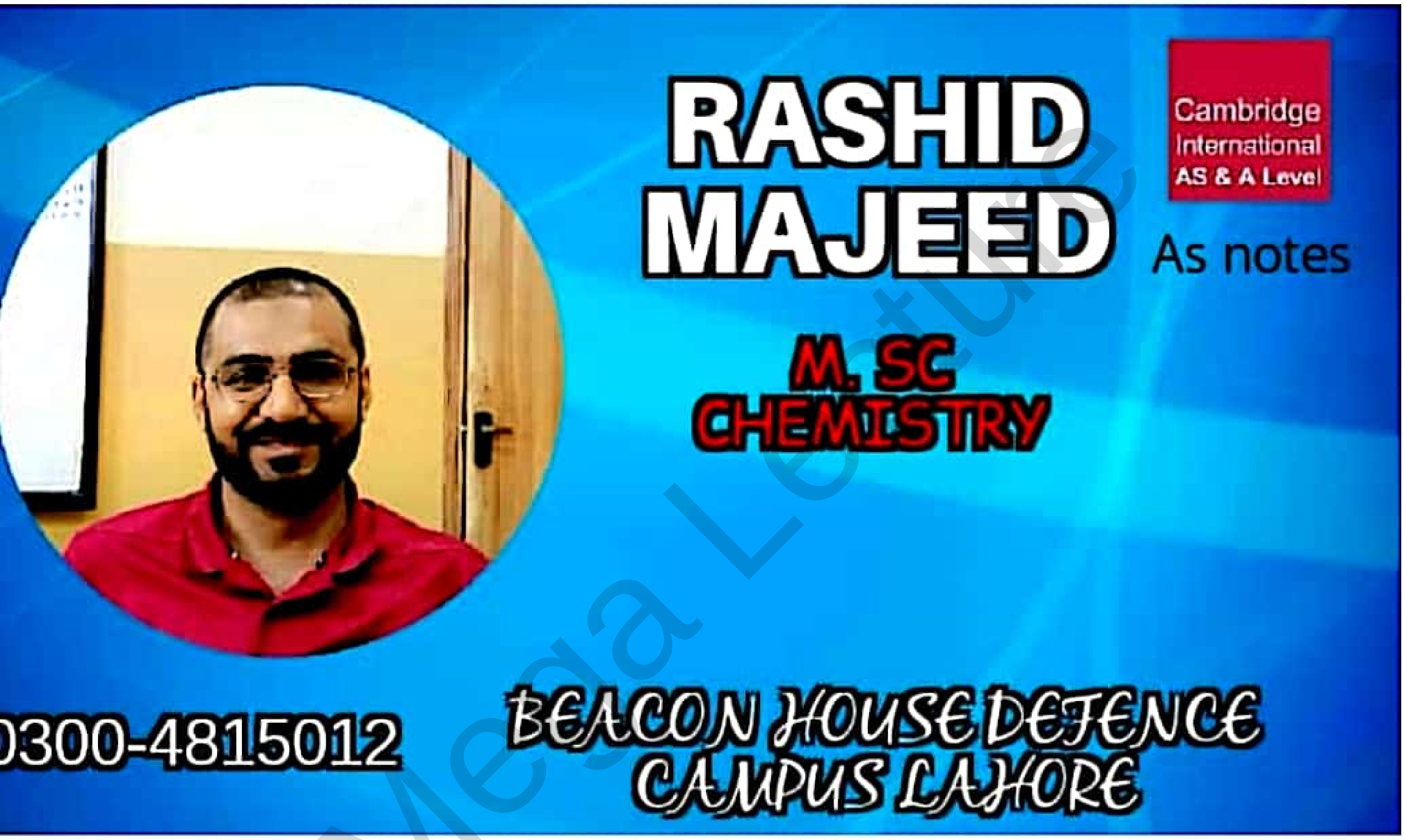

RASHID
MAJEED
Cambridge
International
AS & A Level
As notes
M. SC
CHEMISTRY
0300-4815012
BEACON HOUSE DEFENCE
CAMPUS LAHORE

5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

	Learning outcomes Candidates should be able to:
5.1 Enthalpy change, ΔH	a) explain that chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH is negative) or endothermic (ΔH is positive) b) explain and use the terms: (i) *enthalpy change of reaction* and *standard conditions*, with particular reference to: formation, combustion, hydration, solution, neutralisation, atomisation (ii) *bond energy* (ΔH positive, i.e. bond breaking) **(iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)** c) calculate enthalpy changes from appropriate experimental results, including the use of the relationship $\Delta H = -mc\Delta T$ **d) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy**
5.2 Hess' Law, including Born-Haber cycles	a) apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to: (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion (ii) average bond energies **(iii) the formation of a simple ionic solid and of its aqueous solution** **(iv) Born-Haber cycles (including ionisation energy and electron affinity)** b) construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy

