

Thermochemistry

1. Introduction to Energy changes

Energy is the capacity to do **work**. There are many/various **forms** of energy like heat, electric, mechanical, and/ or chemical energy. There are two types of energy:

- (i) Kinetic Energy (KE); the energy in motion.
- (ii) Potential Energy (PE); the stored/internal energy.

Energy like matter, is **neither created nor destroyed** but can be transformed /changed from one form to the other/ is interconvertible. This is the **principle of conservation** of energy. e.g. Electrical energy into heat through a filament in bulb. Chemical and physical processes take place with **absorption** or **evolution**/production of energy mainly in form of **heat**

The study of energy changes that accompany physical/chemical reaction/changes is called **Thermochemistry**. Physical/chemical reaction/changes that involve energy changes are called **thermochemical reactions**. The SI unit of energy is the **Joule (J)**. Kilo Joules (**kJ**) and mega Joules (**MJ**) are also used. The Joule (J) is defined as the:

- (i) quantity of energy transferred when a force of one **newton** acts through a distance of one **metre**.
- (ii) quantity of energy transferred when one **coulomb** of electric charge is passed through a potential difference of one **volt**.

All thermochemical reactions should be carried out at standard conditions of:

- (i) **298K /25°C** temperature
- (ii) **101300Pa/101300N/m² /760mmHg/1** atmosphere pressure.

2. Exothermic and endothermic processes/reactions

Some reactions / processes take place with evolution/production of energy. They are said to be **exothermic** while others take place with **absorption** of energy. They are said to be **endothermic**.

Practically exothermic reactions / processes cause a rise in temperature (by a rise in thermometer reading/mercury or alcohol level rise)

Practically endothermic reactions / processes cause a fall in temperature (by a fall in thermometer reading/mercury or alcohol level decrease)

To demonstrate/illustrate exothermic and endothermic processes/reactions

- a) Dissolving Potassium nitrate(V)/ammonium chloride crystals

Procedure:

Measure 20cm³ of water in a beaker. Determine and record its temperature T₁. Put about 1.0g of Potassium nitrate(V) crystals into the beaker. Stir the mixture carefully and note the highest temperature rise /fall T₂. Repeat the whole procedure by using ammonium chloride in place of Potassium nitrate (V) crystals.

Sample results

Temperture (°C)	Using Potassium nitrate(V) crystals	Using Ammonium chloride crystals
T ₂ (Final temperature)	21.0	23.0
T ₁ (Initial temperature)	25.0	26.0
Change in temperature(T ₂ –T ₁)	4.0	3.0

Note:

- (i)Initial(T₁) temperature of dissolution of both potassium nitrate(V) crystals and ammonium chloride crystals is **higher** than the final temperature(T₂)
- (ii) Change in temperature(T₂ –T₁) is **not** a mathematical “-4.0” or “-3.0”.
- (iii)Dissolution of both potassium nitrate(V) and ammonium chloride crystals is an **endothermic** process because initial(T₁) temperature is **higher** than the final temperature(T₂) thus causes a **fall/drop** in temperature.

b) Dissolving concentrated sulphuric(VI) acid/sodium hydroxide crystals

Procedure:

Measure 20cm³ of water in a beaker. Determine and record its temperature T₁. **Carefully** put about 1.0g/four pellets of sodium hydroxide crystals into the beaker. Stir the mixture carefully and note the highest temperature rise /fall T₂. Repeat the whole procedure by using 2cm³ of concentrated sulphuric(VI) acid in place of sodium hydroxide crystals.

CAUTION:

- (i)Sodium hydroxide crystals are **caustic** and cause painful blisters on contact with skin.
- (ii) Concentrated sulphuric (VI) acid is **corrosive** and cause painful wounds on contact with skin.

Sample results

Temperture (°C)	Using Sodium hydroxide pellets	Using Concentrated sulphuric(VI) acid
T ₂ (Final temperature)	30.0	32.0
T ₁ (Initial temperature)	24.0	25.0
Change in temperature(T ₂ –T ₁)	6.0	7.0

Note:

- (i)Initial (T₁) temperature of dissolution of both concentrated sulphuric (VI) acid and sodium hydroxide pellets is **lower** than the final temperature (T₂).
- (ii)Dissolution of both Sodium hydroxide pellets and concentrated sulphuric (VI) acid is an **exothermic** process because final (T₂) temperature is **higher** than the initial temperature (T₁) thus causes a **rise** in temperature.

The above reactions show heat loss **to** and heat gain **from** the surrounding as illustrated by a **rise** and **fall** in temperature/thermometer readings.

Dissolving both potassium nitrate(V) and ammonium chloride crystals causes heat **gain from** the **surrounding** that causes **fall** in thermometer reading.

Dissolving both Sodium hydroxide pellets and concentrated sulphuric (VI) acid causes heat **loss to** the **surrounding** that causes **rise** in thermometer reading.

At the same temperature and pressure, heat absorbed and released is called enthalpy/ heat content denoted **H**.

Energy change is measured from the heat content/enthalpy of the **final** and **initial** products. It is denoted ΔH (delta H).i.e.

$$\text{Enthalpy/energy/ change in heat content } \Delta H = H_{\text{final}} - H_{\text{initial}}$$

For chemical reactions:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

For exothermic reactions, the heat contents of the **reactants** is **more** than/**higher** than the heat contents of **products**, therefore the ΔH is negative ($-\Delta H$)

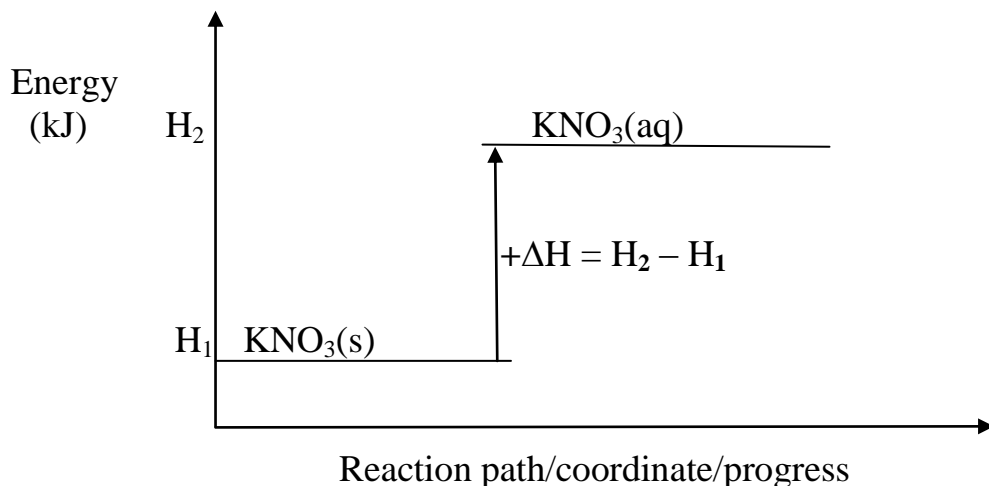
For endothermic reactions, the heat contents of the **reactants** is **less** than/**lower** than the heat contents of **products**, therefore the ΔH is positive ($+\Delta H$)

