Note : **(i)** $\Delta_{\text{neutralisation}}H^{\ominus}$ for weak acids (HCN, CH_3COOH, benzoic acid) and weak bases (NH_4OH, amines) is lower than that for strong acids and bases. The reason is that heat is absorbed in complete ionisation of weak acids and bases (unlike in case of strong acids and bases where no heat is required for ionisation).

(ii) $\Delta_{\text{neutralisation}}H^{\ominus}$ for the reaction between HCl and NaOH in aprotic solvents (solvents which doesn't ionizes) e.g. benzene etc. is less than −13.7 kcal/mol because HCl is a polar covalent substance and doesnt get ionizes in aprotic solvent so requires non-zero $\Delta_{\text{ionisation}}H^{\ominus}$ for neutralization.

(iii) $\Delta_{\text{neutralisation}}H^{\ominus}$ for the reaction between HF and NaOH is −16.27 kcal/mol which is greater than the expected value of −13.7 kcal/mol (obviously to be compared in terms of magnitude). The difference is due to a very high heat of hydration of flouride ion due to its small size.

Hess's Law of Constant Heat Summation Section - 3

It states that change in enthalpy for any chemical reaction is constant, whether the reaction occurs in one step (directly) or in several steps (indirectly).

OR

The enthalpy change in a reaction depends upon initial and final states and is independent of the route followed to complete the reaction.

It is the direct consequence of *law of conservation of energy*. Δ_rH of overall reaction will be obtained by "*appropriate summation*" of the changes in enthalpies of various intermediate steps.

Illustrating the concept :

Find the enthalpy change for formation of $NO_2(g)$.

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad ; \qquad \Delta_f H = ?$$

Using given thermochemical equations, and applying Hess's Law :

(i) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$; $\Delta_rH_1 \equiv (\Delta_f H)_{NO}$

(ii) $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$; $\Delta_rH_2 \equiv (\Delta_c H)_{NO} \neq (\Delta_f H)_{NO_2}$

Adding two equations, we get : $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Rightarrow \quad \Delta_rH = \Delta_rH_1 + \Delta_rH_2$

Illustrating the concept

Find Δ_rH of reaction : $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

(i) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$; $\Delta_rH_1 = -68.3 \text{ kcal/mol} \equiv (\Delta_f H)_{H_2O} \equiv (\Delta_c H)_{H_2}$

(ii) $H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta_rH_2 = 10.52 \text{ kcal/mol} \equiv (\Delta_{vap}H)_{H_2O}$

From Hess's Law : $\Delta_rH = \Delta_rH_1 + \Delta_rH_2 = (-68.3) + (10.52) = -57.78 \text{ kcal/mol}$

Illustration - 3 *Enthalpy of neutralisation of acetic acid by NaOH is 50.6 kJ/mol. Calculate ΔH for ionisation of CH_3COOH. Given, the heat of neutralisation of a strong acid with a strong base is –57.3 kJ/mol.*

SOLUTION : The neutralisation of a strong acid by a strong base is represented as :

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_{\text{Neutralisation}} H^\ominus = -57.3 \text{ kJ/mol}$$

Now acetic acid is a weak acid, so its neutralisation is represented in two stages: First complete ionisation of weak acid and then complete neutralisation of the fully ionised acid by the base.

1. $CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H^+(aq) \quad ; \quad \Delta_{\text{Ionisation}} H^\ominus = ?$

2. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_{\text{Neutralisation}} H^\ominus = -57.3 \text{ kJ/mol}$

Now adding the two equations to get the equation of neutralisation;

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(\ell) \quad ; \quad \Delta_{\text{Neutralisation}} H^\ominus = -50.6 \text{ kJ/mol}$$

From Hess's Law : $\Delta_{\text{ionisation}} H^\ominus + (-57.3) = -50.6 \quad \Rightarrow \quad \Delta_{\text{ionisation}} H^\ominus = +6.7 \text{ kJ/mol}$

Illustration - 4 *Find the heat of formation of ethyl alcohol from following data :*

$C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta_r H = -94$ *kcal/mol*

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_r H = -68$ *kcal/mol*

$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell) \; ; \quad \Delta_r H = -327$ *kcal/mol*

SOLUTION : Always write the balanced thermodynamic equation for which $\Delta_r H$ is to be calculated.

$$2C(s) + 3H_2(g) + \frac{1}{2} O_2(g) \longrightarrow C_2H_5OH(\ell) \; ; \; \Delta_f H = ?$$

Given : **I.** $C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta_r H_1 = -94 \text{ kcal/mol} \equiv (\Delta_f H)_{CO_2} \equiv (\Delta_c H)_C$

II. $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_r H_2 = -68 \text{ kcal/mol} \equiv (\Delta_f H)_{H_2O} \equiv (\Delta_c H)_{H_2}$

III. $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell) \quad ; \quad \Delta_r H_3 = -327 \text{ kcal} \equiv (\Delta_c H)_{C_2H_5OH}$

