Thermochemistry

TYPES OF REACTIONS:

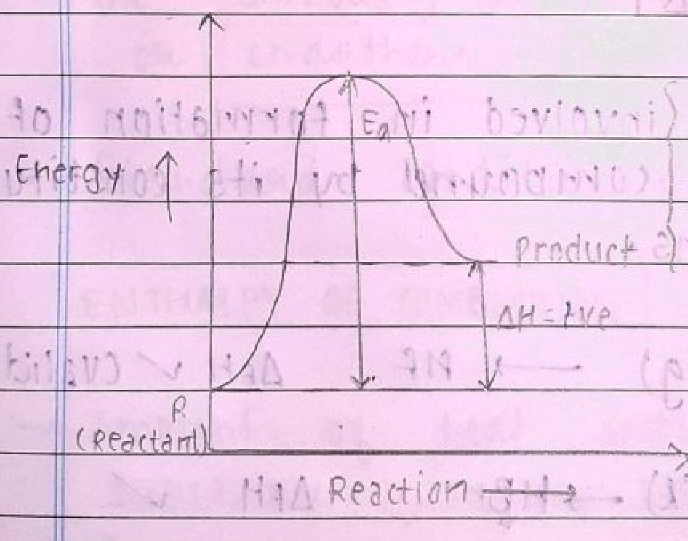
On the basis of heat absorbed or released, chemical reaction at constant pressure are of two types:

1) ENDOTHERMIC REACTION
2) EXOTHERMIC REACTION

The overall change in enthalpy of reaction can be calculated as following:

$$\Delta_r H = \Sigma H_{PRODUCT} - \Sigma H_{REACTANT}$$

- ENDOTHERMIC REACTION:



ΔH = Product − Reactant ($\Delta H = H_P - H_R$)

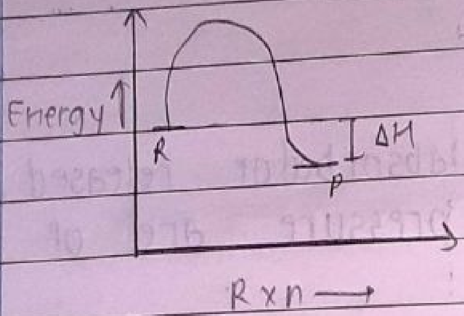
$H_P > H_R$

$\Delta H = +ve$

Examples: Dissociation rxn, fusion rxn, Sublimation, Photosynthesis, evaporation.

Representation: A + B + x Cal → C + D

EXOTHERMIC



$\Delta H = -ve$

$H_P < H_R$

$A + B \rightarrow C + D + x\,cal$

$A + B - x\,cal \rightarrow C + D$

$A + B \rightarrow C + D \;,\; \Delta H = -x\,cal$

EXAMPLES: i) Combustion, Neutralisation, Respiration
Formation rxns.

HEAT OF FORMATION

The amount of heat involved in formation of 1 mole of a compound by its constituent molecules and atoms.

$\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF$ $\Delta_f H$ ✓ (valid)

$\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(l) \longrightarrow HBr$ $\Delta_f H$ ✓

$C_{graphite} + O_2(g) \longrightarrow CO_2$ $\Delta_f H$ ✓

$\frac{3}{2} H_2(g) + \frac{1}{4} P_4 \text{(white)} + 2O_2(g) \longrightarrow H_3PO_4$ $\Delta_f H$ ✓

* There are total 11 gas in Periodic Table

Constituent element	Acceptable Physical State (Reference State)
H_2, O_2, N_2, Cl_2, F_2	Gas
Br_2	Liquid
I_2	Solid
P_4	White phosphorous
Metal	Ms [except Hg(l)]
S	S_8 (Rhombic)
C	C (graphite)

- The enthalpy of constituent elements consider as zero. Then the value of ΔH_f may be +ve / -ve.

- The enthalpy of formation may be exothermic or endothermic

- Standard condition means; P = 1 atm ; T = 25°C / 298K

ENTHALPY OF COMBUSTION:

→ Amount of heat evolved when 1 mole of substance is completely burned or oxidised in presence of excess of Oxygen.

→ Example:

$$CH_4(g) + \underset{\text{excess}}{2O_2(g)} \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta_{comb}H$$

	$\Delta_{comb}H$	ΔH_f
$C_{diamond} + O_2(g) \rightarrow CO_2(g)$	✓	X
$C_{graphite} + O_2(g) \rightarrow CO_2(g)$	✓	✓
$C_{graphite} + \frac{1}{2}O_2(g) \rightarrow CO(g)$	X	✓

- Always exothermic
- $\Delta H = \Sigma(\Delta H_c)_R - \Sigma(\Delta H_c)_P$

• CALORIFIC VALUE / FUEL VALUE (C.V.)

Amt. of heat evolved when 1g of a substance (food or fuel) is completely burnt.

$$\text{Calorific Value} = \frac{\Delta H_{comb}}{\text{Molar Mass}}$$

Unit :- KJ/g or KCal/g

- Always negative
- Maximum value of C.V. = Maximum efficiency or best fuel.

