Energetics

Chemical reaction

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              Chemical reaction
                     |
         _____|_____
        |                         |
   Exothermic                Endothermic
   reaction                  Reaction
```

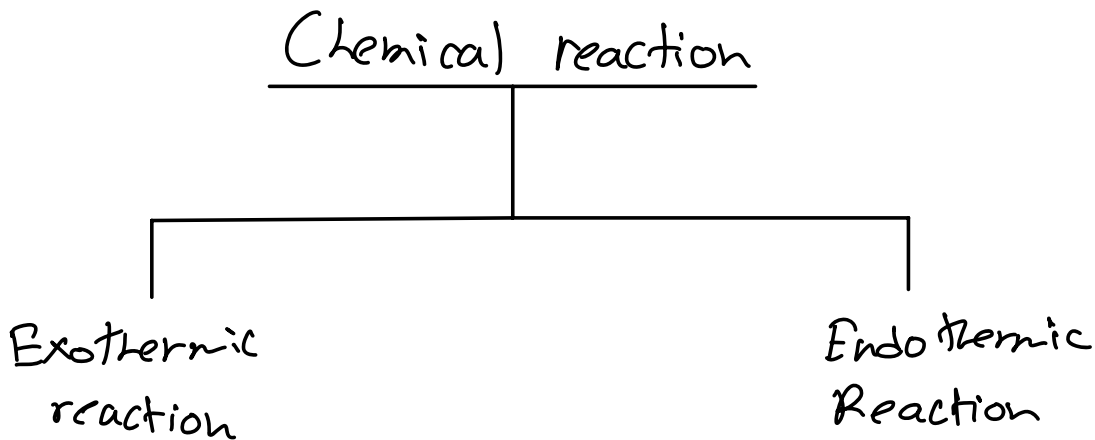## Exothermic reaction

⊝ The type of reaction by which energy is given out from the system to the surrounding are called exothermic reactions.

⊝ During the exothermic reaction, temperature of the reaction mixture increases.

⊝ Reactants have more energy than the products.

⊝ Heat energy is transferred from

the system to the surrounding.

⊖ During the clemical reactions we have to break the bonds in the reactants and new bonds are formed in the products.

~~⊘~~ Bond breaking is endo thermic.
~~⊘~~ Bond formation is exothermic
~~⊘~~ Bond breaking energy is less than the bond formation energy.
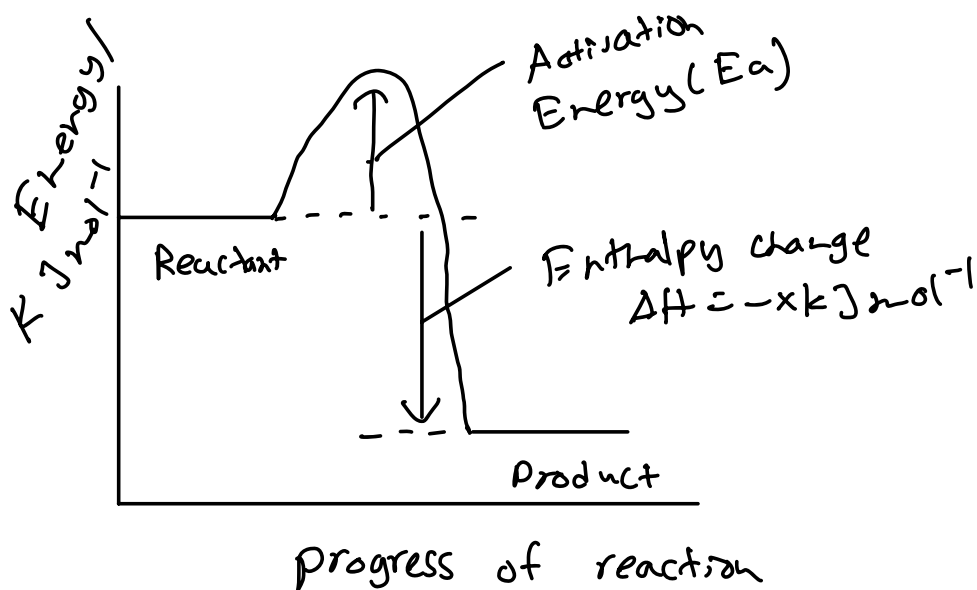~~⊘~~ overall heat energy is given out.
⊖ Enthalpy change is the energy difference between reactant and products.
⊖ The value of enthalpy change always negative.
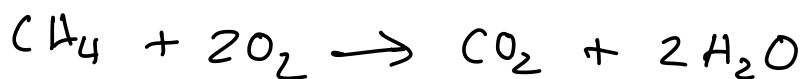⊖ Most of the exothermic reactions have low activation energy.
⊖ Most of the exothermic reactions are spontaneous.

⊖ $\Delta H = H_{product} - H_{reactant}$
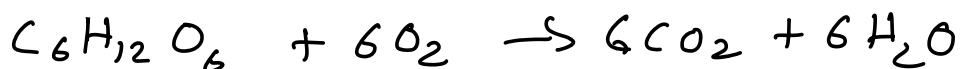(enthalpy of   (Enthalpy of
the product)   the reactant)

Progress of reaction

Examples of exothermic reactions

① Combustion reaction

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

② Respiration

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

③ Neutralisation Reaction

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
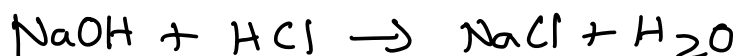
④ Reaction of metal with acid

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

⑤ Reactions of metal oxides wit water

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_2$$

⑥ Fermentation

$$C_6H_{12}O_{6\ (aq)} \longrightarrow 2\,C_2H_5OH_{(aq)} + 2CO_{2\ (g)}$$
$$\text{Absence of}$$
$$\text{oxygen}$$

⑦ Hydration

$$CuSO_4 + 5\,H_2O \rightarrow CuSO_4 \cdot 5\,H_2O$$
$$\text{white} \qquad\qquad\qquad \text{blue}$$

$$CoCl_2 + 6\,H_2O \rightarrow CoCl_2 \cdot 6\,H_2O$$
$$\text{Blue} \qquad\qquad\qquad \text{Pink}$$

⑧ Bond Formation

$$H + H \rightarrow H-H$$
$$Cl + Cl \rightarrow Cl-Cl$$

⑨ Condensation

$$H_2O_{(g)} \rightarrow H_2O_{(l)}$$

⑩ Solidification

$$I_2 (g) \rightarrow I_2 (s)$$

⑪ Freezing

$$H_2O (l) \rightarrow H_2O (s)$$
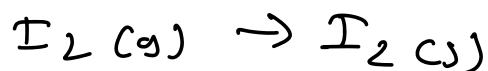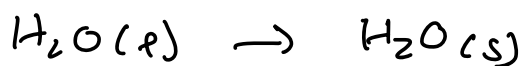
Endothermic Reaction

⊖ The type of reaction by which heat energy is taken in from the surrounding to the system are called endothermic reaction.

⊖ During the endothermic reaction, temperature of the reaction mixture decreases.