Now adding *appropriately* to get the required equation (Using *Hess's Law*) :

Operate : 2 (I) + 3(II) – (III) to get :

$$2C(s) + 3H_2(g) + \frac{1}{2} O_2(g) \longrightarrow C_2H_5OH(\ell)$$

From Hess's Law : $\Delta_f H = 2(\Delta_r H_1) + 3(\Delta_r H_2) - \Delta_r H_3 = 2(-94) + 3(-68) - (-327) = \mathbf{-65 \text{ kcal/mol}}$

Illustration - 5 *From the following data, calculate the standard enthalpy change for the combustion of cyclopropane at* 298 *K* :

The enthalpy of formation of $CO_2(g)$, $H_2O(\ell)$ *and propene*(g) *are* –393.5, –285.8 *and* 20.42 *kJ* mol^{-1} *respectively.*

The enthalpy of isomerisation of cyclopropane to propene is – 33.0 *kJ* mol^{-1}.

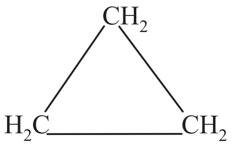
SOLUTION :

$$CH_3CH = CH_2(g) + \frac{9}{2} O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(\ell) \qquad \ldots\text{(i)}$$

$$\Delta_c H^\ominus_{(\text{Propene})} = \left[3\Delta_f H^\ominus_{(CO_2)} + 3\,\Delta_f H^\ominus_{(H_2O)}\right] - \left[\Delta_f H^\ominus_{(\text{Propene})} + \frac{9}{2}\,\Delta_f H^\ominus_{O_2}\right]$$

$$= 3(-393.5) + 3(-285.8) - (20.42) = -2058.32 \text{ kJ mol}^{-1}$$

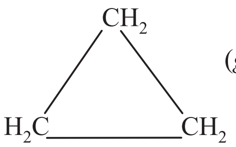
To the above reaction, if we add the reaction :



$(g) \longrightarrow CH_3CH=CH_2(g)$ $\quad \Delta_{\text{isomerization}}H^{\ominus} = -33.0 \text{ kJ mol}^{-1}$

Propene

we get :



$(g) + \frac{9}{2}O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(\ell)$

Hence, $\Delta_c H^{\ominus}_{(\text{cyclopropane})} = (-2058.32 - 33.0) \text{ kJ mol}^{-1} = -2091.32 \text{ kJ mol}^{-1}$

Heat of Reaction and Bond Energy Section - 4

Let us consider that the bond energy of AB molecule is x kcal/mol.

Bond Formation : $A + B \longrightarrow A - B$; $\Delta_r H = -x$ (*Bond formation is exothermic*)

Bond Dissociation : $A - B \longrightarrow A + B$; $\Delta_r H = +x$ (*Bond dissociation is endothermic*)

During a chemical reaction, atoms and molecules are rearranged to form new molecules. During the course of chemical reaction, old bonds are broken (of reactants) and new ones are formed (of products).

A given chemical reaction can be analysed energetically into two parts :

(i) *Bond Breaking* (endothermic, $\Delta_r H > 0$)

(ii) *Bond Formation* (exothermic, $\Delta_r H < 0$)

If $\Delta_r H_1$ is the enthalpy change during bond breaking (i) and $\Delta_r H_2$ is the enthalpy change during bond formation (ii), then overall enthalpy change of the reaction ($\Delta_r H$) is given by Hess's Law:

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2$$

As discussed, $\Delta_r H$ can be calculated using Hess's law of constant heat summation or using :

$$\Delta_r H = \sum H_{\text{Poducts}} - \sum H_{\text{Reactants.}}$$

$\Delta_r H$ can also be theoretically calculated using bond energies in the following manner :

(i) On the reactants side, calculate the energy required to break all the bonds. If there is an element in Solid / Liquid state, also consider the energy required to convert it into gaseous state.

(ii) On the products side, calculate the energy released when products are formed. If there is an elements/compound in Solid/Liquid state, also consider the energy released when it is converted from gaseous state to the required state.

(iii) Add total energy released and absorbed to get $\Delta_r H$.

Illustration - 6 *Find $\Delta_r H$ of the reaction :* $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2\,HF(g)$;

Average bond energies of O–F, O–H, O = O, H–F are 44, 111, 118 *and* 135 *kcal/mol respectively.*

SOLUTION : $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2\,HF(g)$; $\Delta_r H = ?$

(i) Bond Breaking: (endothermic) : $\Delta_r H_1$

$F-O-F(g) \longrightarrow O(g) + 2\,F(g)$; $\Delta_r H = +2 \times 44$ [bond energy of O–F = 44]

$H-O-H(g) \longrightarrow O(g) + 2\,H(g)$; $\Delta_r H = +2 \times 111$ [bond energy of O–H = 111]

$\Rightarrow \Delta_r H_1 = 2 \times 44 + 2 \times 111 = +310 \text{ kcal.}$