- $H_2 \rightarrow$ CV ↑ (150 KJ/g) but not used as domestic or industrial fuel due to some technical problems.

|| श्री सर्वोपरिने श्रीस्वामिनारायणभगवते नमः ||

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श्रीहरिकृष्णधाम (राजकोट)

Calculation of $\Delta_r H^\circ$ from value of $\Delta_f H^\circ$:

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ_{product} - \Sigma \Delta_f H^\circ_{reactant}$$

Que: $\Delta_f H^\circ \rightarrow CO_2(g) \rightarrow -393.5$

$CO(g) \rightarrow -110.5$ $\quad H_2 \rightarrow 0$

$H_2O(g) \rightarrow -241.8$

Std. enthalpy change for

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

$[-110.5 + (-241.8)] - [-393.5 + 0]$

$(-352.3) - (393.5)$

$\boxed{41.2}$ ← FINAL ANSWER.

Que: $C_2H_4(g) \rightarrow 52$

$CO_2(g) \rightarrow -394$

$H_2O(l) \rightarrow -286$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$[2 \times (-286) + 2(-394)] - [3(0) + 52]$

$[(-572) + (-788)] - (52)$

$-1360 - 104$

$\boxed{14.12}$ ← FINAL ANSWER

* નિત્ય અભ્યાસ રાખીએ, તો ધારીએ તે કરી શકીએ. *

ENTHALPY OF NEUTRALISATION (ΔH_{neut})

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

SA + SB → Salt + Water

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

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

$$H^+ + OH^- \rightarrow H_2O$$

$HCl + NaOH \rightarrow NaCl + H_2O + 13.7\ \frac{kcal}{gm\ eq}$

(SA) (SB)

NV NV

→ When one gm. 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^{-1}

eg: SA + SB

$HCl(aq) + NaOH(aq) \rightarrow NaCl + H_2O + 13.7$

NV = 2 NV = 2 → $\Delta H = 2(-13.7)$

NV = 3 NV = 2 → $\Delta H = 2(-13.7)$

→ If neutralisation is carried out b/w SA and WB or WA and SB then value of enthalpy of neutralisation is less than 13.7 K Cal/gm eq.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O \quad \Delta H_{neu} < 13.7 \text{ Kcal}$$
SA WB

ENTHALPY OF HYDROGENATION ($\Delta H_{Hydro.}$)

→ The heat evolved during the complete hydrogenation of one mol unsaturated O.C. into its saturated compd.

→ Unsaturated O.C. (= / ≡ Bond) $\xrightarrow{\text{Change}}$ Saturated O.C. (– Bond)

Eg:-
$C_2H_2 + 2H_2 \longrightarrow C_2H_6$ ΔH_{Hydro} ✓
$C_2H_2 + H_2 \longrightarrow C_2H_4$ ΔH_{Hydro} ✗
$C_2H_4 + H_2 \longrightarrow C_2H_6$ ΔH_{Hydro} ✓

→ Hydrogenation is always exothermic process.

→ ENTHALPY OF ATOMIZATION (ΔH_{atom})

→ The amount of heat required to dissociate 1 mol substance into gaseous atoms.

eg:

$\frac{1}{2}H_2(g) \longrightarrow 1H(g)$ ΔHatom ✗

$H_2(g) \longrightarrow 2H(g)$ ΔHatom ✓

$\frac{1}{2}Cl_2(g) \longrightarrow 1Cl(g)$ ΔHatom ✗

$Cl_2(g) \longrightarrow 2Cl(g)$ ΔHatom ✓

- Always endothermic rxn (ΔH = +ve)

Que: ΔHcomb of $C_2H_4 \rightarrow -1409.5$ KJ
$C_2H_6 \rightarrow -1558.3$
$H_2 \rightarrow -285.6$

ΔHHydro. of ethene is

$C_2H_4 + H_2 \longrightarrow C_2H_6$

$(-1409.5) - [(-1558.3 + (-285.6)]$

$(-1409.5) - 1272.7$

$= \boxed{-136.8}$

Que 200 ml of 0.1 M H_2SO_4 is mixed with 150 mL of 0.2 M NaOH solⁿ. find out the value of heat evolved in Kilojoule/gm equivalent.

0.1 M H_2SO_4, 200 ml — 0.2 M NaOH, 150 ml

NV

gmeq: $M_1V_1n_1$

$0.1 \times 200 \times 10^{-3} \times 2$ — $0.2 \times 150 \times 10^{-3} \times 1$

0.4 — 0.03×57.1 KJ/gmeq

ENTHALPY OF TRANSFORMATION

- **Enthalpy of fusion: (ΔH_{fusion})**

- The energy required to convert 1 mole of solid substance into liquid state at its MP temperature is called Enthalpy of fusion.

