From definition : $\Delta_r H = \Sigma (H_{products}) - \Sigma (H_{reactants}) = \Sigma a_i (H)_{m,\ products} - \Sigma b_i (H)_{m,\ reactants}$

[H_m is the molar enthalpy of the compound and a_i &b_i the stoichiomeric coefficients of products and reactants respectively]

$\Rightarrow \quad \Delta_r H^\ominus = \Delta_f H^\ominus = H^\ominus_{HCl} - \left(\frac{1}{2} H^\ominus_{H_2} + \frac{1}{2} H^\ominus_{Cl_2}\right)$ [see definition of $\Delta_f H^\ominus$ in Section - 2]

$\Rightarrow \quad \Delta_f H^\ominus = H^\ominus_{HCl} - 0$ [Enthalpy of elements in standard state = 0]

$\Rightarrow \quad H^\ominus_{(HCl)} = \Delta_f H^\ominus_{(HCl)}$

Hence the enthalpy of a compound is the standard heat of formation of the compound OR *enthalpy of a compound is often taken as standard enthalpy of formation of that compound.*

Enthalpy of a compound A at standard conditions = $\Delta_f H^\ominus$ of A

Note : By convention, $\Delta_f H^\ominus (H^+ (aq)) = 0$

Illustration - 1 *How much heat is evolved by the preparation of* 100 *gm of iron by the following reaction* ?

$$2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe(s) + Al_2O_3\,(s)\ ; \qquad \Delta_r H = -202.6\ kcal/mol$$

SOLUTION :

From thermochemical reaction, it is clear that 202.6 kcal of heat is involved when two moles of *Fe* (iron) is formed.

$\Rightarrow \quad$ 2 moles of Fe $\equiv$ 202.6 kcal $\quad \Rightarrow \quad$ 1 mole of Fe $\equiv$ 101.3 kcal

$\Rightarrow \quad$ 100/56 mole of Fe $\equiv 101.3 \times 100/56 = 180.9$ kcal

Heat of Reaction — Section - 2

The heat of a reaction can be assigned special names in the following manner :

(a) Standard Heat of Formation ($\Delta_f H^\ominus$) :

The heat evolved or absorbed when one mol of any compound is formed from its elements in their standard states. It is usually denoted by $\Delta_f H^\ominus$. $\Delta_f H^\ominus$ can be given –ve or +ve sign, depending upon whether formation is exothermic or endothermic.

$$C(s,\ graphite) + 2\,H_2\,(g) \longrightarrow CH_4\,(g) \quad ; \qquad \Delta_f H^\ominus = -74.3\ kJ/mol$$

$$\frac{1}{2} H_2\,(g) + \frac{1}{2} I_2\,(s) \longrightarrow HI\,(g) \quad ; \qquad \Delta_f H^\ominus = 25.92\ kJ/mol$$

Note : To write chemical equations for formation, balance the reaction for one mole of compound whose formation is to be studied.

(b) Standard Heat of Combustion ($\Delta_c H^\ominus$) :

The heat evolved (or enthalpy change) when one mole of any substance is completely burnt in excess of oxygen.

$\Delta_c H^\ominus$ will always bear –ve sign for it being enthalpy change of an exothermic reaction.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(\ell)\ ; \qquad \Delta_c H^\ominus = -212\ kcal/mol$$

$$C(s,\ graphite) + O_2(g) \longrightarrow CO_2\,(g) \quad ; \qquad \Delta_c H^\ominus = -94\ kcal/mol$$

Note : To write chemical equations for combustion, balance the reaction for one mole of compound whose combustion is to be studied.

Illustration - 2 *Calculate* $\Delta_r H^\ominus$ *for the reaction :* $C_6H_6(\ell) + \frac{15}{2} O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(\ell)$

Given the standard heat of formations $(\Delta_f H^\ominus)$ *of* $H_2O(\ell)$, $CO_2(g)$ *and* $C_6H_6(\ell)$ *are –57.80 kcal/mol, –94.05 kcal/mol and 19.8 kcal/mol respectively.*

SOLUTION :

Whenever, standard heat of formation $(\Delta_f H^\ominus)$ *of a compound is given it means that enthalpy of that particular compound at standard state is given*. Also, note that in the question, molar enthalpy changes are given.