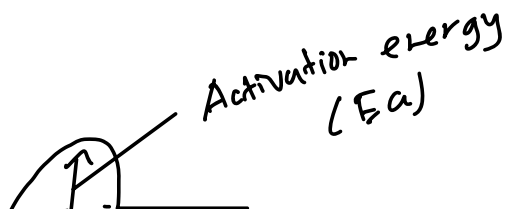
⊖ Reactants have less energy than the products.

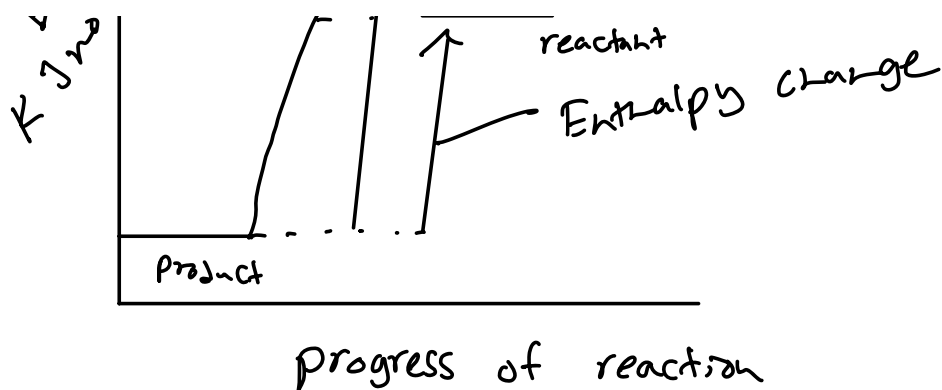⊖ Heat energy is transferred from the surrounding to the system.

⊖ During the chemical reactions we

have to break the bonds in the reactants and new bonds are formed in the products.

⊘ Bond breaking is endothermic.
⊘ Bond formation is exothermic.
⊘ Bond breaking energy is more than the bond formation energy.
⊘ overall heat energy is taken in.
⊖ Enthalpy change is the energy difference between reactant and products.
⊖ The value of enthalpy change always negative.
⊖ Most of the exothermic reactions have high activation energy.
⊖ Most of the exothermic reactions are not spontaneous.

⊖ $\Delta H = H\ product - H\ reactant$
  (enthalpy of   (Enthalpy of
   the product)   the reactant)

Energy / ↑
Activation energy
(Ea)

The y-axis is labelled $KJ/mol^?$. The graph shows "reactant", "Enthalpy change", and "Product" with the x-axis labelled "progress of reaction".

Examples of endothermic Reaction

① Photosynthesis

$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}O_6 + 6O_2$$

② Thermal Decomposition

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$$

③ Dehydration

$$CuSO_4 \cdot 5H_2O \xrightarrow{\text{heat}} CuSO_4 + H_2O$$

Blue   white
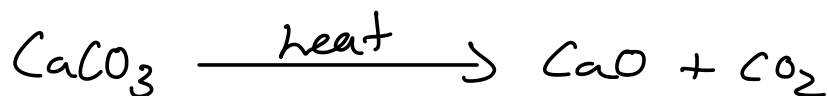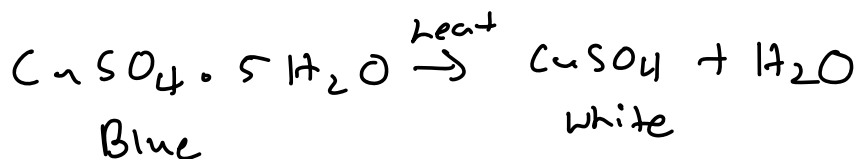
④ Melting

⑤ Boiling

⑥ Evaporation

⑦ Bond Breaking

$$H-H \rightarrow H + H$$

$$Cl-Cl \rightarrow Cl + Cl$$
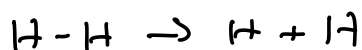
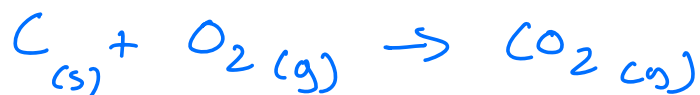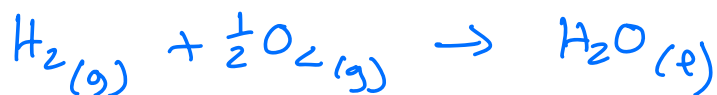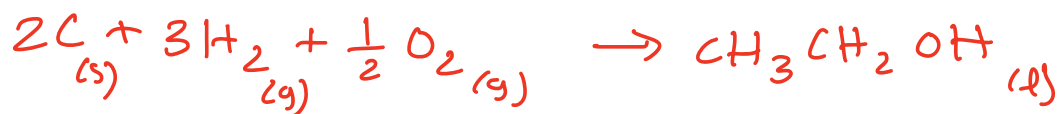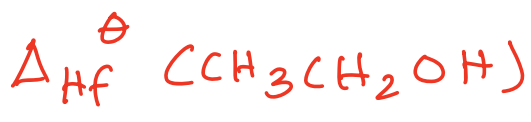⑧ NH_4Cl in H_2O

Energy Profile Diagram for a two step reaction

$$A \xrightarrow[\text{Exo}]{\text{step 1}} B \xrightarrow[\text{Exo}]{\text{step 2}} C$$

(ΔH_1) (ΔH_2) overall endothermic reaction

Energy KJmol⁻¹ [axis label — $Energy\ KJmol^{-1}$]

A

ΔA

Ea_1

H_1

B

Ea_2

H_2

C

Overall enthalpy change

Progress of reaction

② $A \xrightarrow[\text{Endothermic}]{\text{Step 1}} B \xrightarrow[\text{Exothermic}]{\text{step 2}} C$

(ΔH_1) (ΔH_2)

overall exothermic reaction

Energy KJmol⁻¹

E_{A1} E_{A2}
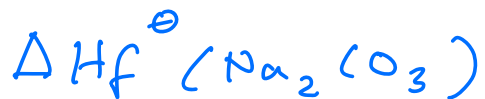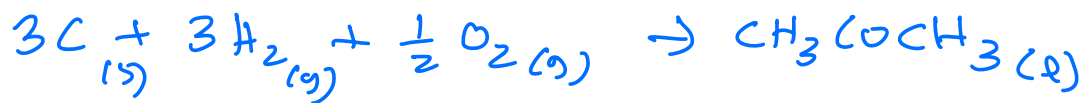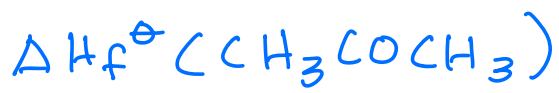
B

Progress of reaction