5.3 Entropy change, ΔS	**a) explain that entropy is a measure of the 'disorder' of a system, and that a system becomes more stable when its energy is spread out in a more disordered state** **b) explain the entropy changes that occur:** **(i) during a change in state e.g. (s) → (l); (l) → (g); (s) → (aq)** **(ii) during a temperature change** **(iii) during a reaction in which there is a change in the number of gaseous molecules** **c) predict whether the entropy change for a given process is positive or negative** **d) calculate the entropy change for a reaction, ΔS, given the standard entropies, S, of the reactants and products**
5.4 Gibbs free energy change, ΔG	**a) define the standard Gibbs free energy change of reaction by means of the equation $\Delta G = \Delta H - T\Delta S$** **b) calculate ΔG for a reaction using the equation $\Delta G = \Delta H - T\Delta S$** **c) state whether a reaction or process will be spontaneous/feasible by using the sign of ΔG** **d) predict the effect of temperature change on the spontaneity/feasibility of a reaction, given standard enthalpy and entropy changes**

Chemical energetics

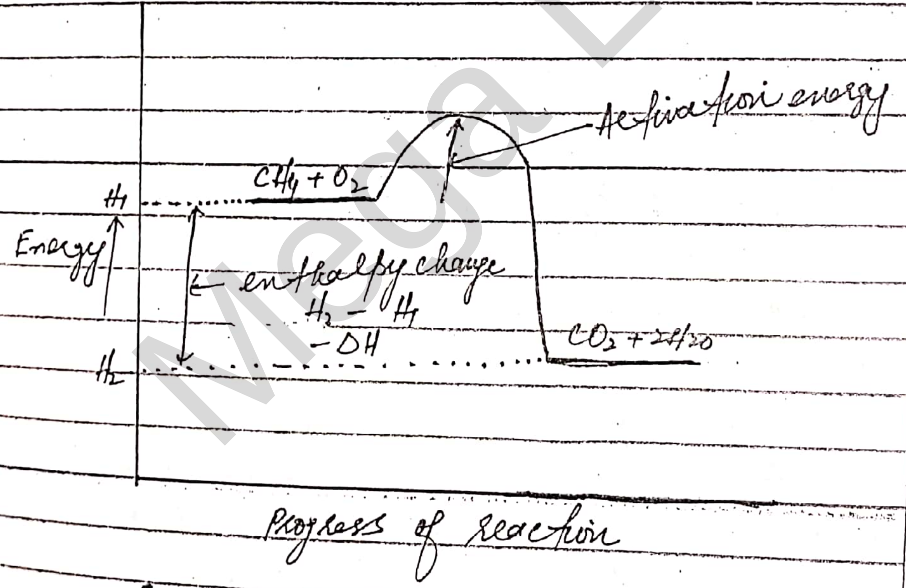
Most chemical reactions involve change in energy or enthalpy, i.e, energy is either released or absorbed during a chemical reaction.

⇒ Those reactions in which energy is released to the surroundings are called exothermic reactions.

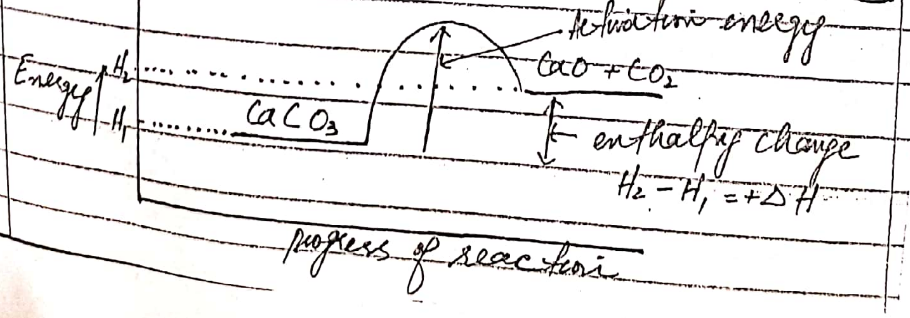
⇒ Those reactions in which energy is absorbed from the surroundings are called endothermic reactions.