Using the definition of enthalpy change as : $\Delta_r H = \Sigma H_{(\text{products})} - \Sigma H_{(\text{reactants})}$

For the given reaction : $\Delta_r H^\ominus = \Sigma(H^\ominus_{\text{products}}) - \Sigma(H^\ominus_{\text{reactants}})$

or $\Delta_r H^\ominus = \Sigma\left(\Delta_f H^\ominus{}_{\text{products}}\right) - \Sigma\left(\Delta_f H^\ominus{}_{\text{reactants}}\right)$

$$C_6H_6(\ell) + \frac{15}{2} O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(\ell)$$

	$C_6H_6(\ell)$	$O_2(g)$	$6\,CO_2(g)$	$3\,H_2O(\ell)$
$\Delta_f H^\ominus$	19.8	0	(–94.05)	(–57.8)

$\Rightarrow$ $\Delta_r H^\ominus = [6 \times (-94.05) + 3 \times (-57.8)] - [19.8] = -757.50$ kcal/mol.

(c) Heat of Dissociation ($\Delta_{\text{bond}} H^\ominus$) :

It is the amount of energy required to break one mole of bonds in a molecule (in gas phase) into gasesous atoms.

$H-H(g) \longrightarrow 2H(g)\,;\ \Delta_{\text{bond}} H^\ominus = 103$ kcal/mol $\qquad C-C(g) \longrightarrow 2C(g)\,;\ \Delta_{\text{bond}} H^\ominus = 80$ kcal/mol

Note : (i) $\Delta_{\text{bond}} H^\ominus$ is always positive i.e. energy is always required to break the bond between two atoms.

(ii) Whenever a bond is formed between two atoms in gasesous state, energy is always released.

(d) Heat of Phase change :

It is the amount of energy required to change the phase of a substance under the particular conditions for the phase change.

$H_2O(s) \longrightarrow H_2O(\ell)$; $\Delta_{\text{fus}} H^\ominus = 6$ kJ/mol at 273 K and 1 atm

$H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta_{\text{vap}} H^\ominus = 40.8$ kJ/mol at 373 K and 1 atm

$CO_2(s) \longrightarrow CO_2(g)$; $\Delta_{\text{sub}} H^\ominus = 108$ kcal/mol at 195 K and 1 atm

Note : (i) $\Delta_{\text{fus}} H^\ominus$: Amount of heat required to melt one mole of a substance at a constant temperature and 1 atm pressure.

(ii) $\Delta_{\text{vap}} H^\ominus$: Amount of heat required to vaporize one mole of a substance at a constant temperature and 1 atm pressure.

(iii) $\Delta_{\text{sub}} H^\ominus$: Amount of heat required to sublime one mole of a substance at a constant temperature and 1 atm pressure.

(e) Heat of Atomization ($\Delta_a H^\ominus$) :

It is the amount of energy required to break the bonds in a molecule (in gas phase) into gasesous atoms.

$Na(s) \longrightarrow Na(g)\,;\ \Delta_a H^\ominus = 108$ kJ/mol $\qquad H-H(g) \longrightarrow 2H(g)\,;\ \Delta_a H^\ominus = 435$ kJ/mol

$CH_4(g) \longrightarrow C(g) + 4\,H(g)\,;\ \Delta_a H^\ominus = 1665$ kJ/mol

Note : (i) For a monoatomic molecule (i.e. atom) in solid phase, $\Delta_a H^\ominus$ is also called as $\Delta_{\text{sub}} H^\ominus$.

(ii) For a diatomic molecule, $\Delta_a H^\ominus$ is also called as $\Delta_{\text{bond}} H^\ominus$.

(iii) For a polyatomic molecule, it is the enery required to break all the bonds to form gasesous atoms.

(f) Average Heat of Dissociation ($\Delta_{\text{mean, bond}}H^{\ominus}$) :

It is the average amount of energy required to break one mole of bonds in a polyatomic molecule (in gas phase) into gasesous atoms.

$$CH_4(g) \longrightarrow C(g) + 4H(g) \quad ; \quad \Delta_a H^{\ominus} = 1665 \text{ kJ/mol}$$

Note : (i) In general, in a polyatomic molecule, the energy required to break a bond changes in the successive bond dissociations. For example :

$$CH_4(g) \longrightarrow CH_3(g) + H(g) \;;\; \Delta_{\text{bond}}H_1^{\ominus} \qquad CH_3(g) \longrightarrow CH_2(g) + H(g) \;;\; \Delta_{\text{bond}}H_2^{\ominus}$$

$$CH_2(g) \longrightarrow CH(g) + H(g) \;;\; \Delta_{\text{bond}}H_3^{\ominus} \qquad CH(g) \longrightarrow C(g) + H(g) \;;\; \Delta_{\text{bond}}H_4^{\ominus}$$

