TYPES OF HEAT OF REACTION :

(A) Heat of formation, Enthalpy of formation (ΔH_f) or ($\Delta_f H$)

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

The reference state of oxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$, respectively some reactions with standard molar enthalpies of formation are :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell) \qquad \Delta H_f \quad \surd$$

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow \underset{1\text{ mole}}{HNO_3} \qquad \Delta H_f \quad \surd$$

$$Na_{(s)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \longrightarrow \underset{1\text{ mole}}{NaOH} \qquad \Delta H_f \quad \surd$$

APPLICATION OF ΔH_f :

Calculation of ΔH of any general reaction.

Let us considered a general reaction $aA + bB \longrightarrow cC + dD$

$$\Delta H_{reaction} = \Sigma\Delta H_{f(products)} - \Sigma\Delta H_{f(reactant)} = [c\Delta H_{f(C)} + d\Delta H_{f(D)}] - [a\Delta H_{f(A)} + b\Delta H_{f(B)}]$$

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GOLDEN KEY POINTS

- Standard condition means, P = 1 atm, T = 25°C or 298 K
  Standard heat of formation is represent by ΔH_f^o.
- If no condition is given then value of ΔH_f is considerd as ΔH_f^o.
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

Elements	Reference state	
C	$C_{(graphite)}$	
S	$S_{8(Rhombic)}$	Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)
P	$P_{4(white)}$	
O	$O_{2(g)}$	
H	$H_{2(g)}$	
Br	$Br_{2(l)}$	
Metal	$M_{(s)}$ [except $Hg_{(l)}$]	

* The formation reaction may be exothermic or endothermic.

(B) Heat of combustion (ΔH_{comb}) :

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised) in excess of oxygen.

Example :

$\underset{(1mole)}{C_{graphite}} + O_2 \longrightarrow CO_2, \Delta H_{comb}$	√	and	ΔH_f	√
$\underset{(1mole)}{C_{diamond}} + O_2 \longrightarrow CO_2, \Delta H_{comb}$	√	and	ΔH_f	X
$C_{(1mole)} + ½O_2 \longrightarrow CO, \Delta H_{comb}$	X	and	ΔH_f	√
$CO_{(1mole)} + ½O_2 \longrightarrow CO_2, \Delta H_{comb}$	√	and	ΔH_f	X

Note :

(I) Heat of combustion reaction is always exothermic.

(II) If conditions are not given then ΔH_{comb} considered as ΔH^{o}_{comb}.

(III) If in a reaction heats of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\boxed{\Delta H = \Sigma(\Delta H_{comb})_R - \Delta(\Delta H_{comb})_P}$$

APPLICATION OF HEAT OF COMBUSTION :

Calorific value or fuel value (C.V.) :

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\boxed{\text{Calorific value} = \frac{\Delta H_{comb}}{\text{Molecular weight}}}$$

Unit : KJ g^{-1} or K cal g^{-1}

GOLDEN KEY POINTS

* Heat of combustion reaction is always exothermic.
* If conditions are not given then ΔH_{comb} is considered as ΔH^{o}_{comb}.
* Maximum value of calorific value = Maximum efficiency or best fuel.
* H_2 has the highest calorific value (150 KJ/gm) but it is not used as domestic or industrial fuel due to some technical problems.

(C) Heat of neutralisation (ΔH_{neut}) :

The heat evolved when one equivalent of an acid is completely neutralised by one equivalent of a base in dilute solution is called as heat of neutralisation.

$$SA + SB \longrightarrow Salt + Water$$

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl + H_2O$$

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

$$\boxed{H^+ + OH^- \longrightarrow H_2O}$$

(i) When one equivalent of SA is neutralised by one equivalent of SB then evolve heat remain constant and its value is –13.7 kcal/equivalent or –57.2 KJ/equivalent.

eg.