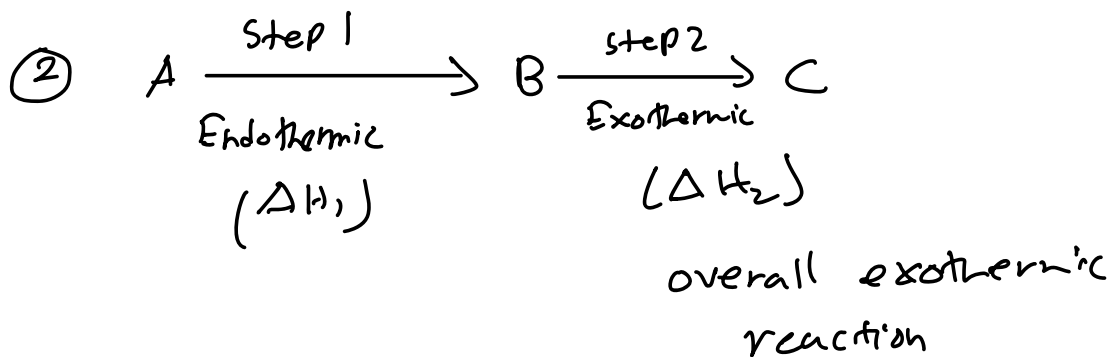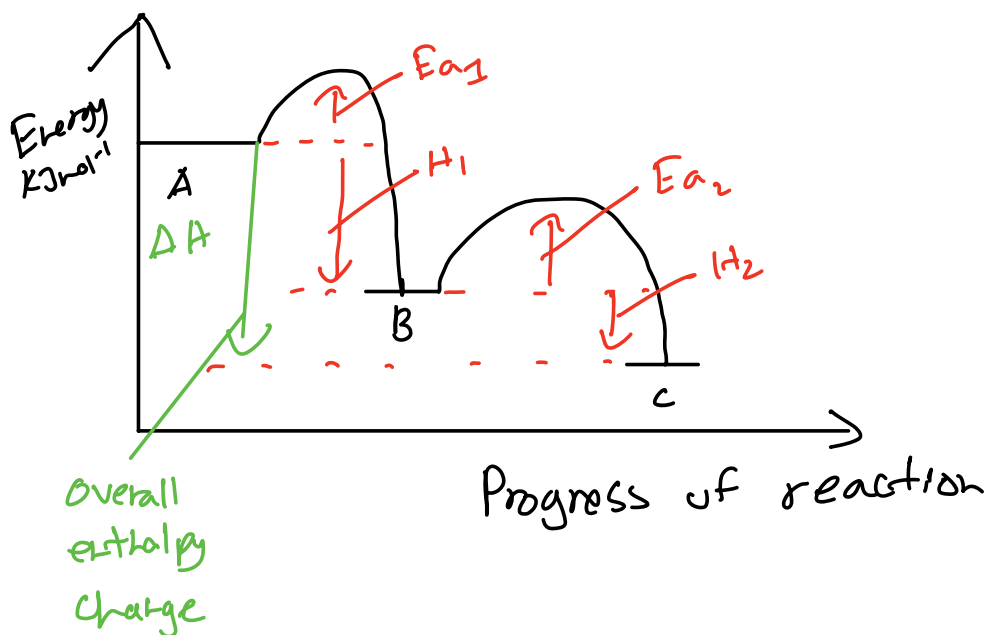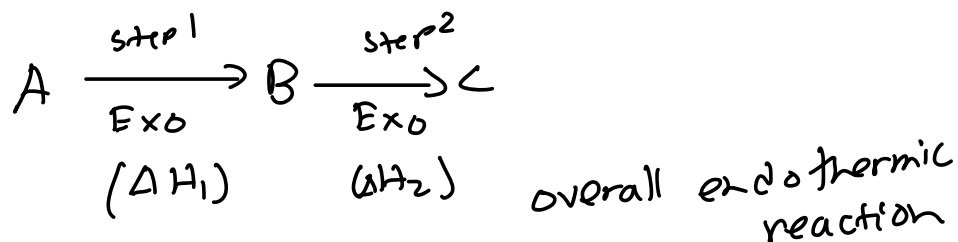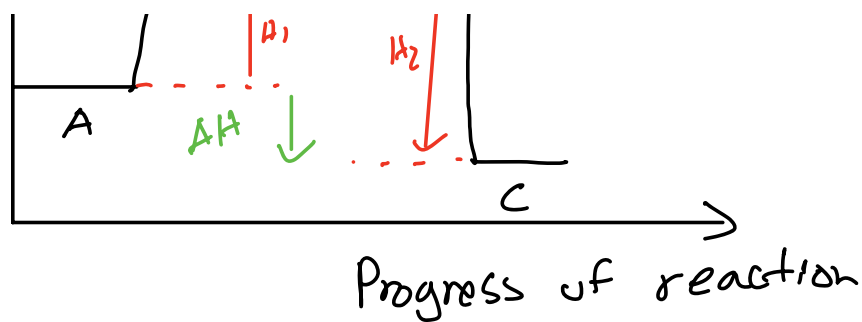
Standard enthalpy change of formation ($\Delta H_f^{\ominus}$)

Standard enthalpy change of formation is the enthalpy change when one mole compound is formed from its elements in their standard state under standard condition ($25\,^{\circ}C$ and 1 atm).

$\Delta H_f^{\ominus}$ (CH_3CH_2OH)

$$2C_{(s)} + 3H_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} \longrightarrow CH_3CH_2OH_{(l)}$$

$\Delta H_f^{\ominus}$ (H_2O)

$$H_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} \longrightarrow H_2O_{(l)}$$

$\Delta H_f^{\ominus}$ (CO_2)

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$$

$\underline{\Delta H_f^\ominus (CH_3COCH_3)}$

$$3C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3COCH_{3(l)}$$

$\underline{\Delta H_f^\ominus (Na_2CO_3)}$

$$2Na_{(s)} + C_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Na_2CO_{3(s)}$$
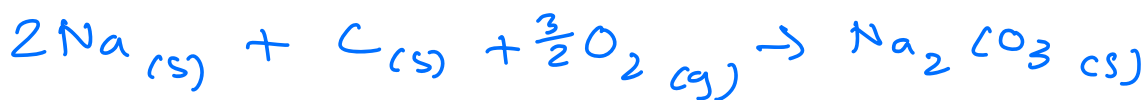
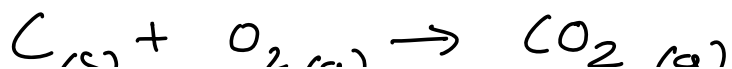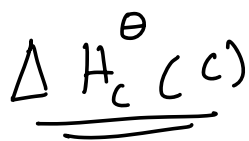☺ The value of $\Delta H_f^\ominus$ of an element is zero.

$$\Delta H_f^\ominus (H_2) = 0$$
$$\Delta H_f^\ominus (O_2) = 0$$

☺ the value of $\Delta H_f^\ominus$ can be positive or negative.

Standard enthalpy change of combustion $\Delta H_c^\ominus$

Standard enthalpy change of combustion is the enthalpy change when one mole of a substance is completely burnt in an excess oxygen under standard condition.
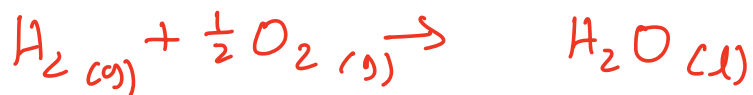
$\underline{\underline{\Delta H_c^\ominus (C)}}$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$\Delta H_c^{\ominus} (H_2)$

$$H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \rightarrow \quad H_2O_{(l)}$$

$\Delta H_c^{\ominus} (CH_4)$

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow \quad CO_{2\,(g)} + 2H_2O_{(l)}$$

$\Delta H_c^{\ominus} (CH_3CH_2OH)$

$$CH_3CH_2OH_{(l)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 3H_2O_{(l)}$$
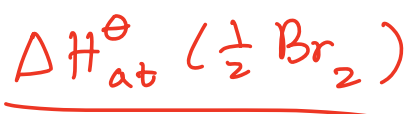
Standard enthalpy change of atomisation $(\Delta H_{at}^{\ominus})$

Standard enthalpy change of atomisation is the enthalpy change when one mole of gaseous atom is formed from its elements in their standard state under standard condition.