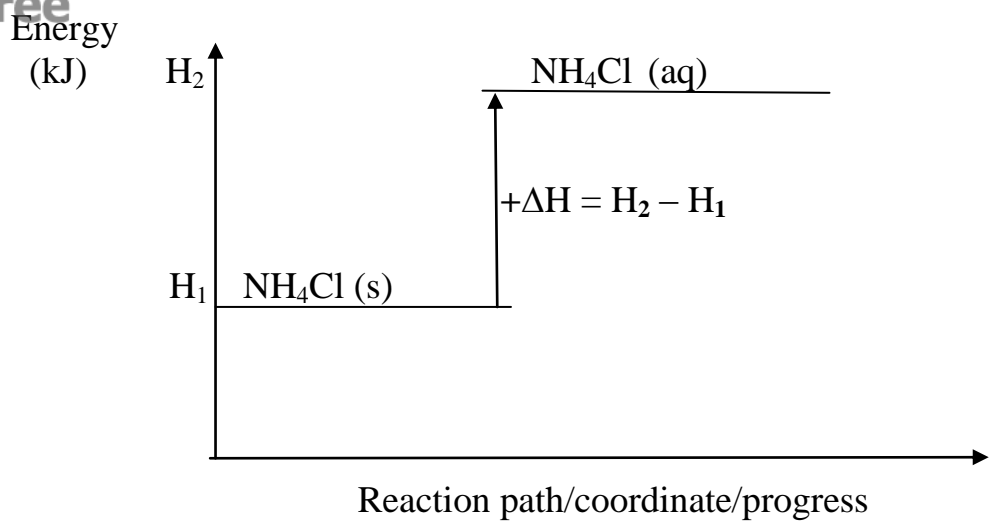
Graphically, in a **sketch** energy level diagram:

(i)For endothermic reactions the heat content of the reactants should be relatively/slightly **lower** than the heat content of the products

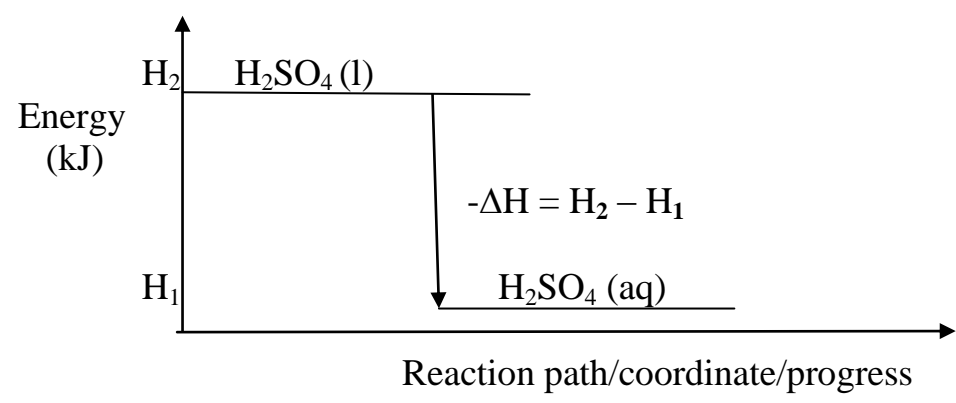
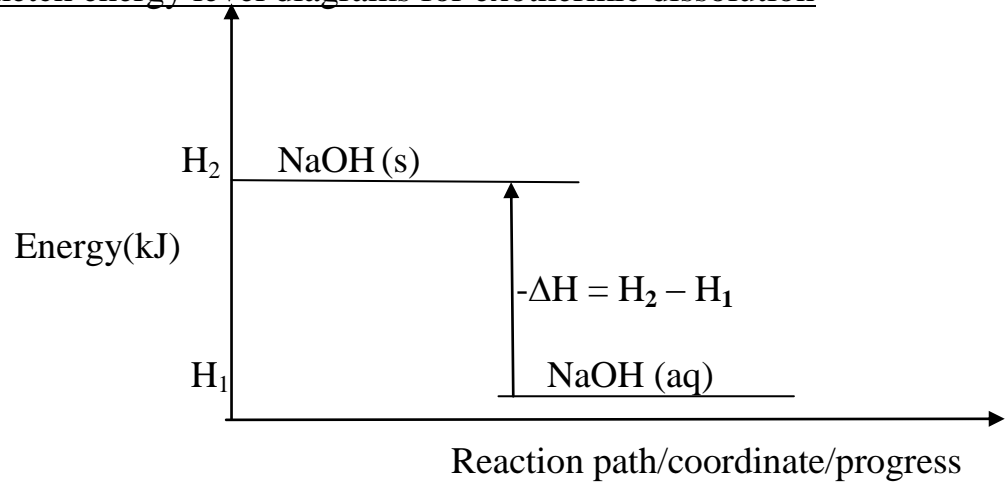
(ii)For exothermic reactions the heat content of the reactants should be relatively/slightly **higher** than the heat content of the products

Sketch energy level diagrams for endothermic dissolution





Sketch energy level diagrams for exothermic dissolution



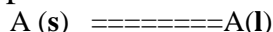
3. Energy changes in physical processes

Melting/freezing/fusion/solidification and **boiling/vaporization/evaporation** are the two physical processes. Melting /freezing point of pure substances is fixed

/constant. The boiling point of pure substance depend on **external atmospheric pressure**.

Melting/fusion is the physical change of a **solid to liquid**. Freezing is the physical change of a **liquid to solid**.

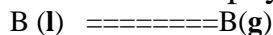
Melting/freezing/fusion/solidification are therefore two **opposite but same** reversible physical processes. i.e



Boiling/vaporization/evaporation is the physical change of a **liquid to gas/vapour**.

Condensation/liquidification is the physical change of **gas/vapour to liquid**.

Boiling/vaporization/evaporation and condensation/liquidification are therefore two **opposite but same** reversible physical processes. i.e



Practically

(i) Melting/liquidification/fusion involves **heating** a solid to **weaken** the strong bonds holding the solid particles together. Solids are made up of very strong bonds holding the particles **very close** to each other (**Kinetic Theory of matter**). On heating these particles gain energy/heat from the surrounding heat source to form a liquid with **weaker** bonds holding the particles close together but with some degree of **freedom**. Melting/freezing/fusion is an **endothermic** (+ΔH) process that require/absorb energy from the surrounding.

(ii) Freezing/fusion/solidification involves cooling a a liquid to reform /rejoin the very strong bonds to hold the particles **very close** to each other as solid and thus lose their degree of **freedom** (**Kinetic Theory of matter**). Freezing /fusion / solidification is an **exothermic** (-ΔH) process that require particles holding the liquid together to lose energy to the surrounding.

(iii) Boiling/vaporization/evaporation involves **heating** a liquid to completely **break/free** the bonds holding the liquid particles together. Gaseous particles have high degree of **freedom** (**Kinetic Theory of matter**). Boiling /vaporization / evaporation is an **endothermic** (+ΔH) process that require/absorb energy from the surrounding.

(iv) Condensation/liquidification is **reverse** process of boiling /vaporization / evaporation. It involves gaseous particles losing energy to the surrounding to form a liquid. It is an **exothermic**(+ΔH) process.

The quantity of energy required to **change** one mole of a solid **to** liquid or to **form** one mole of a solid **from** liquid at constant temperature is called **molar enthalpy/latent heat of fusion**. e.g.





The quantity of energy required to **change** one mole of a liquid **to** gas/vapour or to **form** one mole of a liquid **from** gas/vapour at constant temperature is called **molar enthalpy/latent heat of vapourization**. e.g.



The following experiments illustrate/demonstrate practical determination of melting and boiling

a) To determine the boiling point of water

Procedure:

Measure 20cm³ of tap water into a 50cm³ glass beaker. Determine and record its temperature. Heat the water on a strong Bunsen burner flame and record its temperature after every thirty seconds for four minutes.