SA		SB	
HCl(aq)	+	NaOH(aq)	$\longrightarrow$ NaCl + H_2O + 13.7 Kcal
NV = 1 eq.		NV = 1 eq.	$\longrightarrow \Delta H = -13.7$ Kcal
NV = 2 eq.		NV = 2 eq.	$\longrightarrow \Delta H = 2\,(-13.7)$ Kcal
NV = 3 eq.		NV = 3 eq.	$\longrightarrow \Delta H = 3\,(-13.7)$ Kcal
NV = 4 eq.		NV = 5 eq. = (4 + 1) eq.	$\longrightarrow \Delta H = 4\,(-13.7)$ Kcal
NV = 5 eq.=(3+2)eq		NV = 3 eq.	$\longrightarrow \Delta H = 3\,(-13.7)$ Kcal

(ii) If one of the acid or base or both are weak then heat of neutralization is usually less than –13.7 KCal eq^{-1} or –57.3 KJ eq^{-1} because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.

eg. $\underset{}{\overset{\text{WA}}{CH_3COOH(aq)}} + \overset{\text{SB}}{NaOH(aq)} \rightarrow CH_3COONa(aq) + H_2O;\ \Delta H = -13.4\ \text{KCal eq}^{-1}$

(iii) For a reaction HF + NaOH $\rightarrow$ NaF + H_2O; $\Delta H = -16.17$ kcal; this is because of hydration of F^- ion.

(D) Heat of hydrogenation ($\Delta H_{Hydrogenation}$) :

The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.

Unsaturated organic compound $\xrightarrow{\text{Change}}$ Saturated organic compound

(= or ≡ Bond) (– Bond)

$C_2H_2 + 2H_2 \longrightarrow C_2H_6$, ΔH_{hydro} √

$C_2H_2 + H_2 \longrightarrow C_2H_4$, ΔH_{hydro} X

$C_2H_4 + H_2 \longrightarrow C_2H_6$, ΔH_{hydro} √

Note : Heat of hydrogenation is exothermic process.

DPP 11 Que 1

(E) Heat of atomization (ΔH_{atom}) :

The amount of heat required to dissociate 1 mol gaseous molecules into gaseous atoms is called as heat of atomization.

Example : $\frac{1}{2}H_{2(g)} \longrightarrow 1H_{(g)}$ ΔH_{atom} X

$H_{2(g)} \longrightarrow 2H_{(g)}$ ΔH_{atom} √

$\frac{1}{2}Cl_{2(g)} \longrightarrow 1Cl_{(g)}$ ΔH_{atom} X

$Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ ΔH_{atom} √

Note : It is an endothermic reaction.

(F) Heat of Transformation :

(i) **Heat of fusion (ΔH_{fusion}) :** The required amount of heat to convert 1 mol solid into liquid at its melting point is called as heat of fusion.

Example : $1H_2O_{(s)} \longrightarrow H_2O_{(\ell)}$ ΔH_{fusion} √

Note : Heat of fusion is always endothermic reaction i.e. (ΔH = +ve)

(ii) Heat of vapourization (ΔH_{Vapour}) : The required amount of heat to convert 1 mol liquid into gas at its boiling point is called as heat of vapourization.

Example : $1H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$ $\quad \Delta H_{vapour}$ $\quad \surd$

Note : Heat of vapourization is always endothermic reaction i.e. (ΔH = +ve)

(iii) Heat of sublimation (ΔH_{sub}) : The required amount of heat to convert 1 mol solid into gas at a certain temperature is called as heat of sublimation.

Example : $H_2O_{(s)} \longrightarrow H_2O_{(g)}$ $\quad \Delta H_{Sub}$ $\quad \surd$

Note : Heat of sublimation is always endothermic reaction i.e. (ΔH = +ve)

(G) Heat of hydration (ΔH_{hydra}) :

Amount of heat evolved when **one mol** of anhydrous salt combines with fixed number of water molecules to convert into its specific hydrated crystal is called as heat of hydration.

Example :

- $1\ CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s) \quad \Delta H = -ve$

  anhydrous salt   hydrated salt

- $1\ MgSO_4(s) + 7H_2O(\ell) \longrightarrow MgSO_4.7H_2O(s) \quad \Delta H = -ve$

  anhydrous salt   hydrated salt

- $1CaCl_2(s) + 6H_2O(l) \longrightarrow CaCl_2.6H_2O(s) \quad \Delta H = -ve$

  anhydrous salt   hydrated salt

Special Note : Heat of hydration is exothermic.

(H) Heat of solution ($\Delta H_{sol.}$) :

Amount of heat absorbed or evolved when **one mol** of substance is dissolved in such a large volume of solvent that further addition of solvent does not produce any more heat change is called as **'Heat of solution'**.