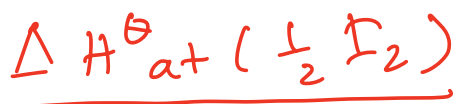
$\Delta H_{at}^{\ominus} (\tfrac{1}{2} H_2)$

$$\tfrac{1}{2} H_{2\,(g)} \rightarrow H_{(g)}$$
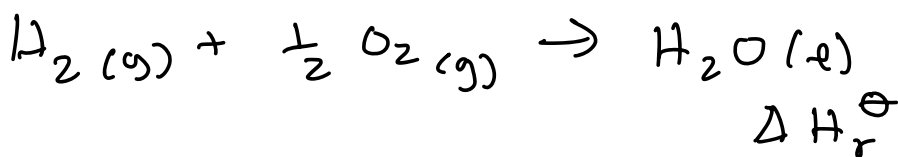
✳ The value of

$\Delta H^{\ominus}_{at} \left(\frac{1}{2} Br_2 \right)$

$\Delta H^{\ominus}_{at}$ always positive.

$\frac{1}{2} Br_{2 (\ell)} \rightarrow Br_{(g)}$

$\Delta H^{\ominus}_{at} \left(\frac{1}{2} I_2 \right)$
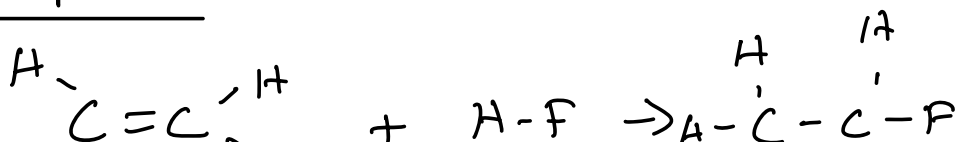
$\frac{1}{2} I_{2 (s)} \rightarrow I_{(g)}$
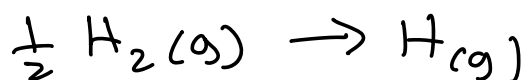
Standard enthalpy change of reaction ($\Delta H^{\ominus}_r$)

$\Delta H^{\ominus}_r$ is the enthalpy change when the amounts of reactants shown in the equation react to give products under standard condition. The reactants and products must be in their standard state.

$$H_{2 (g)} + \frac{1}{2} O_{2 (g)} \rightarrow H_2O_{(\ell)}$$
$$\Delta H^{\ominus}_r$$

Enthalpy change calculation

Example - 1

$$\underset{H}{\overset{H}{\diagdown}} C = C \underset{H}{\overset{H}{\diagup}} + A-F \rightarrow A - \overset{H}{\underset{|}{C}} - \overset{A}{\underset{|}{C}} - F$$

$$H' \quad \quad \ ^`H \quad\quad\quad\quad\quad \bar{|} \quad | $$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H \quad H$$
$$H \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \Delta H^{\ominus} = -73 \ kJ\,mol^{-1}$$

Bond	Bond energy
C—H	410
C=C	610
H—F	562
C—C	350
C—F	

Example-2

$$H_T \overset{H}{\underset{H}{\overset{+}{C}}} + \overset{O}{\overset{||}{C}}_T H + H_+ C\equiv N \rightarrow A-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{O-H}{C}}-C\equiv N$$
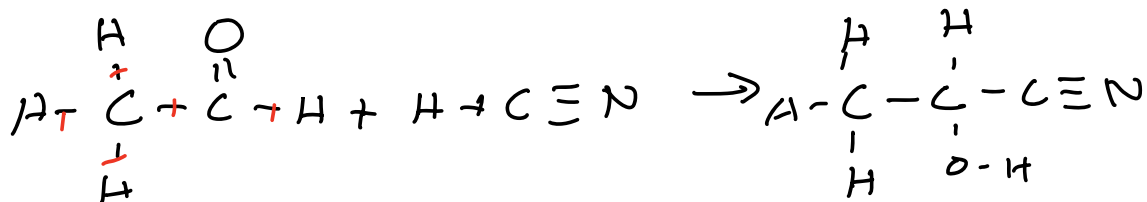
Bond	Bond energy $(kJ\,mol^{-1})$
C≡N	890
C=O	740
C—O	360

O – H	460
C – C	350
C – H	410

$$\left(5(410) + 350 + 740 + 890 \right) -$$

$$\left(4(410) + 2(350) + 360 + 460 + 890 \right)$$

$$\Rightarrow \sim 20 \text{ KJ mol}^{-1}$$

Example-3

Molecular formula of sulfur S_8

$$\Delta H_c^{\ominus} (S_8) = -2376 \text{ KJ nol}^{-1}$$

Energy required to break 1 nole S_8
into gaseous atoms $= 2232 \text{ KJ nol}^{-1}$
$O = O$ bond energy $= 496 \text{ KJ nol}^{-1}$
what is the value of $S = O$ bond ?

