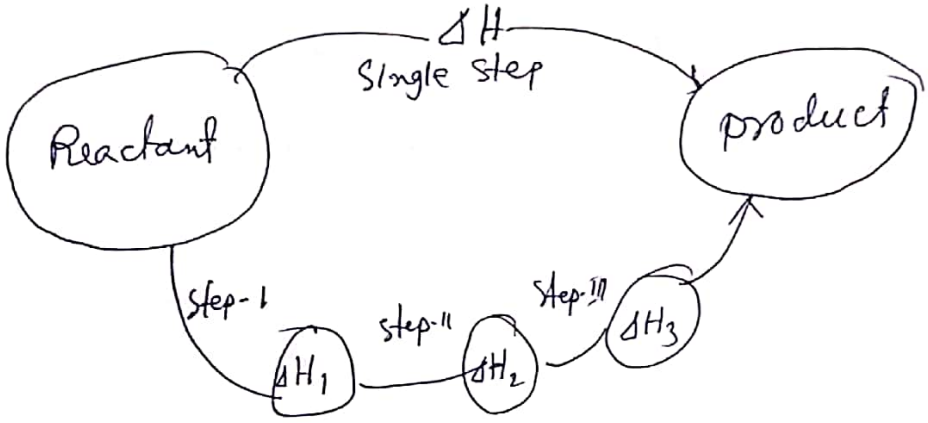
(1) Thermochemistry ✠ 2nd Sem (G)
19-5-20

Hesses law :— The total heat evolved or absorbed in a chemical reaction is always same whether the reaction is completed in single step or in several steps. This is known as Hesses law of heat summation.




According to Hesses law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

example — Suppose a reaction is of

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.3 \text{ Kcal}$$

If the reaction takes in two steps,

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H = -68.0 \text{ Kcal}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -26.3 \text{ Kcal}$$

Total $\Delta H = -94.3$ Kcal.

NB: — Hesses law helps to determine the heat of formation of compound.

Very important for exam

# Kirchoffs equation



In thermochemistry kirchoffs equation is very important, Enthalpy and Internal energy have direct relation with heat capacity.

We have heat capacity at constant pressure as

$$\left(\frac{dH}{dT}\right)_p = C_p \quad \text{——— (1)}$$

In case of two different stage 1 and 2 we have

$$\left(\frac{dH_1}{dT}\right)_p = C_{p_1} \quad \text{——— (2)}$$

$$\left(\frac{dH_2}{dT}\right)_p = C_{p_2} \quad \text{——— (3)}$$

(3)-(2) $\Rightarrow$ $\left(\frac{dH_2}{dT}\right)_p - \left(\frac{dH_1}{dT}\right)_p = C_{p_2} - C_{p_1}$

or $\left(\frac{d\Delta H}{dT}\right)_p = \Delta C_p$

or $\boxed{d\Delta H = \Delta C_p \, dT}$ ——— (4)

On integration $\int_1^2 d\Delta H = \Delta C_p \int_1^2 dT$

$$\Delta H_2 - \Delta H_1 = \Delta C_p \int_1^2 dT$$

$$\Delta H_2 = \Delta H_1 + \Delta C_p \int_1^2 dT$$

In case of reactant and product

$$\left.\begin{aligned} \Delta H_R &= \Delta H_P + \Delta C_p \int_1^2 dT \\ \text{Similarly} \quad \Delta E_R &= \Delta E_P + \Delta C_v \int_1^2 dT \end{aligned}\right\} \text{——— (5)}$$

Equation (5) is known as Kirchoffs eqn