Example 1 : $1CuSO_{4(s)} + aq \longrightarrow CuSO_4(aq) \quad \Delta H_{solution}$ √

$1CuSO_{4(s)} + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s) \quad \Delta H_{hydration}$ √

Example 2 : $MgSO_{4(s)} + 7H_2O(\ell) + aq \longrightarrow MgSO_4(aq) \quad \Delta H_{solution}$ √

$MgSO_4.7H_2O(s) + aq \longrightarrow MgSO_4(aq) \quad \Delta H_{solution}$ √

Special Note : Heat of solution may be endothermic or exothermic.

(I) **Bond energy / Bond dissociation energy :** (Bond Enthalpy):

The required amount of energy to dissociate **one mole gaseous bond** into separate **gaseous atoms** is called as **bond dissociation energy**.

Example :

$1H-H_{(g)} \longrightarrow 2H_{(g)}$	ΔH_{H-H}	√
$1Cl-Cl_{(g)} \longrightarrow 2Cl_{(g)}$	ΔH_{Cl-Cl}	√
$1H-Cl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}$	ΔH_{H-Cl}	√
$1H-Cl_{(g)} \longrightarrow H^+_{(g)} + Cl^-_{(g)}$	ΔH_{H-Cl}	X
$1H-Cl_{(g)} \longrightarrow \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)}$	ΔH_{H-Cl}	X
$1H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)}$	Δ_{H_2-O}	X

GOLDEN KEY POINTS

- The **bond energy** may be defined as the **average** amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.
- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then ΔH of that reaction can be calculate as follows.

$$\Delta H = \Sigma(B.E)_R - \Sigma(B.E.)_P$$

$\Delta H_R = \Sigma(\Delta H_{BOND})_R - \Sigma(\Delta H_{Bond})_P$

- **In the case of poly atomic molecule** we calculate the average bond energy.

$$(BE)_{av} = \text{Average bond energy} = \frac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}$$

Example :

$H-O-H_{(g)} + 112\ KJ \longrightarrow H-O_{(g)} + H_{(g)}$

$H-O_{(g)} + 108\ KJ \longrightarrow H_{(g)} + O_{(g)}$

$$(BE)_{av} = \text{Average bond energy} = \frac{112+108}{2} = 110\ KJ/mol$$

9) Lattice Enthalpy The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

27. Hess's Law of constant heat summation: The change in enthalpy is same whether the reaction takes place in one step or in several steps. Because ΔH is a state function and it is pathway independent. It depends only on initial state of the reactants and the final state of the product.

If a series of reactions are added together, the net change in the heat of the reaction is the sum of the enthalpy changes for each step. i.e.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \text{-------}$$

Rules for using Hess's Law:

1) If the reaction is multiplied (or divided) by some factor, ΔH must also be multiplied (or divided) by that same factor.

2) If the reaction is reversed (flipped), the sign of ΔH must also be reversed.

For example:

C (s) + 1/2O2 (g) = CO (g) ΔrH0 =-110.5 kJmol-1

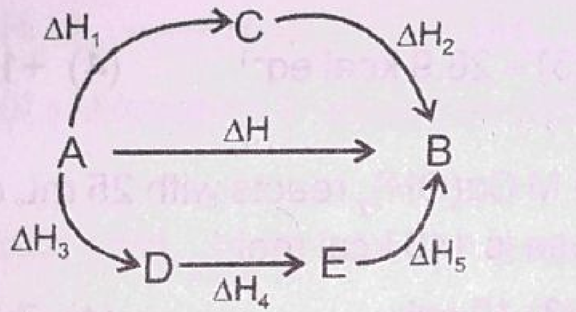
CO (g) + 1/2O2 (g) = CO2 (g) ΔrH0 =-283.0 kJmol-1

C (s) + O2 (g) = CO2 (g) ΔrH0 = -393.5 kJmol-1

(II) Hess law of constant heat summation :

The heat change in a complete chemical reaction always remain same whether reaction completes in on step or more.

Example - 1 :

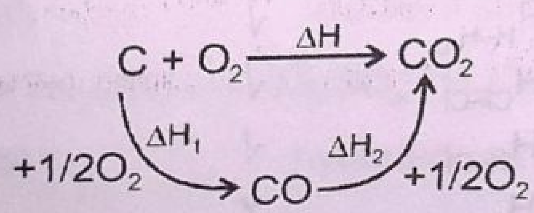


$$\Delta H = \Delta H_1 + \Delta H_2$$

or $$\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$$

or $$\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$$

Example - 2 :



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