$$S_8 + 8 O_2 \rightarrow 8 SO_2$$

$$-2376 \text{ KJ nol}^{-1}$$

$$2232 + 8(496) - 16x = -2376$$

$$-16x = -8576$$
$$x = 536 \quad kJ\,mol^{-1}$$

Example - 5

$$2 \quad \underset{F'\ \overset{|}{P}\ F}{N} \quad \rightarrow \quad 2N \quad + \quad 6F$$
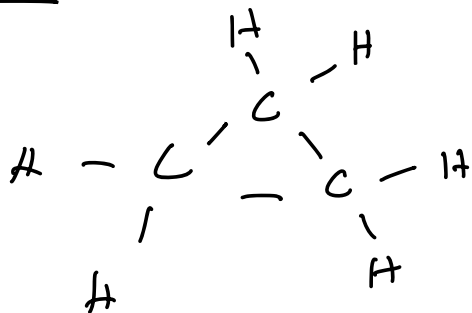
$$\Delta H = 1668$$

$$2(3x) = 1668$$
$$x = 278$$

Ans

Example - 6

$$\Delta H_f^{\ominus}\ (\text{cyclo propane}) = +53\cdot3$$
$$kJ\,mol^{-1}$$

$$3C + 3H_2 \rightarrow C_3H_6$$

$H-H = 436$ kJ mol^{-1} $C-H = 410$

$C-C = ?$

$\Delta H_{at}^{\ominus}$ (graphite) $= 717$ kJ mol^{-1}

$3(717) + 3(436) - (6 \times 410 + 3x) = 53.3$

$x = 315.23$ Ans

Enthalpy change calculation by using standard enthalpy change of formation

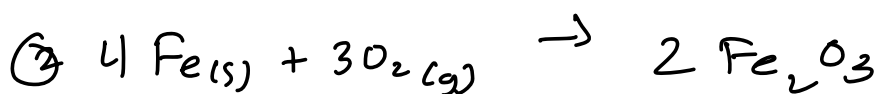$$\Delta H_r^{\ominus} = \Delta H_f^{\ominus} (product) - \Delta H_f^{\ominus} (reactant)$$

$$2H_2O_{2\,(l)} \rightarrow 2H_2O_{(l)} + O_{2\,(g)}$$
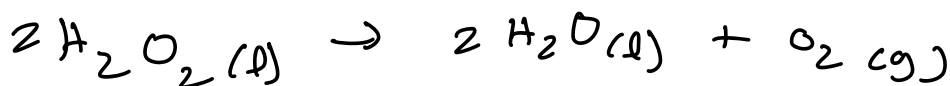
$\Delta H_f^{\ominus} (H_2O_2) = -187.8$ kJ mol^{-1}

$\Delta H_f^{\ominus} (H_2O) = -285.8$ kJ mol^{-1}

$\Delta H_r^{\ominus} =$

   $2(-285.8) - 2(-187.4)$

   $\Rightarrow -196$ kJ mol^{-1}

③ $4Fe_{(s)} + 3O_{2\,(g)} \rightarrow 2Fe_2O_3$

$\Delta H^{\circ} = -1648$

$$\Delta H_f^\ominus (Fe_2 O_3) = -824 \, kJ \, mol^{-1}$$

③ $3 FeO + 2 Al \rightarrow 3 Fe_{(s)} + Al_2 O_{3 \,(s)}$

$$\Delta H_f^\ominus (FeO) = -266 \, kJ \, mol^{-1}$$
$$\Delta H_f^\ominus (Al_2 O_3) = -1676 \, kJ \, mol^{-1}$$

$$\Delta H_r^\ominus = -1676 - 3(-266)$$
$$\Rightarrow -878 \, kJ \, mol^{-1}$$

$$\underline{\underline{Ans}}$$

④ $TiO_{2 \,(s)} + 2C_{(s)} \rightarrow Ti_{(s)} + 2CO_{(g)}$
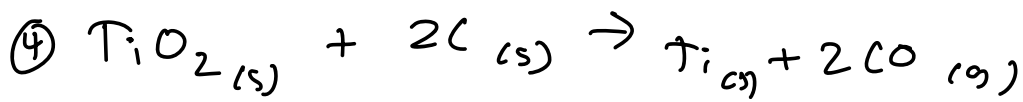
$$\Delta H_f^\ominus (TiO_2) = -900$$

$$\Delta H_f^\ominus (CO) \sim -110$$

$$\Delta H_r^\ominus \sim +720 \, kJ \, mol^{-1}$$
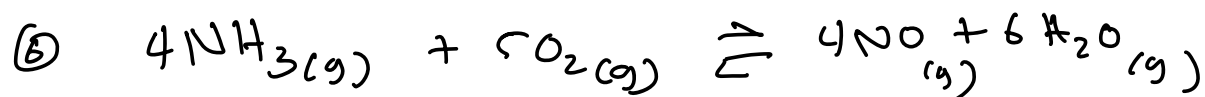
⑤ $3 Mg_{(s)} + KClO_{3 \,(s)} \rightarrow 3 MgO_{(s)} + KCl_{(s)}$
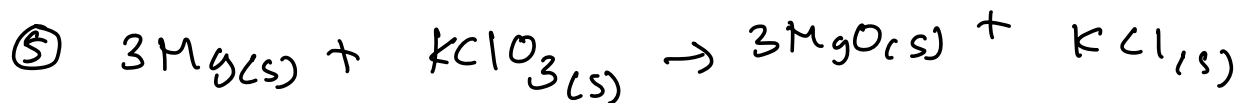
$$\Delta H_f^\ominus (MgO) = -602 \, kJ \, mol^{-1}$$
$$\Delta H_f^\ominus (KCl) = -437 \, kJ \, mol^{-1}$$
$$\Delta H_f^\ominus (KClO_3) = -391 \, kJ \, mol^{-1}$$

$$\Delta H_r^{\ominus} = -1852 \text{ kJmol}^{-1}$$

⑤ $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

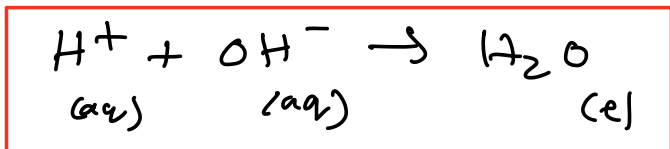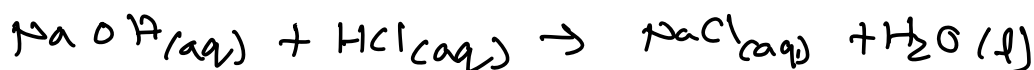$$\Delta H_f^{\ominus}(NH_3) = -46.1 \text{ kJmol}^{-1}$$
$$\Delta H_f^{\ominus}(NO) = +90.3$$
$$\Delta H_f^{\ominus}(H_2O) = -241.8$$

$$\Delta H_r^{\ominus} = -905.2 \text{ kJmol}^{-1}$$

## Standard Enthalpy change of neutralisation ($\Delta H_n^{\ominus}$)

⊖ $\Delta H_n^{\ominus}$ is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard condition.

⊖ Value of $\Delta H_n^{\ominus}$ always negative (exothermic)

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

$$\boxed{H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}}$$

Hess's Law

The overall enthalpy change for a reaction is independent of the route taken / is independant of the number of steps involved. Provided the initial and final conditions are the same.