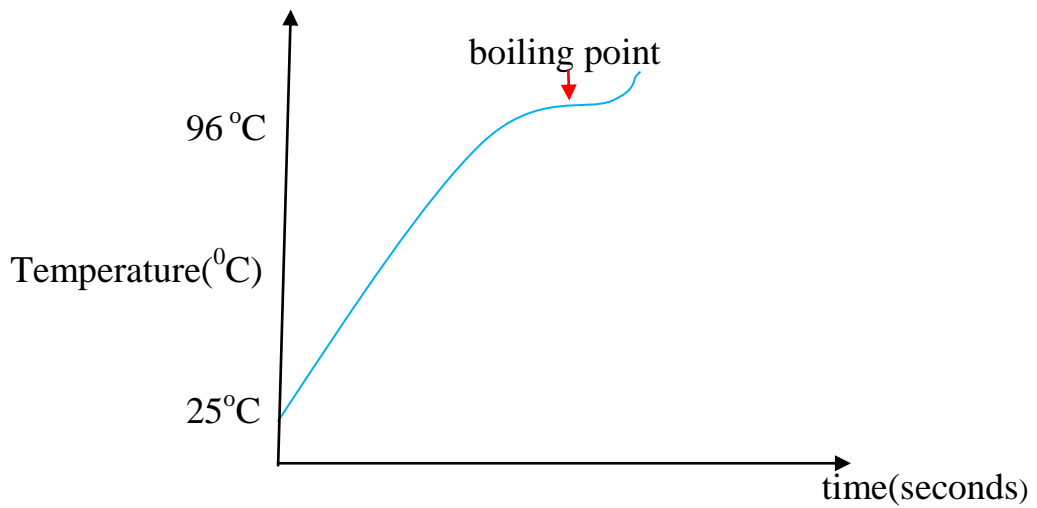
Sample results

Time(seconds)	0	30	60	90	120	150	180	210	240
Temperature(°C)	25.0	45.0	85.0	95.0	96.0	96.0	96.0	97.0	98.0

Questions

1. Plot a graph of temperature against time(y-axis)

Sketch graph of temperature against time



2. From the graph show and determine the boiling point of water

Note:

Water boils at 100°C at sea level/one atmosphere pressure/101300Pa **but** boils at **below** 100°C at **higher** altitudes. The sample results above are from Kiriari

Girls High School-Embu County on the slopes of Mt Kenya in Kenya. Water here boils at 96°C.

3. Calculate the molar heat of vaporization of water. (H= 1.0, O= 16.0)

Working:

Mass of water = density x volume => (20 x 1) /1000 = **0.02kg**

Quantity of heat produced

= mass of water x specific heat capacity of water x temperature change

=> 0.02kg x 4.2 x (96 – 25) = **5.964kJ**

Heat of vaporization of one mole H₂O = $\frac{\text{Quantity of heat}}{\text{Molar mass of H}_2\text{O}}$

$$\Rightarrow \frac{5.964\text{kJ}}{18} = \mathbf{0.3313 \text{ kJ mole}^{-1}}$$

To determine the melting point of candle wax

Procedure

Weigh exactly 5.0 g of candle wax into a boiling tube. Heat it on a strongly Bunsen burner flame until it completely melts. Insert a thermometer and remove the boiling tube from the flame. Stir continuously. Determine and record the temperature after every 30seconds for four minutes.

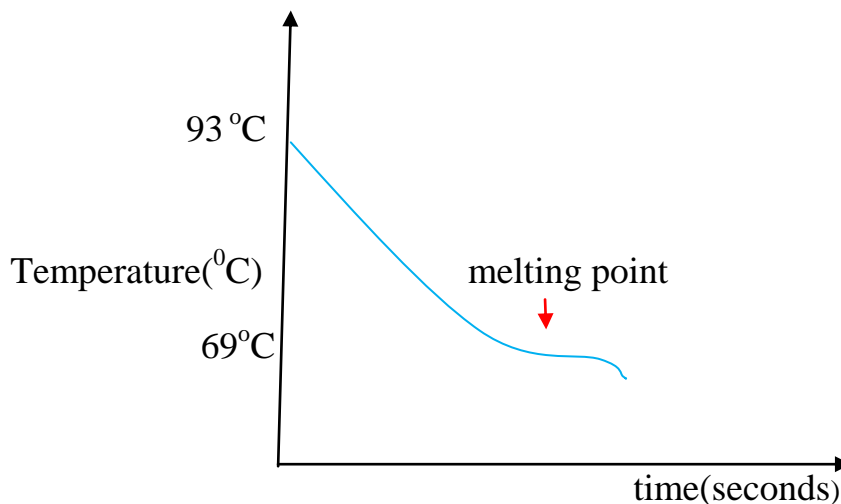
Sample results

Time(seconds)	0	30	60	90	120	150	180	210	240
Temperature(°C)	93.0	85.0	78.0	70.0	69.0	69.0	69.0	67.0	65.0

Questions

1. Plot a graph of temperature against time(y-axis)

Sketch graph of temperature against time



2. From the graph show and determine the melting point of the candle wax

4. Energy changes in chemical processes

Thermochemical reactions measured at **standard** conditions of 298K(25°C) and 101300Pa/101300Nm²/ 1 atmospheres/760mmHg/76cmHg produce standard **enthalpies** denoted ΔH° .

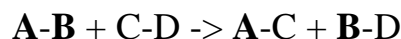
Thermochemical reactions are named from the type of reaction producing the energy change. Below are some thermochemical reactions:

- (a) Standard enthalpy/heat of reaction ΔH°_r
- (b) Standard enthalpy/heat of combustion ΔH°_c
- (c) Standard enthalpy/heat of displacement ΔH°_d
- (d) Standard enthalpy/heat of neutralization ΔH°_n
- (e) Standard enthalpy/heat of solution/dissolution ΔH°_s
- (f) Standard enthalpy/heat of formation ΔH°_f

(a) Standard enthalpy/heat of reaction ΔH°_r

The molar standard enthalpy/heat of reaction may be defined as the energy/heat change when one mole of products is formed at standard conditions

A chemical reaction involves the reactants forming products. For the reaction to take place the bonds holding the reactants must be broken so that new bonds of the products are formed. i.e.



Old Bonds **broken** A-B and C-D on reactants

New Bonds **formed** A-C and B-D on products

The energy required to break one mole of a (covalent) bond is called **bond dissociation energy**. The SI unit of bond dissociation energy is $\mathbf{kJmole^{-1}}$

The higher the bond dissociation energy the stronger the (covalent)bond

Bond dissociation energies of some (covalent)bonds

Bond	Bond dissociation energy (kJmole^{-1})		Bond dissociation energy (kJmole^{-1})
H-H	431	I-I	151
C-C	436	C-H	413
C=C	612	O-H	463
C = C	836	C-O	358
N = N	945	H-Cl	428
N-H	391	H-Br	366
F-F	158	C-Cl	346
Cl-Cl	239	C-Br	276
Br-Br	193	C-I	338
H-I	299	O=O	497
Si-Si	226	C-F	494

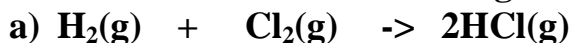
The molar enthalpy of reaction can be calculated from the bond dissociation energy by:

(i) **adding** the total bond dissociation energy of the **reactants** (endothermic process/ $+\Delta H$) and total bond dissociation energy of the **products** (exothermic process/ $-\Delta H$).

(ii) **subtracting** total bond dissociation energy of the **reactants** from the total bond dissociation energy of the **products** (exothermic process/ $-\Delta H$ less/minus endothermic process/ $+\Delta H$).

Practice examples/Calculating ΔH_r

1. Calculate ΔH_r from the following reaction:



Working

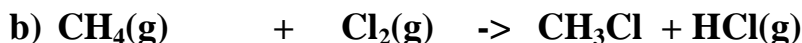
$$\begin{aligned} \text{Old bonds broken (endothermic process}/+\Delta H) \\ = (\text{H-H} + \text{Cl-Cl}) \Rightarrow (+431 + (+239)) = \underline{+670\text{kJ}} \end{aligned}$$

$$\begin{aligned} \text{New bonds broken (exothermic process}/-\Delta H) \\ = (2(\text{H-Cl})) \Rightarrow (-428 \times 2) = \underline{-856\text{kJ}} \end{aligned}$$

$$\Delta H_r = (+670\text{kJ} + -856\text{kJ}) = \underline{186\text{kJ}} = \underline{-93\text{kJ mole}^{-1}}$$

The above reaction has negative $-\Delta H$ enthalpy change and is therefore practically exothermic.