Here : $\Delta_{\text{bond}}H_1^{\ominus} \neq \Delta_{\text{bond}}H_2^{\ominus} \neq \Delta_{\text{bond}}H_3^{\ominus} \neq \Delta_{\text{bond}}H_4^{\ominus}$ and $\Delta_{\text{mean, bond}}H^{\ominus} = \frac{1}{4}\Delta_a H^{\ominus}$

(g) Heat of Lattice($\Delta_{\text{lattice}}H^{\ominus}$) and Heat of Hydration($\Delta_{\text{hyd}}H^{\ominus}$) :

$\Delta_{\text{lattice}}H^{\ominus}$: It is the energy required to break one mole of an ionic compound into ions in their gaseous atoms.

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \quad ; \quad \Delta_{\text{lattice}}H^{\ominus} = 787 \text{ kJ/mol}$$

$\Delta_{\text{hyd}}H^{\ominus}$: It is the energy released when atoms (gaseous) in one mole of an ionic compound gets hydated.

$$Na^+(g) + Cl^-(g)\,(\equiv NaCl) \longrightarrow Na^+(aq.) + Cl^-(aq.) \quad ; \quad \Delta_{\text{hyd}}H^{\ominus} = -783 \text{ kJ/mol}$$

Note : $\Delta_{\text{lattice}}H^{\ominus}$ is always positive and $\Delta_{\text{hyd}}H^{\ominus}$ is always negative.

(h) Heat of Solution ($\Delta_{\text{sol}}H^{\ominus}$) :

It is the change in enthalpy when one mole of a substance (solute) is completely dissolved in excess of water.

$$NaCl(s) + aq \longrightarrow Na^+(aq) + Cl^-(aq) \;;\; \Delta_{\text{sol}}H^{\ominus} = 5 \text{ kJ} \qquad HCl(g) + aq \longrightarrow HCl(aq) \;;\; \Delta_{\text{sol}}H^{\ominus} = -x \text{ kJ}$$

Note : (i) $\Delta_{\text{sol}}H^{\ominus} = \Delta_{\text{lattice}}H^{\ominus} + \Delta_{\text{hyd}}H^{\ominus}$ (can be positive or negative)

(ii) Generally, when gases are dissolved, heat is evolved. In case of salts (solids), heat is absorbed except when anhydrous salts are dissolved.

(i) Heat of Ionisation ($\Delta_{\text{ionisation}}H^{\ominus}$) :

It is the amount of heat absorbed when one mole of a compound completely dissociates into ions in a solution.

$$HCN(aq) \longrightarrow H^+(aq) + CN^-(aq) \quad ; \quad \Delta_{\text{ionisation}}H^{\ominus} = +p$$

$$NH_4OH(aq) \longrightarrow NH_4^+(aq) + OH^-(aq) \quad ; \quad \Delta_{\text{ionisation}}H^{\ominus} = +q$$

(j) Heat of Neutralisation ($\Delta_{\text{neutralisation}}H^{\ominus}$) :

It is the amount of heat liberated when one gm-equivalent of acid completely neutralises by one gm-equivalent of base. In water, all strong acids (HCl, H_2SO_4, HNO_3) and strong bases [NaOH, $Ca(OH)_2$, etc] ionise completely.

$\Delta_{\text{neutralisation}}H^{\ominus}$ is constant for strong acid and base neutralization and is equal to –13.7 kcal/mol = –57.27 kJ/mol.

Neutralisation can be treated as : $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \;;\; \Delta_{\text{neutralisation}}H^{\ominus} = -13.7 \text{ kcal/mol}$

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*. $\Delta_r H$ 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) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$; $\Delta_r H_1 \equiv (\Delta_f H)_{NO}$

(ii) $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$; $\Delta_r H_2 \equiv (\Delta_c H)_{NO} \neq (\Delta_f H)_{NO_2}$

Adding two equations, we get : $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Rightarrow \quad \Delta_r H = \Delta_r H_1 + \Delta_r H_2$

Illustrating the concept

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

(i) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$; $\Delta_r H_1 = -68.3 \text{ kcal/mol} \equiv (\Delta_f H)_{H_2O} \equiv (\Delta_c H)_{H_2}$

(ii) $H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta_r H_2 = 10.52 \text{ kcal/mol} \equiv (\Delta_{vap} H)_{H_2O}$

From Hess's Law : $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 = (-68.3) + (10.52) = -57.78 \text{ kcal/mol}$

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.*