$$A \xrightarrow{\Delta H_1} B \xrightarrow{\Delta H_2} C$$

$$\Delta H \searrow D \nearrow \Delta H_3$$
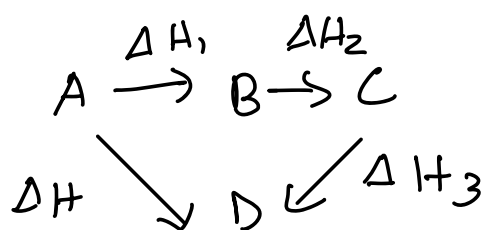
According to Hess's Law

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

Example - 1
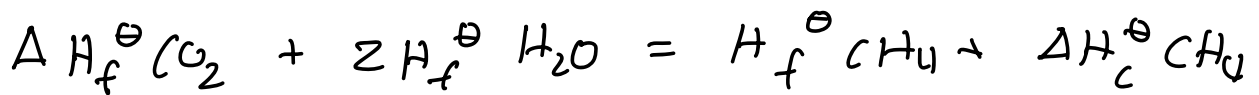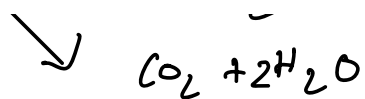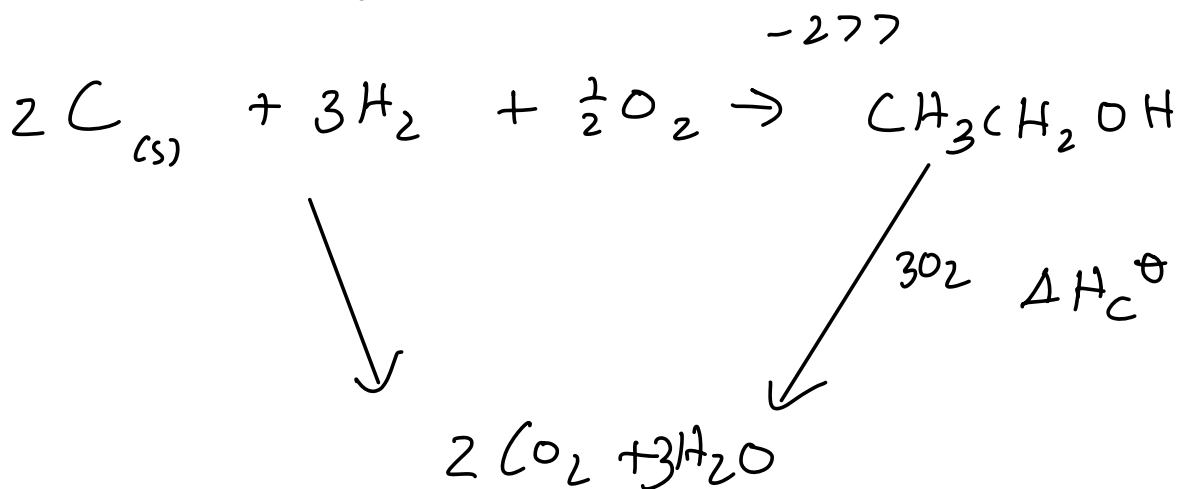
$$\Delta H_f^{\ominus} (CO_2) = -394 \text{ kJmol}^{-1}$$
$$\Delta H_f^{\ominus} (H_2O) = -286 \text{ kJmol}^{-1}$$
$$\Delta H_f^{\ominus} (CH_4) = -74 \text{ kJmol}^{-1}$$
$$\Delta H_c^{\ominus} (CH_4) = ?$$

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_4 \qquad \Delta H_f^{\ominus} = -74$$

$$\downarrow \quad CO_2 + 2H_2O$$

$$\Delta H_f^{\ominus} CO_2 \;+\; 2H_f^{\ominus} H_2O \;=\; H_f^{\ominus} CH_4 + \Delta H_c^{\ominus} CH_4$$
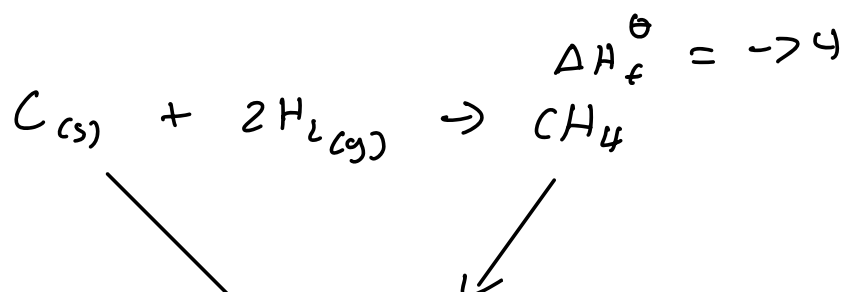
Example - 2

$$\Delta H_f^{\ominus} (CO_2) \;=\; -393 \;\; KJ\,mol^{-1}$$
$$\Delta H_f^{\ominus} (H_2O) \;=\; -286 \;\; KJ\,mol^{-1}$$
$$\Delta H_f^{\ominus} (CH_3 CH_2 OH) \;=\; -277 \;\; KJ\,mol^{-1}$$

Calculate the value of

$$\Delta H_c^{\ominus} (CH_3 CH_2 OH)$$

$$\qquad\qquad\qquad\qquad\qquad -277$$
$$2C_{(S)} \;+\; 3H_2 \;+\; \tfrac{1}{2}O_2 \;\rightarrow\; CH_3CH_2OH$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad 3O_2 \quad \Delta H_c^{\ominus}$$

$$2CO_2 + 3H_2O$$

$$2(-393) + (3 \times -286) \;=\; -277 + H_c^{\ominus}$$

$$H_c^\ominus (CH_3CH_2OH) = -1367 \text{ kJmol}^{-1}$$

Example 4

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

$$\Delta H_f^\ominus (SO_2) = -297$$

$$S_{(s)} + 1\tfrac{1}{2} O_{2(g)} \rightarrow SO_{3(g)}$$

$$\Delta H_f^\ominus (SO_3) = -395$$

$$2 SO_2 + O_2 \rightarrow 2SO_3$$