The thermochemical reaction is thus:



Working

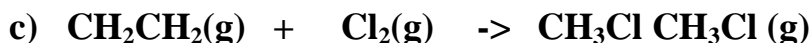
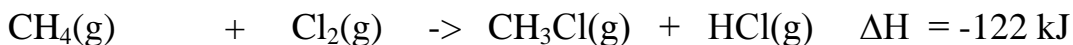
$$\begin{aligned} \text{Old bonds broken (endothermic process}/+\Delta H) \\ = (4(\text{C-H}) + \text{Cl-Cl}) \\ \Rightarrow ((4 \times +413) + (+239)) = \underline{+1891\text{kJ}} \end{aligned}$$

$$\begin{aligned} \text{New bonds broken (exothermic process}/-\Delta H) \\ = (3(\text{C-H}) + \text{H-Cl} + \text{C-Cl}) \\ \Rightarrow ((3 \times -413) + 428 + 346) = \underline{-2013\text{kJ}} \end{aligned}$$

$$\Delta H_r = (+1891\text{kJ} + -2013\text{kJ}) = \underline{-122\text{kJ mole}^{-1}}$$

The above reaction has negative $-\Delta H$ enthalpy change and is therefore practically exothermic.

The thermochemical reaction is thus:



Working

$$\text{Old bonds broken (endothermic process}/+\Delta H)$$

$$\begin{aligned}
 &= (4(\text{C-H}) + \text{Cl-Cl} + \text{C=C}) \\
 &\Rightarrow ((4 \times 413) + (239) + (612)) = + \underline{2503\text{kJ}} \\
 \text{New bonds broken (exothermic process/-}\Delta\mathbf{H}) & \\
 &= (4(\text{C-H} + \text{C-C} + 2(\text{C-Cl})) \\
 &\Rightarrow ((3 \times 413) + 436 + 2 \times 346) = -\underline{2367 \text{kJ}} \\
 \Delta H_r &= (+ 2503\text{kJ} + -2367 \text{kJ}) = +\underline{136 \text{kJ mole}^{-1}}
 \end{aligned}$$

The above reaction has negative $+\Delta H$ enthalpy change and is therefore practically endothermic.

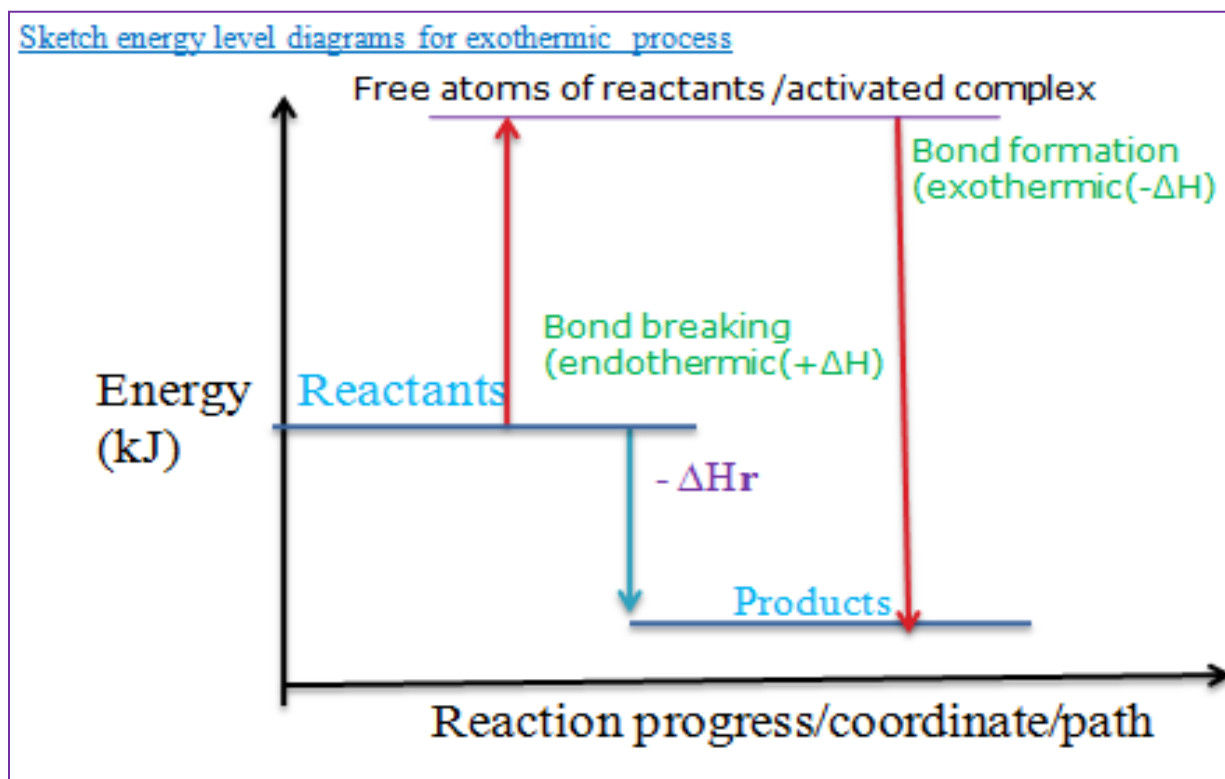
The thermochemical reaction is thus:

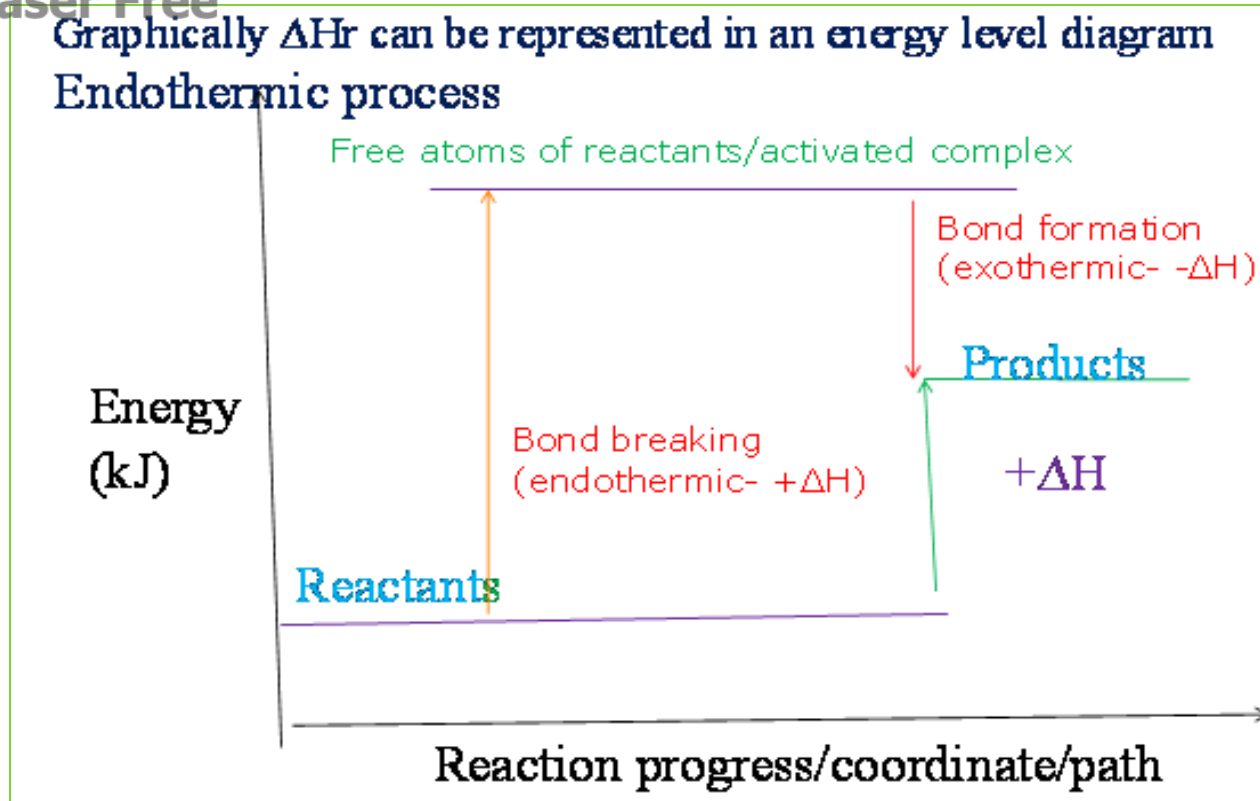


Note that:

(i) a reaction is **exothermic** if the bond dissociation energy of **reactants** is **more** than bond dissociation energy of products.

