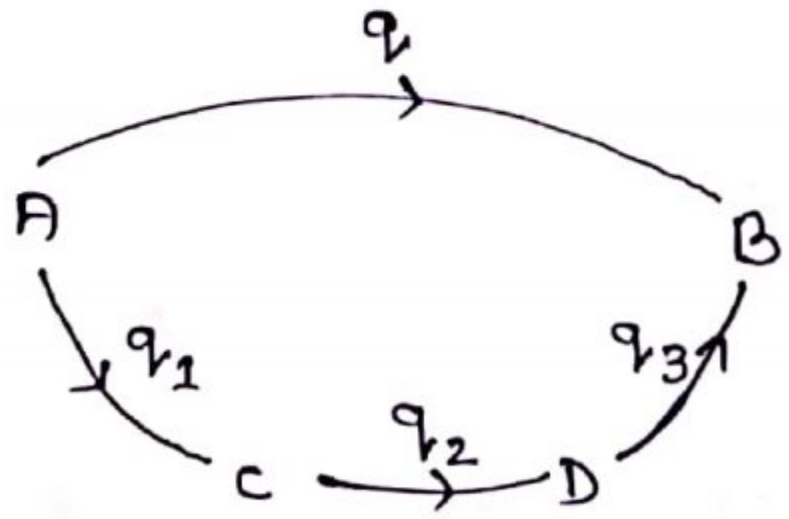
This law states that —

'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'.

Let us suppose in a process, the system changes from state 'A' to state 'B' in one step and the heat exchange in this change is 'q'.

Now suppose the systems changes from state A to state B in three steps involving a change from A to C, C to D and finally D to B. If q_1, q_2 and q_3 are the heats exchanged in the first, second and third steps, respectively, then A/c to Hess's law —

$$q = q_1 + q_2 + q_3 .$$



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Application of Hess's law:-

(1) Calculation of enthalpy of reactions :—

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

Hess's law, starts that the heat evolved in the Combustion of 1 mole of Carbon is the same, viz. 393.5 kJ ($\Delta H = -393.5$ kJ) whether the reaction takes place in the single step as—

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad (\Delta H = -393.5\ kJ)$$

or in two steps as—

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \qquad (\Delta H = x\ kJ)$$

$$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g) \qquad (\Delta H = y\ kJ)$$
$$(\Delta H = -282.0\ kJ)$$

then A/c to Hess's law—

$$\Delta H = x + y$$

$$-393.5 = x - 282.0$$

$$\therefore \quad x = -393.5 + 282.0\ kJ$$

$$x = -111.5\ kJ$$

Thus, ΔH for the Combustion of Carbon to Carbon monoxide(CO) is -111.5 kJ.

(2). Determination of Enthalpy of slow reaction:-

This law is useful to determine enthalpy of those reaction which take place extremely slow.

The transformation of S(rhombic) in to S(monoclinic) is so slow that direct measurement of enthalpy is not possible. But the enthalpies of combustion of S(rhomic) and S(monocliaic) are found to be -297.5 KJ and -300.0 KJ mol^{-1} respectively.

(i) $S(rhombic) + O_2 \longrightarrow SO_2(g)$ $\quad \Delta H = -297.5$ KJ

(ii) $S(monoclinic) + O_2 \longrightarrow SO_2(g)$ $\quad \Delta H = -300.0$ KJ

On substrating (ii) from (i) we get -

$S(rhombic \longrightarrow S(monoclinic)$

$$\Delta H = -297.5 - (-300.0)\ KJ$$
$$= -297.5 + 300.0\ KJ$$
$$(\Delta H = +2.5\ KJ.)$$

(3) Calculation of Enthalpy of formation :-

The enthalpy of formation of compounds can be calculated by the application of Hess's law when it is not possible to determine these experimently.

It is impossible to determine experimentally the enthalpy of formation of Benzene from its elements.

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(i) $C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$ $\quad \Delta H = -3267.7\ kJ$

(ii) $C + O_2 \longrightarrow CO_2$ $\quad \Delta H = -393.5\ kJ$

(iii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ $\quad \Delta H = -285.9\ kJ$

Now, Eqs (ii) is multiplied by 6 and Eqs - (iii) is multiplied by 3.

(iv) $6C + 6O_2 \longrightarrow 6CO_2$ $\quad \Delta H = -2361.0\ kJ$

(v) $3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$ $\quad \Delta H = -857.7\ kJ$

Now adding (iv) and (v) we get -

(vi) $6C + 3H_2 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$ $\quad \Delta H = -3218.7\ kJ$

Now, Substracting eqs - (i) from eqs - (vi) we get -

$$6C + 3H_2 + \frac{15}{2}O_2 - C_6H_6 - \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O - 6CO_2 - 3H_2O$$

$\Delta H = -3218.7 - (-3267.7)\ kJ$

or $6C + 3H_2 \longrightarrow C_6H_6$ $\quad \Delta H = -3218.7 + 3267.7\ kJ$

$(\Delta H = 49.0\ kJ)$

from

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