$$2\times-297 \diagup\!\!\diagdown 2\times-395$$

$$2\, S + 3\, O_2$$

$$\Rightarrow -196 \quad \underline{Ans}$$

Example 5

$$I_{2(g)} + 3Cl_{2(g)} \rightarrow 2 ICl_{3(s)}$$

$$\Delta H^\ominus = -214$$

$$I_{2(s)} \rightarrow I_{2(g)}$$

$$\Delta H^{\ominus} = +38$$

$$I_{2(g)} + 3Cl_{2(g)} \xrightarrow{-214} 2ICl_{3(s)}$$

$$38 \nearrow \qquad \nearrow x$$

$$I_{2} + Cl_{2}$$
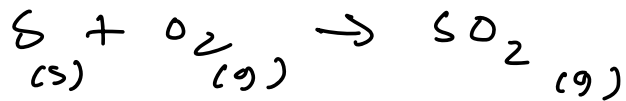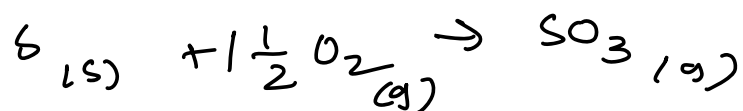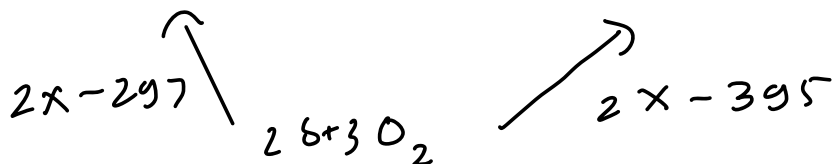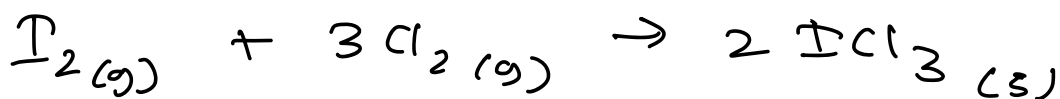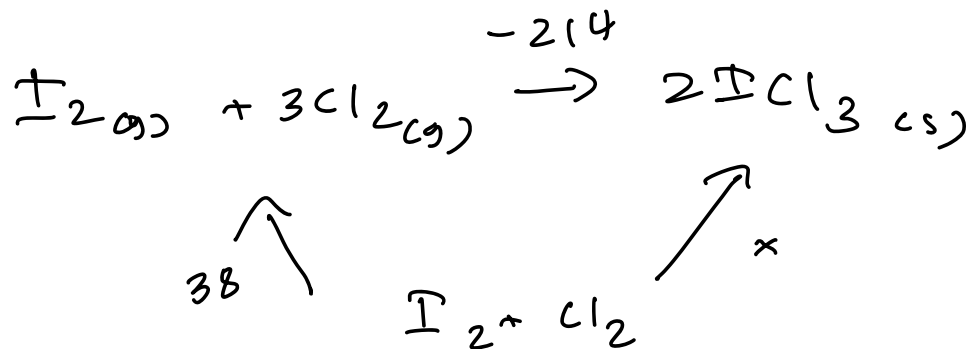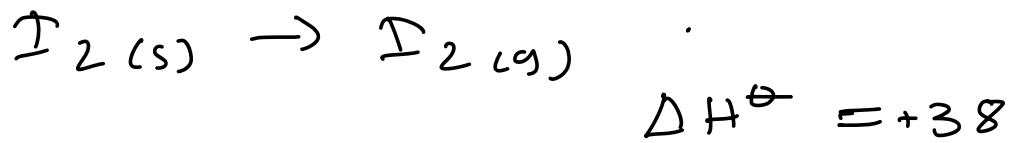
$$\frac{38 - 214}{2} = -88 \text{ kJ mol}^{-1}$$

$$\underline{\underline{Ans}}$$

Example 6

$$I_{2(s)} + Cl_{2(g)} \rightarrow 2ICl_{(s)}$$

$$\Delta H^{\ominus} = +14$$

$$ICl_{(s)} + Cl_{2(g)} \rightarrow ICl_{3(s)}$$

$$\Delta H^{\ominus} = -88$$

$$ICl_{(s)} + Cl_{2(g)} \xrightarrow{-88} ICl_{3(s)}$$

$$+7 \nwarrow \qquad \nearrow x$$

$$I_{2} + Cl_{2}$$

$2_{(s)}$ $_{(g)}$

$$CO_2 + H_2 \rightarrow CO + H_2O_{(g)}$$

-286 -283 -44

$$H_2O_{(l)} + CO_{2(g)}$$
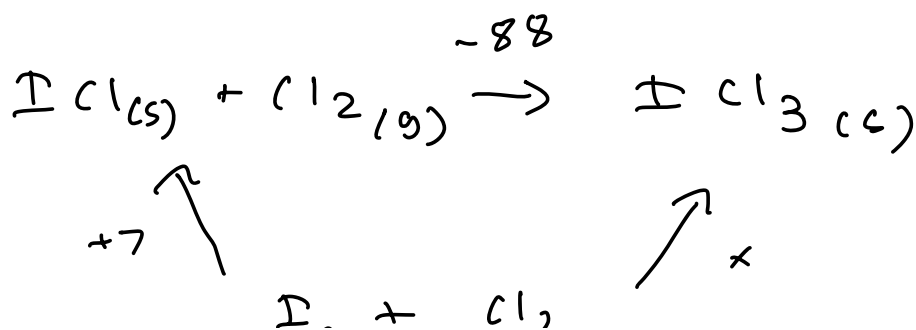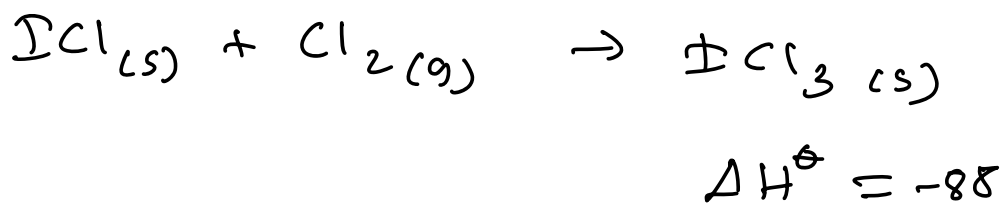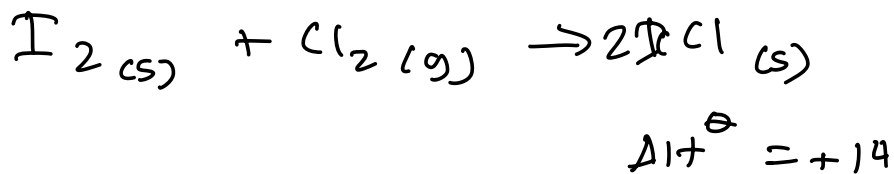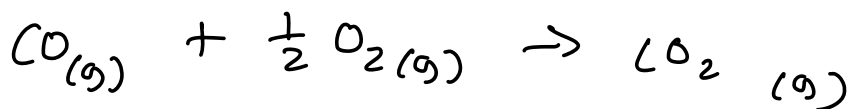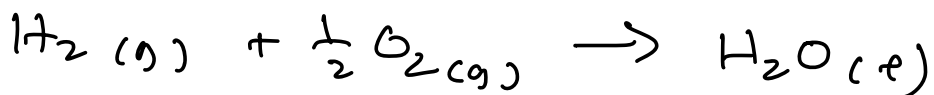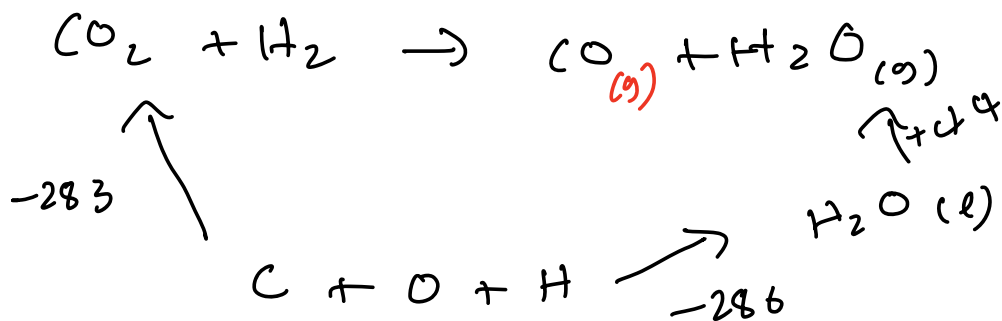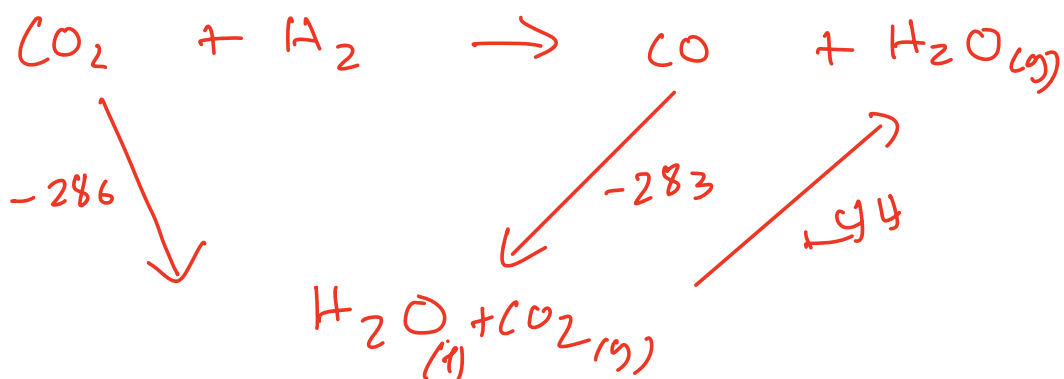
Neutralisation

Example 1

Experiment to determine enthalpy change of neutralisation

- ⊖ $50 cm^3$ of $1.0 \, mol \, dm^{-3}$ HCl is taken in a plastic beaker

  Initial temperature = $21.3°C$

- ⊖ $50 cm^3$ of $1.0 \, mol \, dm^{-3}$ NaOH is added in the plastic beaker

- ⊖ Stir the reaction mixture with the thermometer and record the highest

temperature.