(ii) a reaction is **endothermic** if the bond dissociation energy of **reactants** is **less** than bond dissociation energy of products.





(b) Standard enthalpy/heat of combustion ΔH^0_c

The molar standard enthalpy/heat of **combustion**(ΔH^0_c) is defined as the energy/heat change when one mole of a substance is burnt in oxygen/excess air at standard conditions.

Burning is the reaction of a substance with oxygen/air. It is an exothermic process producing a lot of energy in form of heat.

A substance that undergoes burning is called a **fuel**. A fuel is defined as the combustible substance which burns in air to give heat energy for domestic or industrial use. A fuel may be **solid** (e.g coal, wood, charcoal) **liquid** (e.g petrol, paraffin, ethanol, kerosene) or **gas** (e.g liquefied petroleum gas/LPG, Water gas- CO_2/H_2 , biogas-methane, Natural gas-mixture of hydrocarbons)

To determine the molar standard enthalpy/heat of **combustion**(ΔH^0_c) of ethanol

Procedure

Put 20cm³ of distilled water into a 50cm³ beaker. Clamp the beaker. Determine the temperature of the water T_1 . Weigh an empty burner(empty tin with wick). Record its mass M_1 . Put some ethanol into the burner. Weigh again the burner with the ethanol and record its mass M_2 . Ignite the burner and place it below the clamped 50cm³ beaker. Heat the water in the beaker for about one minute. Put off

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the burner. Record the highest temperature rise of the water, T_2 . Weigh the burner again and record its mass M_3

Sample results:

Volume of water used	20cm ³
Temperature of the water before heating T_1	25.0°C
Temperature of the water after heating T_2	35.0°C
Mass of empty burner M_1	28.3g
Mass of empty burner + ethanol before igniting M_2	29.1g
Mass of empty burner + ethanol after igniting M_3	28.7g

Sample calculations:

1. Calculate:

(a) ΔT the change in temperature

$$\Delta T = T_2 - T_1 \Rightarrow (35.0^\circ\text{C} - 25.0^\circ\text{C}) = 10.0^\circ\text{C}$$

(b) the mass of ethanol used in burning

$$\text{mass of ethanol used} = M_2 - M_1 \Rightarrow 29.1\text{g} - 28.7\text{g} = 0.4\text{g}$$

(c) the number of moles of ethanol used in burning

$$\text{moles of ethanol} = \frac{\text{mass used}}{\text{molar mass of ethanol}} \Rightarrow \frac{0.4}{46} = 0.0087 / 8.7 \times 10^{-3} \text{ moles}$$

2. Given that the specific heat capacity of water is $4.2 \text{ kJ}^{-1}\text{kg}^{-1}\text{K}^{-1}$, determine the heat produced during the burning.

$$\begin{aligned} \text{Heat produced } \Delta H &= \text{mass of water (m)} \times \text{specific heat capacity (c)} \times \Delta T \\ &\Rightarrow 20 \times 4.2 \times 10 = \frac{840 \text{ Joules}}{1000} = 0.84 \text{ kJ} \end{aligned}$$

3. Calculate the molar heat of combustion of ethanol

$$\begin{aligned} \text{Molar heat of combustion } \Delta H_c &= \frac{\text{Heat produced } \Delta H}{\text{Number of moles of fuel}} \\ &\Rightarrow \frac{0.84 \text{ kJ}}{0.0087 / 8.7 \times 10^{-3} \text{ moles}} = 96.5517 \text{ kJmole}^{-1} \end{aligned}$$

4. List two sources of error in the above experiment.

(i) Heat loss to the surrounding lowers the practical value of the molar heat of combustion of ethanol.

A draught shield tries to minimize the loss by protecting wind from wobbling the flame.

(ii) Heat gain by reaction vessels/beaker lowers ΔT and hence ΔH_c

5. Calculate the heating value of the fuel.

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$$\text{Heating value} = \frac{\text{molar heat of combustion}}{\text{Molar mass of fuel}} \Rightarrow \frac{96.5517 \text{ kJmole}^{-1}}{46 \text{ g}} = \mathbf{2.0989 \text{ kJg}^{-1}}$$

Heating value is the energy produced when a unit mass/gram of a fuel is completely burnt

6.Explain other factors used to determine the choice of fuel for domestic and industrial use.

(i) **availability and affordability**-some fuels are more available cheaply in rural than in urban areas at a lower cost.

(ii)**cost of storage and transmission**-a fuel should be easy to transport and store safely. e.g LPG is very convenient to store and use. Charcoal and wood are bulky.

(iii)**environmental effects** –Most fuels after burning produce carbon(IV) oxide gas as a byproduct. Carbon(IV) oxide gas is green house gas that causes global warming. Some other fuel produce acidic gases like sulphur(IV) oxide ,and nitrogen(IV) oxide. These gases cause acid rain. Internal combustion engines exhaust produce lead vapour from leaded petrol and diesel. Lead is carcinogenic.

(iv)**ignition point**-The temperature at which a fuel must be heated before it burns in air is the ignition point. Fuels like petrol have very low ignition point, making it highly flammable. Charcoal and wood have very high ignition point.

7.Explain the methods used to reduce pollution from common fuels.

(i)**Planting trees**-Plants absorb excess carbon(IV)oxide for photosynthesis and release oxygen gas to the atmosphere.

(ii)**using catalytic converters** in internal combustion engines that convert harmful/toxic/poisonous gases like carbon(II)oxide and nitrogen(IV)oxide to harmless non-poisonous carbon(IV)oxide, water and nitrogen gas by using platinum-rhodium catalyst along the engine exhaust pipes.

Further practice calculations

1.Calculate the heating value of methanol CH₃OH given that 0.87g of the fuel burn in air to raise the temperature of 500g of water from 20°C to 27°C.(C=12.0,H=1.0 O=16.0).

$$\text{Moles of methanol used} = \frac{\text{Mass of methanol used}}{\text{Molar mass of methanol}} \Rightarrow \frac{0.87 \text{ g}}{32} = \mathbf{0.02718 \text{ moles}}$$

$$\begin{aligned} \text{Heat produced } \Delta H &= \text{mass of water(m)} \times \text{specific heat capacity (c)} \times \Delta T \\ &\Rightarrow 500 \times 4.2 \times 7 = \frac{14700 \text{ Joules}}{1000} = \mathbf{14.7 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{Molar heat of combustion } \Delta H_c &= \frac{\text{Heat produced } \Delta H}{\text{Number of moles of fuel}} \\ &\Rightarrow \frac{14.7 \text{ kJ}}{0.02718 \text{ moles}} = \mathbf{540.8389 \text{ kJmole}^{-1}} \end{aligned}$$

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$$\text{Heating value} = \frac{\text{molar heat of combustion}}{\text{Molar mass of fuel}} \Rightarrow \frac{540.8389 \text{ kJmole}^{-1}}{32 \text{ g}} = \mathbf{16.9012 \text{ kJg}^{-1}}$$

2. 1.0 g of carbon burn in excess air to raise the temperature of 400g of water by 18°C. Determine the molar heat of combustion and hence the heating value of carbon(C-12.0).

$$\text{Moles of carbon used} = \frac{\text{Mass of carbon used}}{\text{Molar mass of carbon}} \Rightarrow \frac{1.0 \text{ g}}{12} = \mathbf{0.0833 \text{ moles}}$$