Energy profile diagram for exothermic reactions

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O \quad -\Delta H$$

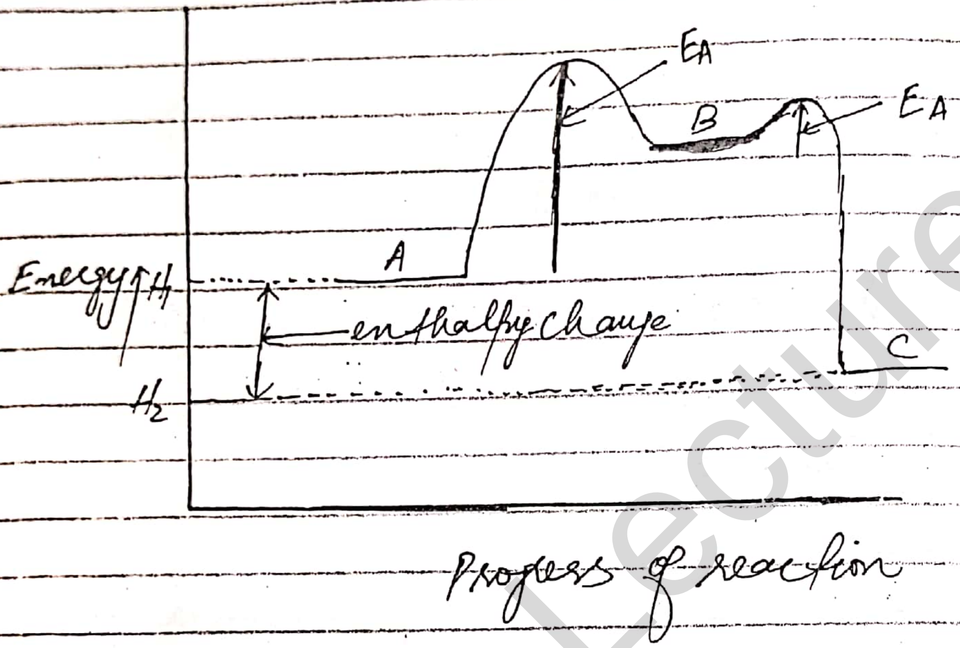


Energy profile diagram for endothermic reactions



Energy profile diagram for those reactions take place in two steps in which first step is endothermic but overall reaction is exothermic.

$$A \xrightarrow{Endo} B \xrightarrow{Exo} C \quad -\Delta H$$



Enthalpy and enthalpy change

Stored energy or internal energy of a substance is called its enthalpy which is represented by H. Enthalpy of a substance cannot be measured, only the energy absorbed or released by a substance during a chemical reaction can be measured which is called enthalpy change represented by ΔH.

Standard conditions for measuring enthalpy change

To make fair comparison of enthalpy changes, we must use the same conditions. These are called standard conditions, e.g;

⇒ a pressure of 1 atm or 10^5 pa or 100 kpa
⇒ a temperature of 25°C or 298 K
⇒ each substance involved in the reaction should have 1 mole
⇒ concentration of solutions should be 1 mol dm^{-3}.

Types of enthalpy changes

Standard enthalpy change of reaction ΔH_r°

Enthalpy change when any number of moles of reactants react to produce any number of moles of products under standard conditions.

$4Al + 3O_2 \longrightarrow 2Al_2O_3 \quad \Delta H_r^\circ$

$2H_2 + O_2 \longrightarrow 2H_2O \quad \Delta H_r^\circ$

Standard enthalpy change of formation ΔH_f°

Enthalpy change when one mole of a compound is formed from its elements under standard

Q2 (4)

conditions e.g.

$2Li_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow Li_2O_{(s)} \quad \Delta H_f^{\ominus} = -596 KJ/mol$

$2Fe_{(s)} + 1\frac{1}{2}O_{2(g)} \longrightarrow Fe_2O_{3(s)} \quad \Delta H_f^{\ominus} = -824.2 KJ mol^{-1}$

Note: Standard enthalpy change of formation of an element in its standard state is zero.

$Na_{(s)} \longrightarrow Na_{(s)} \quad \Delta H_f^{\ominus} = 0$

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

Enthalpy change when one mole of a substance burns in excess of oxygen under standard conditions.

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H_c^{\ominus} = -882 KJ mol^{-1}$

$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad \Delta H_c^{\ominus} = -296.8 KJ mol^{-1}$

Stand enthalpy change of atomization $\Delta H_{atm}^{\ominus}$

Enthalpy change when one mole of a gaseous atoms is formed from its element under standard conditions.

For example

$\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \quad \Delta H_{atm}^{\ominus} = +218 KJ mol^{-1}$

(5) 93

$\frac{1}{2}O_{2(g)} \longrightarrow O_{(g)}$ $\Delta H^\ominus_{atm} = 249\,kJ\,mol^{-1}$

$Na_{(s)} \longrightarrow Na_{(g)}$ $\Delta H^\ominus_{atm} = 108\,kJ\,mol^{-1}$

For diatomic molecules, enthalpy change of atomisation is equal to half of their bond energy.