Highest temp = 27.8 °C

0.005
HCl + NaOH → NaCl + H₂O

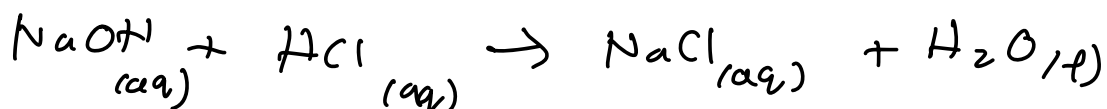$Q = mc\Delta\theta$

⊖ specific heat capacity of water is $4.18 J\ g^{-}c^{-1}$

⊖ The energy required to rise
the temperature of 1 g of a
liquid by 1°C is called the
specific heat capacity.

Reaction

$NaOH_{(aq)} + HCl_{(aq)} → NaCl_{(aq)} + H_2O_{(l)}$

$100 \times 4.18 \times 6.5 = 2717$

$0.05 = 2717$
$1 = -54340 k$
$⇒ -54.34 \ kJ mol^{-}$

Standard enthalpy change of solution (ΔH_{sol})

$\ominus \Delta H^{\ominus}_{sol}$ is the enthalpy change when one mole solute is dissolved in a solvent to form an infinitely dilute solution under normal condition.

Example

volume of H_2O = 100.45 cm^3
water is taken in a plastic beaker.
mass of $NaOH$ = 1.50g
Initial temp = 18°C
Final temp = 21.6°C
Calculate the value of ΔH sol

0.0375 mol

$$\frac{100.45 \times 4.18 \times 3.6}{0.0375 \times 1000} = -40.3 \text{ kJ mol}^{-1}$$
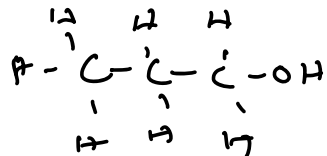
Experiment to determine ΔH_c

mass of H_2O = 100g
mass of spirit burner + propan-1-ol

at start = 86.27 g

mass of burner + propan-1-ol at
end = 86.06 g

Initial temp of water = 25°C
Final temp = 35.7°C

$$\frac{0.21}{60} = 0.0035$$

$$\frac{100 \times 4.18 \times 10.7}{0.0035 \times 1000} = -1278 \; kJ \, mol^{-1}$$

Example-1

$$\Delta H^{\ominus}_{sol} \; (Na_2 S_2 O_3) = -7.6 \; kJ \, mol^{-1}$$
$$(s)$$

$$\Delta H^{\ominus}_{sol} \; (Na_2 S_2 O_3 . 5H_2O) = +47.4 \; kJ \, mol^{-1}$$

$$\Delta H^{\ominus}_{hyd} \; (Na_2 S_2 O_3) = ?$$

$$Na_2 S_2 O_3 \quad + \; 5H_2O \rightarrow Na_2 S_2 O_3 . 5H_2O$$
$$\downarrow_{-7.6} \qquad \swarrow 47.4$$
$$Na, S_2 O_2$$
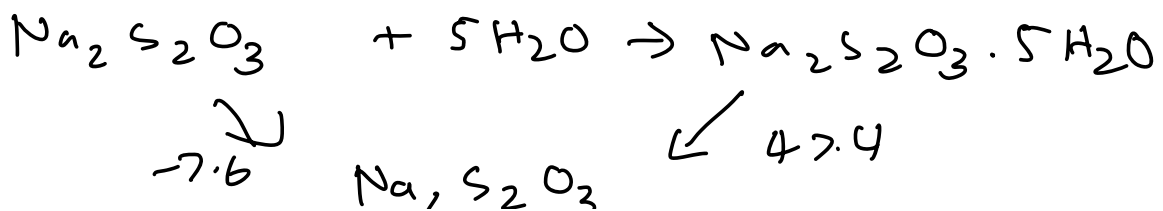
$$-7.6 - 47.4 = -55 \ kJ\,mol^{-1}$$

Example-2
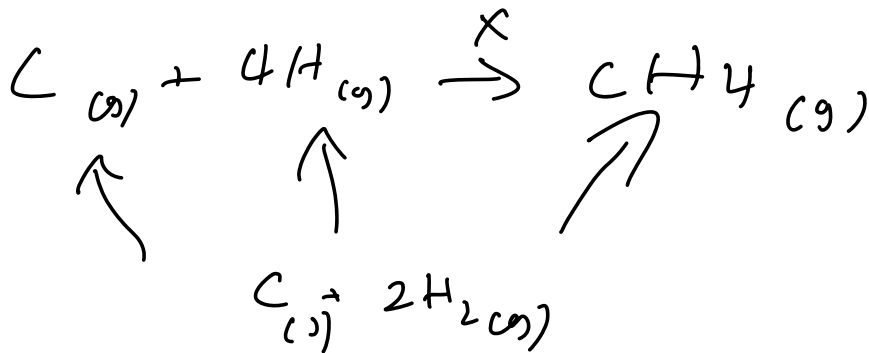
Calculate the Average bond energy
of C-H in CH_4 by using

$$\Delta H_f^{\ominus} (CH_4)$$

$$\Delta H_{at}^{\ominus} (C)$$

$$\Delta H_{at}^{\ominus} (\tfrac{1}{2}H_2)$$

$$C_{(s)} + 4H_{(g)} \xrightarrow{\;X\;} CH_4 \,_{(g)}$$

$$C_{(s)} \; 2H_{2(g)}$$

$$X \;\; - \Delta H_f^{\ominus} (CH_4) = \Delta H_{at}^{\ominus} (C)_{(s)} + 4\Delta H_{at}^{\ominus}(\tfrac{1}{2}H_2)$$

$$\frac{X}{4}$$

Example - 3

$$2 \, KHCO_{3(s)} \xrightarrow{\text{heat}} K_2CO_{3(s)} + CO_{2(g)} + H_2O(l)$$

+HCl ↓

2 KCl + H₂O + CO₂

↙ +2HCl

$\Delta H = ?$

Experiment - 1

0.006

30 cm³ of 2 mol dm⁻³ HCl (excess) was placed in a plastic cup and the temperature recorded was 21°C.

When 0.02 mol K_2CO_3 was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2°C

Calculate the enthalpy change per mole of K_2CO_3.

$$30 \times 4.18 \times 5.2 = 652.08$$

$$-32.6 \, kJ \, mol^{-1}$$

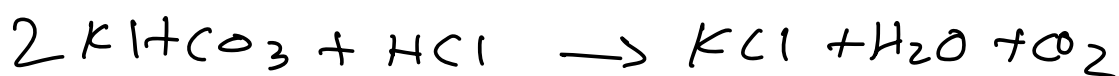$$K_2CO_3 + 2HCl \longrightarrow 2KCl + H_2O + CO_2$$

Experiment-2

The experinent was repeated with 0.02 mol of $KHCO_3$.

All other conditions were the same.

In the second experiment, the temperature decrease from $21.0°C$ to $17.3°C$.

Calculate the enthalpy change per mole of $KHCO_3$.

$$2 KHCO_3 + HCl \longrightarrow KCl + H_2O + CO_2$$

Ans: $+23.2 \ kJ \ mol^{-1}$

$2 \times 23.2 + 32.6 = 79$