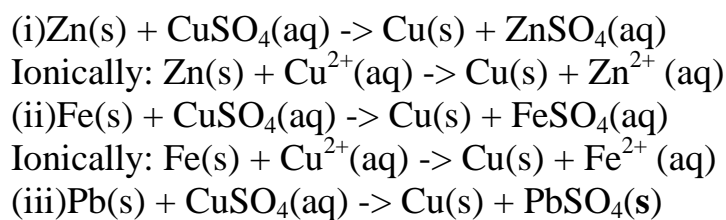
$$\begin{aligned} \text{Heat produced } \Delta H &= \text{mass of water(m)} \times \text{specific heat capacity (c)} \times \Delta T \\ &\Rightarrow 400 \times 4.2 \times 18 = \frac{30240 \text{ Joules}}{1000} = \mathbf{30.24 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{Molar heat of combustion } \Delta H_c &= \frac{\text{Heat produced } \Delta H}{\text{Number of moles of fuel}} \\ &\Rightarrow \frac{30.24 \text{ kJ}}{0.0833 \text{ moles}} = \mathbf{363.0252 \text{ kJmole}^{-1}} \end{aligned}$$

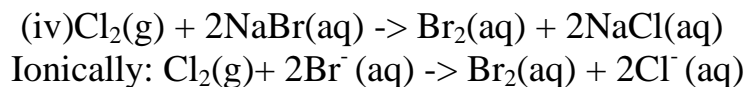
$$\text{Heating value} = \frac{\text{molar heat of combustion}}{\text{Molar mass of fuel}} \Rightarrow \frac{363.0252 \text{ kJmole}^{-1}}{12 \text{ g}} = \mathbf{30.2521 \text{ kJg}^{-1}}$$

(c) Standard enthalpy/heat of displacement ΔH^0_d

The molar standard enthalpy/heat of **displacement** ΔH^0_d is defined as the energy/heat change when one mole of a substance is displaced from its solution. A displacement reaction takes place when a more reactive element/with less electrode potential E^0 / negative E^0 /higher in the reactivity/electrochemical series remove/displace another with less reactive element/with higher electrode potential E^0 / positive E^0 /lower in the reactivity/electrochemical series **from** its solution.e.g.



This reaction stops after some time as insoluble $\text{PbSO}_4(\text{s})$ coat/cover unreacted lead.



Practically, a displacement reaction takes place when a known amount /volume of a solution is added excess of a more reactive metal.

To determine the molar standard enthalpy/heat of **displacement**(ΔH^0_d) of copper

Procedure

Place 20cm³ of 0.2M copper(II)sulphate(VI)solution into a 50cm³ plastic beaker/calorimeter. Determine and record the temperature of the solution T₁. Put all the Zinc powder provided into the plastic beaker. Stir the mixture using the thermometer. Determine and record the highest temperature change to the nearest 0.5°C- T₂ . Repeat the experiment to complete table 1 below

Experiment	I	II
Final temperature of solution(T ₂)	30.0°C	31.0°C
Final temperature of solution(T ₁)	25.0°C	24.0°C
Change in temperature(ΔT)	5.0	6.0

Questions**1.(a) Calculate:****(i)average ΔT**

$$\text{Average } \Delta T = \text{change in temperature in experiment I and II} \\ \Rightarrow \frac{5.0 + 6.0}{2} = \mathbf{5.5^{\circ}\text{C}}$$

(ii)the number of moles of solution used

$$\text{Moles used} = \frac{\text{molarity} \times \text{volume of solution}}{1000} = \frac{0.2 \times 20}{1000} = \mathbf{0.004 \text{ moles}}$$

(iii)the enthalpy change ΔH for the reaction

$$\text{Heat produced } \Delta H = \text{mass of solution(m)} \times \text{specific heat capacity (c)} \times \Delta T \\ \Rightarrow 20 \times 4.2 \times 5.5 = \frac{462 \text{ Joules}}{1000} = \mathbf{0.462 \text{ kJ}}$$

(iv)State two assumptions made in the above calculations.

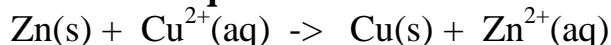
Density of solution = density of water = 1gcm⁻³

Specific heat capacity of solution=Specific heat capacity of solution=4.2 kJ⁻¹kg⁻¹K

This is because the solution is assumed to be **infinite dilute**.

2. Calculate the enthalpy change for one mole of displacement of Cu²⁺ (aq) ions.

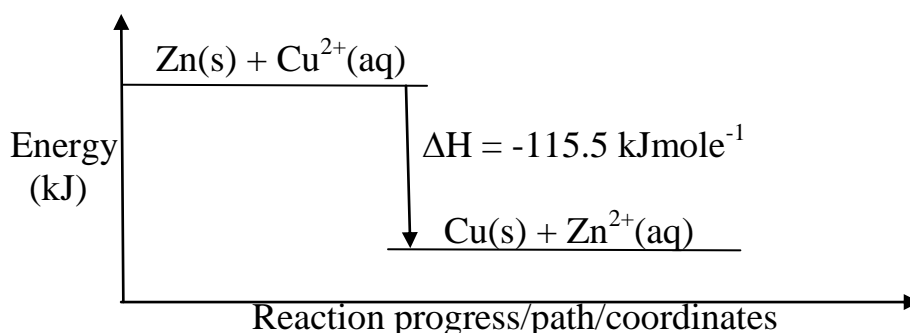
$$\text{Molar heat of displacement } \Delta H_d = \frac{\text{Heat produced } \Delta H}{\text{Number of moles of fuel}} \\ \Rightarrow \frac{0.462 \text{ kJ}}{0.004} = \mathbf{115.5 \text{ kJmole}^{-1}}$$

3. Write an ionic equation for the reaction taking place.

4.State the observation made during the reaction.

Blue colour of copper(II)sulphate(VI) fades/becomes less blue/colourless.
Brown solid deposits are formed at the bottom of reaction vessel/ beaker.

5.Illustrate the above reaction using an energy level diagram.



6. Iron is less reactive than Zinc. Explain the effect of using iron instead of Zinc on the standard molar heat of displacement ΔH_d of copper(II)sulphate (VI) solution.

No effect. Cu²⁺ (aq) are displaced from their solution. The element used to displace it does not matter. The reaction however faster if a more reactive metal is used.

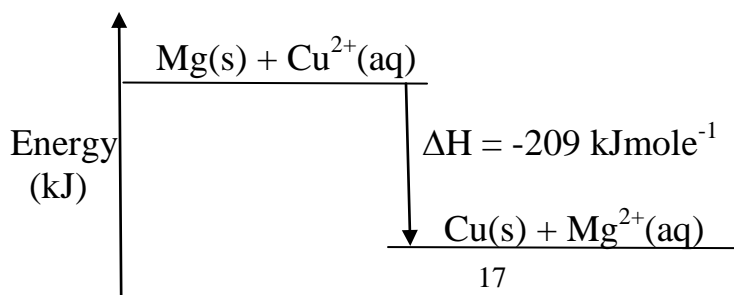
7.(a)If the standard molar heat of displacement ΔH_d of copper(II)sulphate (VI) solution is 209kJmole⁻¹ calculate the temperature change if 50cm³ of 0.2M solution was displaced by excess magnesium.

$$\text{Moles used} = \frac{\text{molarity} \times \text{volume of solution}}{1000} = \frac{0.2 \times 50}{1000} = \mathbf{0.01 \text{ moles}}$$

$$\begin{aligned} \text{Heat produced } \Delta H &= \text{Molar heat of displacement } \Delta H_d \times \text{Number of moles} \\ &=> 209 \text{kJmole}^{-1} \times 0.01 \text{ moles} = \mathbf{2.09 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \Delta T (\text{change in temperature}) &= \frac{\text{Heat produced } \Delta H}{\text{Molar heat of displacement } \Delta H_d \times \text{Number of moles}} \\ &=> \frac{2.09 \text{ kJ}}{0.01 \text{ moles}} = \mathbf{9.9524 \text{ Kelvin}} \end{aligned}$$

(b)Draw an energy level diagram to show the above energy changes



$\xrightarrow{\text{Reaction progress/path/coordinates}}$

8. The enthalpy of displacement ΔH_d of copper(II)sulphate (VI) solution is 126 kJ mole^{-1} . Calculate the molarity of the solution given that 40 cm^3 of this solution produces 2.204 kJ of energy during a displacement reaction with excess iron filings.