For example bond energy of Cl-Cl bond is 242 $kJ\,mol^{-1}$ while enthalpy change of atomisation of chlorine is 121 $kJ\,mol^{-1}$

Standard enthalpy change of neutralization $\Delta H^\ominus_{neut}$

Enthalpy change when one mole of water is formed by the neutralization of an acid by an alkali under standard conditions

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$ $\Delta H^\ominus_{neut} = -57.1\,kJ\,mol^{-1}$

$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$ $\Delta H^\ominus_{neut} = -57.1\,kJ\,mol^{-1}$

Process of neutralization becomes less exothermic as the strength of acid and alkali decreases.

For example,

9/4

Standard enthalpy change of solution ΔH°_{sol}

Enthalpy change when one mole of a substance is completely dissolved in a solvent to give an infinitely dilute solution under standard conditions.

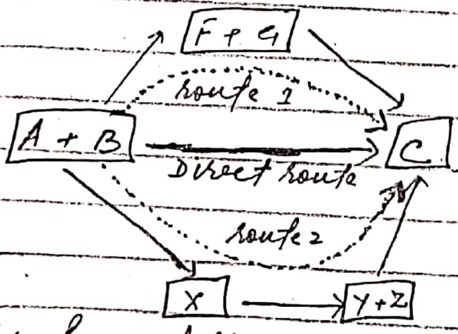
$$HCl_{(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} \quad \Delta H^\circ_{sol} = -74.4\,kJ\,mol^{-1}$$

An infinitely dilute solution is one which does not produce any further enthalpy change when more solvent is added.

Hess's law

Hess's law states that 'the total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same.

We can illustrate Hess's law by drawing enthalpy cycles



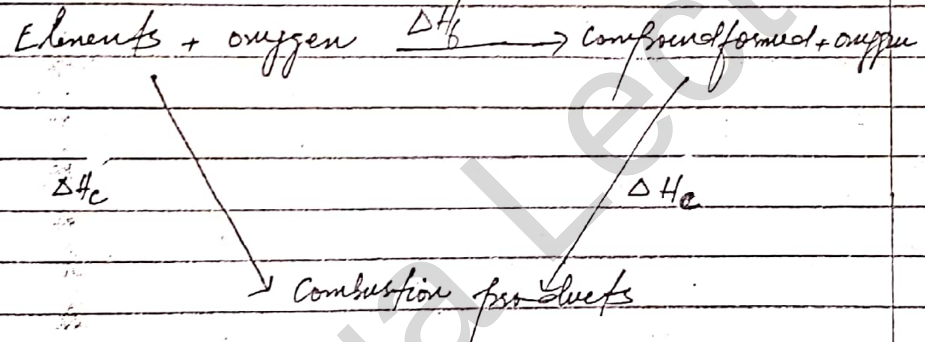
Hess's law tells us that the enthalpy change of reaction for the direct route is same as for the indirect route.

Application of Hess's law

1st application

Calculation of enthalpy of formation from enthalpy change of combustion

Following cycle is used to calculate the enthalpy of formation using enthalpy of combustion.



Following steps are taken

⇒ Write the equation for enthalpy of formation at the top, add oxygen to both sides of the equation to balance the combustion reactions

⇒ Draw the cycles with the combustion products at the bottom

⇒ Draw in all arrows, making sure they go in the correct directions

⇒ Apply Hess's law

Solved examples

Calculate the enthalpy of formation of ethane C_2H_6 using the following enthalpy of combustions.

ΔH_c^{θ} of Carbon = $-393.5\ KJ\ mol^{-1}$

ΔH_c^{θ} of H_2 = $-285.8\ KJ\ mol^{-1}$

ΔH_c of C_2H_6 = $-1559.7\ KJ\ mol^{-1}$

Solution

$$\begin{tikzcd}
3\frac{1}{2}O_2 + 2C + 3H_2 \arrow[rr, "\Delta H_f"] \arrow[dr, "\Delta H_1", "2\Delta H_c^{\theta} C + 3\Delta H_c^{\theta} H_2"'] & & C_2H_6 + 3\frac{1}{2}O_2 \arrow[dl, "\Delta H_c^{\theta} \text{ of } C_2H_6", "\Delta H_2"'] \\
& 2CO_2 + 3H_2O &
\end{tikzcd}$$

using Hess's law

$\Delta H_1 = \Delta H_f + \Delta H_2$

$\Delta H_f = \Delta H_1 - \Delta H_2$

ΔH_f = ΔH_c of reactants − ΔH_c of products

$\Delta H_f = 2(-393.5) + 3(285.8) - (-1559.7)$

$= -84.7\ KJ\ mole^{-1}$

Calculate the enthalpy change of formation of ethanol using enthalpy changes of combustion.