- Endothermic Process

$$H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta H_{fusion} = +ve$$

- **Enthalpy of vaporisation: (ΔH_{vap})**

- Required amount of heat to convert one mole of liquid into gas (vapour) at its BP temp. → Enthalpy of Vapourisation

$$H_2O\,(l) \rightarrow H_2O\,(g)$$

endothermic process (ΔH_{vap} ✓)
($\Delta H = +ve$)

Enthalpy of Sublimation (ΔH_{sub}°)

(anhydrous salt) Required amt of heat to convert 1 mole solid into gas at a certain temperature is called as Enthalpy of Sublimation.

Always endothermic (ΔH : +ve)

$$H_2O(s) \longrightarrow H_2O(g)$$

ENTHALPY OF HYDRATION (ΔH_{hyd}°)

- Amt of heat evolved when 1 mole of anhydrous salt combine with fixed no. of water molecules to convert specific hydrated crystal

- Always exothermic.

$$CuSO_4 + 7H_2O \longrightarrow CuSO_4 \cdot 7H_2O$$
(Blue vitriol)

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$$

$$FeSO_4 + H_2O \longrightarrow FeSO_4 \cdot 7H_2O$$

$$CoSO_4 + H_2O \longrightarrow CoSO_4 \cdot H_2O$$

Green Vitriol Red vitriol

BOND ENTHALPY (ΔH°_{Bond}):

Required amt. of energy to dissociate one mole of gaseous bond into separate gaseous atom → Bond Enthalpy / Bond Dissociation Enthalpy.

Always Endothermic.

Can be calculated as following:

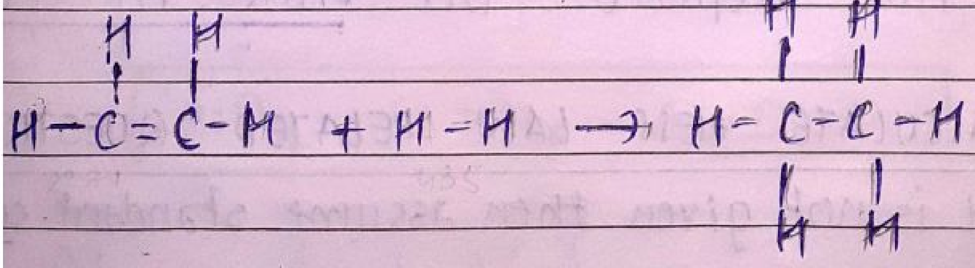
$$\Delta H^\circ_{Bond} = \Sigma H_{reactant} - \Sigma H_{product}$$

Find out the enthalpy of reaction:

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

Given

Bond	Bond E (KJ/mole)
C−H	414
C−C	347
C=C	615
H−H	435



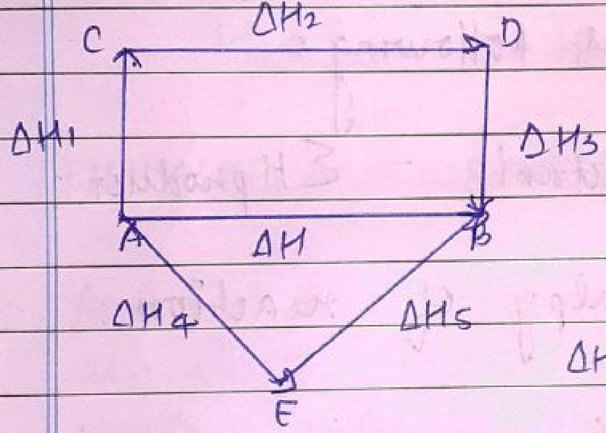
Final ans: −125

HESS LAW :

- The heat (enthalpy) change in a complete chemical reaction always remain same while rxn is carried out in single step or multiple step.

For a chemical reaction

$$A \longrightarrow B \quad \Delta H$$



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

OR

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

OR

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

ΔH does not depend on no. of steps used in the rxn.

ΔH does not depend on intermediate position (depend only on initial & final state)

ΔH does not depend on time of reaction.

RULES TO CALCULATE HESS LAW RELATED QUESTION

If standard is not given then assume standard condition

1) $A \longrightarrow B \quad \Delta H_1$

$B \longrightarrow A \quad \Delta H_2 = -\Delta H_1$

2) $A \rightarrow B \quad \Delta H_1$

$aA \rightarrow bB \quad \Delta H_2 = a\Delta H_1$

3) $A \rightarrow B \quad \Delta H_1$

$B \rightarrow C \quad \Delta H_2$

$A + B \rightarrow B + C \quad (A \rightarrow C) \quad \Delta H_3 = \Delta H_1 + \Delta H_2$

Que: $X \rightarrow 2Y$

1) $X \rightarrow Z \quad , \quad \Delta H = q_1$
2) $Z \rightarrow 2W \quad , \quad \Delta H = q_2$
3) $W \rightarrow Y \quad , \quad \Delta H = q_3$

Value of ΔH of rxn is :

KIRCHOFF's EQN

At constant pressure:

$$(\Delta H)_{T_2} - (\Delta H)_{T_1} = \Delta C_p (T_2 - T_1)$$

At constant Volume:

$$(\Delta E)_{T_2} - (\Delta E)_{T_1} = \Delta C_v (T_2 - T_1)$$