$$\begin{aligned} \text{Number of moles} &= \frac{\text{Heat produced } \Delta H}{\text{Molar heat of displacement } \Delta H_d} \\ &= \frac{2.204 \text{ kJ}}{126 \text{ moles}} = \mathbf{0.0206 \text{ moles}} \end{aligned}$$

$$\begin{aligned} \text{Molarity of the solution} &= \frac{\text{moles} \times 1000}{\text{Volume of solution used}} \\ &= \frac{0.0206 \text{ moles} \times 1000}{40} = \mathbf{0.5167 \text{ M}} \end{aligned}$$

9. If the molar heat of displacement of Zinc(II)nitrate(V) by magnesium powder is $25.05 \text{ kJ mole}^{-1}$, calculate the volume of solution which must be added 0.5 moles solution if there was a 3.0 K rise in temperature.

$$\begin{aligned} \text{Heat produced } \Delta H &= \text{Molar heat of displacement } \Delta H_d \times \text{Number of moles} \\ &= 25.08 \text{ kJ mole}^{-1} \times 0.5 \text{ moles} = \mathbf{1.254 \text{ kJ}} \times 1000 = \mathbf{1254 \text{ J}} \end{aligned}$$

$$\begin{aligned} \text{Mass of solution (m)} &= \frac{\text{Heat produced } \Delta H}{\text{specific heat capacity (c)} \times \Delta T} \\ &= \frac{1254 \text{ J}}{4.2 \times 3} = \mathbf{99.5238 \text{ g}} \end{aligned}$$

$$\text{Volume} = \text{mass} \times \text{density} = 99.5238 \text{ g} \times 1 = \mathbf{99.5238 \text{ cm}^3}$$

Note: The solution assumes to be too dilute /infinite dilute such that the density and specific heat capacity is assumed to be that of water.

Graphical determination of the molar enthalpy of displacement of copper **Procedure:**

Place 20 cm^3 of 0.2 M copper(II)sulphate (VI) solution into a calorimeter/ 50 cm^3 of plastic beaker wrapped in cotton wool/tissue paper.

Record its temperature at time $T = 0$.

Stir the solution with the thermometer carefully and continue recording the temperature after every 30 seconds .

Place all the (1.5 g) Zinc powder provided.

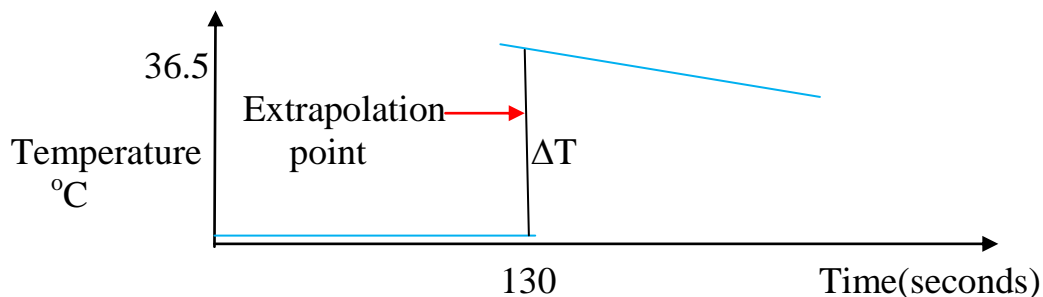
Stir the solution with the thermometer carefully and continue recording the temperature after every 30 seconds for five minutes.

Determine the highest temperature change to the nearest 0.5°C.

Sample results

Time °C	0.0	30.0	60.0	90.0	120.0	150.0	180.0	210.0	240.0	270.0
Temperature	25.0	25.0	25.0	25.0	25.0	xxx	36.0	35.5	35.0	34.5

Sketch graph of temperature against time



Questions

1. Show and determine the change in temperature ΔT

From a well constructed graph $\Delta T = T_2 - T_1$ at 150 second by **extrapolation**

$$\Delta T = 36.5 - 25.0 = 11.5^\circ\text{C}$$

2. Calculate the number of moles of copper(II) sulphate(VI) used given the molar heat of displacement of Cu^{2+} (aq) ions is 125kJmole^{-1}

Heat produced $\Delta H = \text{mass of solution (m)} \times \text{specific heat capacity (c)} \times \Delta T$

$$\Rightarrow 20 \times 4.2 \times 11.5 = \frac{966 \text{ Joules}}{1000} = \mathbf{0.966 \text{ kJ}}$$

$$\text{Number of moles} = \frac{\text{Heat produced } \Delta H}{\text{Molar heat of displacement } \Delta H_d}$$

$$\Rightarrow \frac{.966 \text{ kJ}}{125 \text{ moles}} = \mathbf{0.007728 \text{ moles}}$$

$$\mathbf{7.728 \times 10^{-3} \text{ moles}}$$

2. What was the concentration of copper(II) sulphate(VI) in moles per litre.

$$\text{Molarity} = \frac{\text{moles} \times 1000}{\text{Volume used}} \Rightarrow \frac{7.728 \times 10^{-3} \text{ moles} \times 1000}{20} = \mathbf{0.3864 \text{ M}}$$

4. The actual concentration of copper(II) sulphate(VI) solution was 0.4M. Explain the differences between the two.

Practical value is **lower** than theoretical. Heat/energy **loss** to the surrounding and that absorbed by the reaction vessel **decreases** ΔT hence **lowering** the practical number of moles and molarity against the theoretical value

5.a) In an experiment to determine the molar heat of reaction when magnesium displaces copper, 0.15g of magnesium powder were added to 25.0cm³ of 2.0M copper (II) chloride solution. The temperature of copper (II) chloride solution was 25°C. While that of the mixture was 43°C.

i) Other than increase in temperature, state and explain the observations which were made during the reaction. (3mks)

ii) Calculate the heat change during the reaction (specific heat capacity of the solution = 4.2Jg⁻¹K⁻¹ and the density of the solution = 1g/cm³) (2mks)

iii) Determine the molar heat of displacement of copper by magnesium. (Mg=24.0).

iv) Write the ionic equation for the reaction. (1mk)

v) Sketch an energy level diagram for the reaction. (2mks)

(c) Standard enthalpy/heat of neutralization ΔH^0_n

The molar standard enthalpy/heat of **neutralization** ΔH^0_n is defined as the energy/heat change when one mole of a H⁺ (H₃O⁺) ions react completely with one mole of OH⁻ ions to form one mole of H₂O/water.

Neutralization is thus a reaction of an acid /H⁺ (H₃O⁺) ions with a base/alkali/ OH⁻ ions to form salt and water only.

Strong acids/bases/alkalis are completely dissociated to **many** free ions (H⁺ /H₃O⁺ and OH⁻ ions).

Weak acids/bases/alkalis are partially dissociated to **few** free ions (H⁺ (H₃O⁺ and OH⁻ ions) and exist **more** as molecules.

Neutralization is an exothermic (- ΔH) process. The energy produced during neutralization depend on the amount of free ions (H⁺ H₃O⁺ and OH⁻) ions existing in the acid/base/alkali reactant:

(i) for weak acid-base/alkali neutralization, some of the **energy** is used to dissociate /ionize the **molecule** into free H⁺ H₃O⁺ and OH⁻ ions therefore the overall energy evolved is comparatively **lower/lesser/smaller** than strong acid / base/ alkali neutralizations.

(ii) (i)for strong acid/base/alkali neutralization, no **energy** is used to dissociate /ionize since **molecule** is wholly/fully dissociated/ionized into free H^+ H_3O^+ and OH^- ions. The overall energy evolved is comparatively **higher/more** than weak acid-base/ alkali neutralizations. For strong acid-base/alkali neutralization, the enthalpy of neutralization is **constant** at about $57.3kJmole^{-1}$ irrespective of the acid-base used. This is because ionically:

$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$ for any wholly dissociated acid/base/alkali
Practically ΔH_n^θ can be determined as in the examples below:

To determine the molar enthalpy of neutralization ΔH_n of Hydrochloric acid
Procedure

Place 50cm³ of 2M hydrochloric acid into a calorimeter/200cm³ plastic beaker wrapped in cotton wool/tissue paper. Record its temperature T_1 . Using a clean measuring cylinder, measure another 50cm³ of 2M sodium hydroxide. Rinse the bulb of the thermometer in distilled water. Determine the temperature of the sodium hydroxide T_2 . Average T_2 and T_1 to get the initial temperature of the mixture T_3 .