ΔH_c^{θ} of Carbon = -393.5 KJ/mole

ΔH_c^{θ} of H_2 = -285.8 KJ/mole

ΔH_c^{θ} of C_2H_5OH = -1367.3 KJ/mol

Solution

$$\begin{tikzcd}
3O_2 + 2C + 3H_2 \arrow[rr, "\Delta H_f^{\theta}"] \arrow[dr, "\Delta H_1", "2\times -393.5 + 3\times -285.8"'] & & C_2H_5OH + 3O_2 \arrow[dl, "\Delta H_c^{\theta} = -1367.3\ KJ\ mol^{-1}", "\Delta H_2"'] \\
& 2CO_2 + 3H_2O &
\end{tikzcd}$$

$\Delta H_f^\theta + \Delta H_2 = \Delta H_1$

$\Delta H_f^\theta = \Delta H_1 - \Delta H_2$

$2(-393.5) + 3(-285.8) - (-1367.3)$

$-787 - 857.4 + 1367$

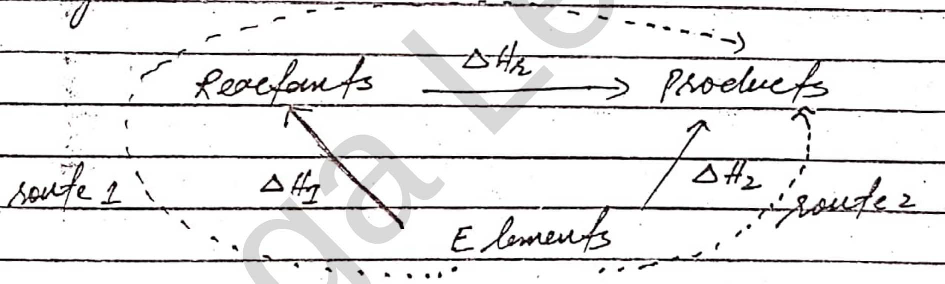
$-1644.4 + 1367$

-277.4 KJ/mole

2nd application of Hess's law

Calculation of enthalpy of reaction using enthalpy of formation

We can calculate the enthalpy change of reaction by using the following enthalpy cycle.



$\Delta H_r + \Delta H_1 = \Delta H_2$

$\Delta H_r = \Delta H_2 - \Delta H_1$

$\Delta H_r = \Delta H_f$ Products $- \Delta H_f$ Reactants

Following steps are followed while calculating enthalpy of reaction

⇒ write the balanced equation at the top

⇒ Draw the cycles with elements at the bottom

⇒ Draw in arrows in correct directions

⇒ Apply Hess's law

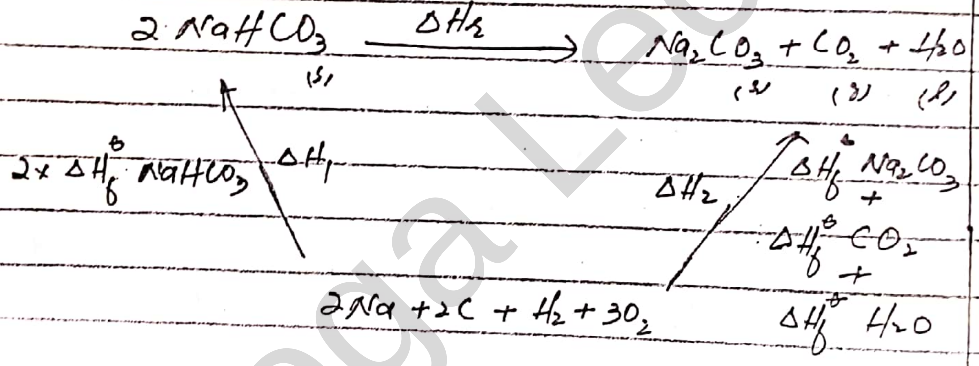
Solved examples

Calculate the standard enthalpy change for the reaction using the relevant enthalpy changes of formation

$$2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$$

ΔH_f° of $NaHCO_3$ = -950.8 KJ mol^{-1}
ΔH_f° of Na_2CO_3 = -1130.7 KJ mol^{-1}
ΔH_f° of CO_2 = -393.5 KJ mol^{-1}
ΔH_f° of H_2O = -285.8 KJ mol^{-1}

Solution



$$\Delta H_3 = \Delta H_2 - \Delta H_1$$
$$(-1130.7) + (-393.5) + (-285.8) - (-1901.6)$$
$$\Delta H_3 = +91.6 \text{ KJ mol}^{-1}$$

Calculate the enthalpy change for the following reaction using the standard enthalpy of formations

$$4CH_3NHNH_{2(l)} + 5N_2O_{4(g)} \longrightarrow 4CO_{2(g)} + 12H_2O_{(l)} + 9N_{2(g)}$$

ΔH_f° of CH_3NHNH_2 = 53 KJ mol^{-1}
ΔH_f° of N_2O_4 = -20 KJ mol^{-1}

ΔH_f° of $CO_2 = -393.5\ KJ\ mol^{-1}$

ΔH_f of $H_2O = -285.8\ KJ\ mol^{-1}$

ΔH_f of $N_2 = 0$

Solution

$$\begin{tikzcd}
4CH_3NHNH_2 + 5N_2O_4 \arrow[rr, "\Delta H_R"] & & 4CO_2 + 12H_2O + 9N_2 \\
& 4C + 24H_2 + 10O_2 + 9N_2 \arrow[ul, "\Delta H_1"', "4\times 53 + 5\times -20"] \arrow[ur, "\Delta H_2", "4\times -393.5 + 12\times -285.8"'] &
\end{tikzcd}$$

$\Delta H_R = \Delta H_2 - \Delta H_1$

$(4\times -393.5 + 12\times -285.8) - (4\times 53 + 5\times -20)$

$-5003.6 - 112$

$-5115.6\ KJ\ mol^{-1}$

3rd application of Hess's law

Calculation of enthalpy change of combustion from enthalpy of formation

Following cycle is used to measure enthalpy change of combustion using enthalpy change of formation

$$\begin{tikzcd}
\text{Reactant} \arrow[rr, "\Delta H_c"] & & \text{Product} \\
& \text{Elements} \arrow[ul, "\Delta H_1"] \arrow[ur, "\Delta H_2"'] &
\end{tikzcd}$$

$\Delta H_c^\circ = \Delta H_2 - \Delta H_1$

ΔH_c° = Enthalpy of formation of Products − enthalpy of formation of reactants

Solved examples

Calculate the enthalpy of combustion of octane C_8H_{18} using following enthalpy of formations

ΔH_f° of C_8H_{18} = -250 KJ mol^{-1}
ΔH_f° of CO_2 = -393 KJ mol^{-1}
ΔH_f° of H_2O = -286 KJ mol^{-1}

Solution

$$\begin{tikzcd}
C_8H_{18} + 12\frac{1}{2}O_2 \arrow[rr, "\Delta H_c"] & & 8CO_2 + 9H_2O \\
& 8C + 9H_2 + 12\frac{1}{2}O_2 \arrow[ul, "\Delta H_f \; -250"] \arrow[ur, "\Delta H_f \; 8\times-393.5 + 9\times-285.8"'] &
\end{tikzcd}$$

$\Delta H_c^\circ = \Delta H_f$ Products $-\ \Delta H_f$ of Reactants

$8\times-393.5 + 9\times-285.8 - (-250)$

-5470.2 KJ mol^{-1}

Calculating enthalpy changes using bond energies

We can use bond energies to calculate enthalpy change of a reaction that we cannot measure directly

Solved examples.

Calculate enthalpy change for the Haber's process used for the manufacture of ammonia, using the bond energies which are given below

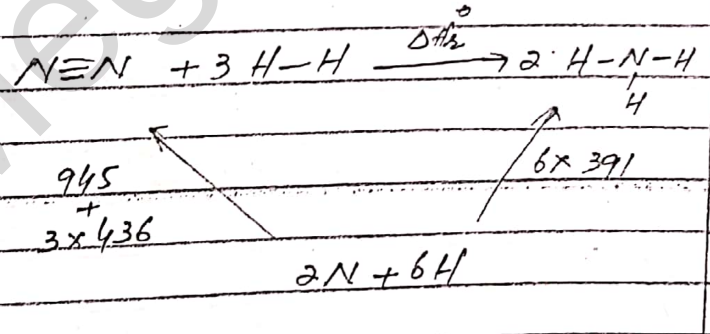
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$N\equiv N = 945\ KJ\ mol^{-1}$

$H-H = 436\ KJ\ mol^{-1}$

$N-H = 391\ KJ\ mol^{-1}$

Solution



ΔH°_r = Bond energy of reactants − Bond energy of products

$(945 + 3\times436) - (6\times391)$

$2253 - 2346$

$= -93\ KJ\ mol^{-1}$

$\frac{}{2} = -46.5\ KJ\ mol^{-1}$

Example

Calculate the enthalpy of combustion of methane CH_4 using following bond energies.

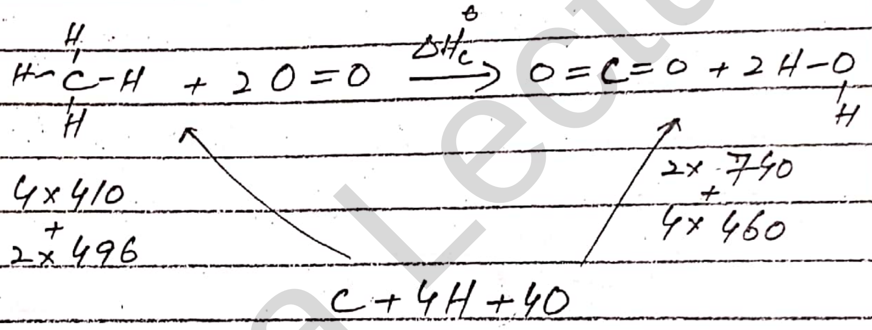
$C-H = 410\ kJ\ mol^{-1}$

$O=O = 496\ kJ\ mol^{-1}$

$C=O = 740\ kJ\ mol^{-1}$

$O-H = 460\ kJ\ mol^{-1}$

Solution



$$CH_4 + 2\,O=O \xrightarrow{\Delta H_c^{\ominus}} O=C=O + 2\,H-O-H$$

$4\times410 + 2\times496$

$2\times740 + 4\times460$

$C + 4H + 4O$

$\Delta H_c^{\ominus}$ = Bond energy of reactants − Bond energy of products

$$(4\times410 + 2\times496) - (2\times740 + 4\times460)$$

$$\Delta H_c^{\ominus} = -688\ kJ\ mol^{-1}$$

Example

A molecule of N_2O_4 is formed by the dimerisation of NO_2. Calculate the N−N single bond energy in N_2O_4 using the following enthalpy of formations.

$\Delta H_f^{\ominus}$ of $NO_2 = 33.2\ kJ\ mol^{-1}$

$\Delta H_f^{\ominus}$ of $N_2O_4 = 9.2\ kJ\ mol^{-1}$

$$-434 = 4x + 158 - 6x$$
$$-434 = -2x + 158$$
$$2x = 434 + 158$$
$$x = \frac{592}{2}$$
$$x = 296\ KJ\ mol^{-1}$$

Example

Calculate the C–H bond energy in methane CH_4 using following information

ΔH°_{atm} of C = 715 KJ mol^{-1}

ΔH°_{f} of CH_4 = −75 KJ mol^{-1}

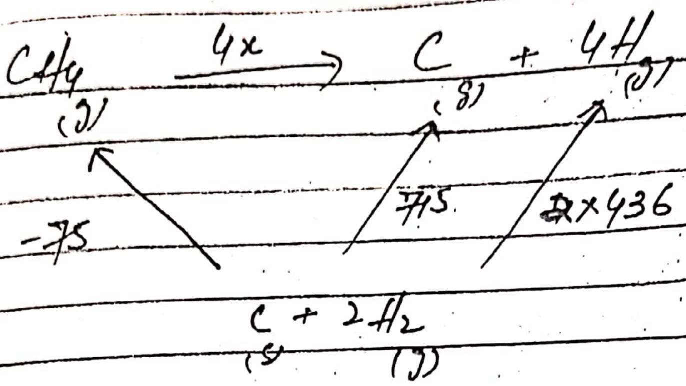
H–H = 436 KJ mol^{-1}

Solution

$$\begin{tikzcd}
C_{(s)} + 2H_{2(g)} \arrow[rr, "-75"] \arrow[dr, "715\quad 2\times436"'] & & CH_{4(g)} \\
& C_{(g)}\quad 4H_{(g)} \arrow[ur, "-4x"'] &
\end{tikzcd}$$

$$-75 = 715 + 2\times436 - 4x$$
$$-75 - 1587 = -4x$$
$$\cancel{-}1662 = \cancel{-}4x$$
$$x = \frac{1662}{4}$$
$$415.5\ KJ\ mol^{-1}$$

Alternative method



$$4x - 75 = 715 + 2\times436$$

$$4x - 75 = 1587$$

$$4x = 1587 + 75$$

$$x = \frac{1662}{4}$$

$$x = 415.5\ kJ\ mol^{-1}$$

1- Measuring enthalpy changes

Calorimetry :- We can measure the enthalpy change of some reactions by a technique called calorimetry. The apparatus used is called a calorimeter.

A simple calorimeter can be a polystyrene cup or a styrofoam beaker or a metal can.

Calorimetry relies on the fact that it takes 4.18 J of energy to increase the temperature of 1g of water by 1°C, which is called the specific heat capacity of water which is $4.18\,J\,g^{-1}\,°C^{-1}$.

The energy transferred as heat is given by the relationship

$$q = mc\Delta T$$

where q = energy transferred in J
m = mass of water
c = specific heat capacity in $J\,g^{-1}\,°C^{-1}$
ΔT = change in temp in °C

Since $1\,cm^3$ of water weighs 1g we can substitute volume of water in cm^3 of water for mass of water in g in the equation.

Similarly aqueous solutions of acids, alkalis and salts are assumed to be largely water. Solutions has same specific heat capacity as water.

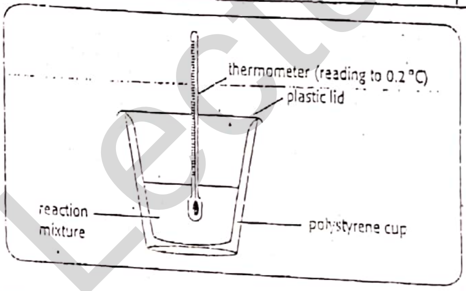
Experimental measurement of enthalpy of neutralization

A typical procedure for neutralization reaction is as follows.

Place 50 cm^3 of 1.0 $mol\,dm^{-3}$ HCl in a polystyrene cup and record its temperature.

Add 50 cm^3 of 1.0 $mol\,dm^{-3}$ NaOH to the acid in the cup.

Stir the reaction mixture with the thermometer and record the highest temperature.



Calculations

Initial temp = 21.3°C
Final temp = 27.8°C
Change in temp ΔT = 6.5°C
m = 50 + 50 = 100 cm^3 = 100 g
C = 4.2 $J\,g^{-1}\,°C^{-1}$
q = $mC\Delta T$

$100 \times 4.2 \times 6.5 = 2717$ J

$\frac{2717}{1000} = 2.717$ kJ

We used 50 cm^3 1.0 $mol\,dm^{-3}$ solution of HCl and NaOH, so number of mole of acid and alkali are

moles = $C \times V$

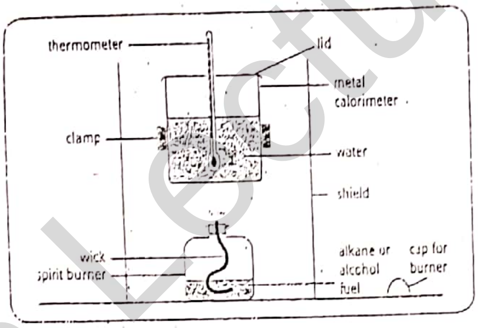
$\frac{0.1 \times 50}{1000} = 0.050$ mole

When 0.050 mol of water formed energy released 2.717 kJ

1 mol of H_2O formed $\frac{2.717}{0.050} = -54$ kJ mol^{-1}

Experimental measurement of enthalpy change of combustion using propan-1-ol

We can find the enthalpy change of combustion by burning a known mass of a substance and using the heat released to raise the temperature of known mass of water.
The apparatus used consists of a spirit burner and a metal calorimeter



To find the standard enthalpy change of combustion we need to know
- => the mass of fuel burnt
- => the temp rise of the water
- => the mass of water
- => Mr of propan-1-ol

mass of water in calorimeter = 100 g
mass of spirit burner + propan-1-ol = 86.27 g
mass of spirit burner + propan-1-ol at the end = 86.0
mass of propan-1-ol burnt = 0.21
initial temp of water = 20.2
final temp of water = 30.9
rise in temp = 10.7

using the relationship $q = mc\Delta T$

$q = 100 \times 4.2 \times 10.7$

$4472.6\ J$

$\frac{4472.6}{1000} = 4.472\ KJ$

Mr of propan-2-ol is 60g
So for 60g of propan-2-ol energy released is $\frac{4.472}{0.21} \times 60$

$= -1300\ KJ\ mol^{-1}$

This is much less than the recorded value due to the heat losses to the surroundings.

Experimental measurement of enthalpy change of solution

The enthalpy change of solution of sodium hydroxide can be found by using a polystyrene cup as a calorimeter. We use known amounts of solute and solvent with the solvent in excess to make sure that all the solute dissolves.

Calculations

mass of polystyrene cup = 23.00g
mass of cup + water = 123.45g
mass of water = 100.45g
mass of cup + water + $NaOH$ = 124.95g
mass of dissolved $NaOH$ = 1.50g
Temperature rise = 3.6°C

$q = 100.45 \times 4.2 \times 3.6 = 1511.57J$

$1.5KJ = \frac{1.5}{1.5} \times 40 = -40KJ\ m$

Solved example

30 cm^3 of 2.00 $mol\,dm^{-3}$ HCl in excess was placed in a conical flask and the temperature recorded as 21°C. When 0.0200 mol of 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 in $kJ\,mol^{-1}$

Solution

$q = mC\Delta T$

$30 \times 4.18 \times 5.2$

$652.08\ J$ per 0.02 mol of K_2CO_3

0.020 mol of K_2CO_3 = 652.08 J

1 mol of K_2CO_3 = $\frac{652.08}{0.02} \times 1$

= 32604 J

= $-32.60\ kJ\,mol^{-1}$