Carefully add all the alkali into the calorimeter/200cm³ plastic beaker wrapped in cotton wool/tissue paper containing the acid. Stir vigorously the mixture with the thermometer.

Determine the highest temperature change to the nearest 0.5°C T_4 as the final temperature of the mixture. Repeat the experiment to complete table 1.

Table I . **Sample results**

Experiment	I	II
Temperature of acid T_1 (°C)	22.5	22.5
Temperature of base T_2 (°C)	22.0	23.0
Final temperature of solution T_4 (°C)	35.5	36.0
Initial temperature of solution T_3 (°C)	22.25	22.75
Temperature change(T_5)	13.25	13.75

(a)Calculate T_6 the average temperature change

$$T_6 = \frac{13.25 + 13.75}{2} = 13.5^\circ C$$

(b)Why should the apparatus be very clean?

Impurities present in the apparatus reacts with acid /base lowering the overall temperature change and hence ΔH_n^θ .

(c)Calculate the:

(i)number of moles of the acid used

$$\text{number of moles} = \frac{\text{molarity} \times \text{volume}}{1000} \Rightarrow \frac{2 \times 50}{1000} = 0.1 \text{ moles}$$

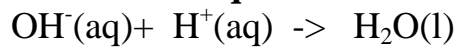
(ii) enthalpy change ΔH of neutralization.

$$\Delta H = (\mathbf{m})\text{mass of solution(acid+base)} \times (\mathbf{c})\text{specific heat capacity of solution} \times \Delta T(T_6) \Rightarrow (50 + 50) \times 4.2 \times 13.5 = \underline{5670 \text{ Joules}} = \underline{5.67 \text{ kJ}}$$

(iii) the molar heat of neutralization the acid.

$$\Delta H_n = \frac{\text{Enthalpy change } \Delta H}{\text{Number of moles}} \Rightarrow \frac{5.67 \text{ kJ}}{0.1 \text{ moles}} = \underline{56.7 \text{ kJ mole}^{-1}}$$

(c) Write the ionic equation for the reaction that takes place



(d) The theoretical enthalpy change is 57.4 kJ. Explain the difference with the results above.

The theoretical value is higher
 Heat/energy loss to the surrounding/environment lowers $\Delta T/T_6$ and thus ΔH_n
 Heat/energy is absorbed by the reaction vessel/calorimeter/plastic cup
 lowers ΔT and hence ΔH_n

(e) Compare the ΔH_n of the experiment above with similar experiment repeated with neutralization of a solution of:

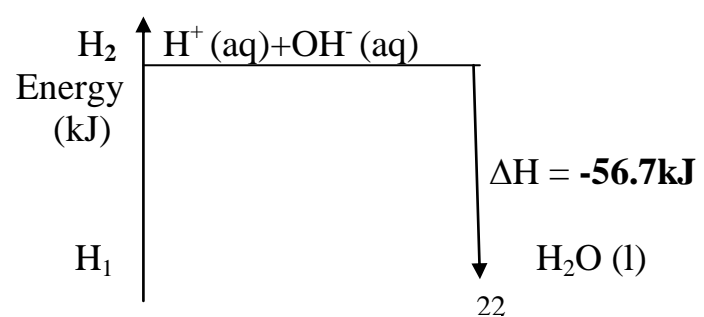
(i) potassium hydroxide with nitric(V) acid

The results would be the same/similar.
 Both are neutralization reactions of strong acids and bases/alkalis that are fully /wholly dissociated into many free $\text{H}^+ / \text{H}_3\text{O}^+$ and OH^- ions.

(ii) ammonia with ethanoic acid

The results would be lower/ ΔH_n would be less.
 Both are neutralization reactions of weak acids and bases/alkalis that are partially /partly dissociated into few free $\text{H}^+ / \text{H}_3\text{O}^+$ and OH^- ions. Some energy is used to ionize the molecule.

(f) Draw an energy level diagram to illustrate the energy changes



Theoretical examples

1. The molar enthalpy of neutralization was experimentally shown to be 51.5kJ per mole of 0.5M hydrochloric acid and 0.5M sodium hydroxide. If the volume of sodium hydroxide was 20cm³, what was the volume of hydrochloric acid used if the reaction produced a 5.0°C rise in temperature?

Working:

$$\text{Moles of sodium hydroxide} = \frac{\text{molarity} \times \text{volume}}{1000} \Rightarrow \frac{0.5 \text{ M} \times 20\text{cm}^3}{1000} = \mathbf{0.01 \text{ moles}}$$

$$\text{Enthalpy change } \Delta H = \frac{\Delta H_n}{\text{Moles sodium hydroxide}} \Rightarrow \frac{51.5}{0.01 \text{ moles}} = \mathbf{0.515\text{kJ}}$$

$$\begin{aligned} \text{Mass of base + acid} &= \frac{\text{Enthalpy change } \Delta H \text{ in Joules}}{\text{Specific heat capacity} \times \Delta T} \\ \Rightarrow & \frac{0.515\text{kJ} \times 1000}{4.2 \times 5} = \mathbf{24.5238\text{g}} \end{aligned}$$

$$\begin{aligned} \text{Mass/volume of HCl} &= \text{Total volume} - \text{volume of NaOH} \\ \Rightarrow & 24.5238 - 20.0 = \mathbf{4.5238 \text{ cm}^3} \end{aligned}$$

3. ΔH_n of potassium hydroxide was practically determined to be 56.7kJmole⁻¹. Calculate the molarity of 50.0 cm³ potassium hydroxide used to neutralize 25.0cm³ of dilute sulphuric(VI) acid raising the temperature of the solution from 10.0°C to 16.5°C.

$$\begin{aligned} \Delta H &= (\mathbf{m})\text{mass of solution(acid+base)} \times (\mathbf{c})\text{specific heat capacity of solution} \times \Delta T \\ \Rightarrow & (50 + 25) \times 4.2 \times 6.5 = \mathbf{2047.5\text{Joules}} \end{aligned}$$

$$\begin{aligned} \text{Moles potassium hydroxide} &= \frac{\text{Enthalpy change } \Delta H}{\Delta H_n} \\ & \frac{2047.5\text{Joules}}{56700\text{Joules}} = \mathbf{0.0361 \text{ moles}} \end{aligned}$$

$$\text{Molarity of KOH} = \frac{\text{moles} \times 1000}{\text{Volume used}} \Rightarrow \frac{0.0361 \text{ moles} \times 1000}{50\text{cm}^3} = \mathbf{0.722\text{M}}$$

3. Determine the specific heat capacity of a solution of a solution mixture of 50.0cm³ of 2M potassium hydroxide neutralizing 50.0cm³ of 2M nitric(V)

acid if a 13.25°C rise in temperature is recorded.(1mole of potassium hydroxide produce 55.4kJ of energy)

$$\text{Moles of potassium hydroxide} = \frac{\text{molarity KOH} \times \text{volume}}{1000}$$

$$\Rightarrow \frac{2 \text{ M} \times 50\text{cm}^3}{1000} = \mathbf{0.1 \text{ moles}}$$

$$\text{Enthalpy change } \Delta H = \Delta H_n \times \text{Moles potassium hydroxide}$$

$$\Rightarrow 55.4\text{kJ} \times 0.1 \text{ moles} = 5.54\text{kJ} \times 1000 = \mathbf{5540 \text{ Joules}}$$

$$\text{Specific heat capacity} = \frac{\text{Enthalpy change } \Delta H \text{ in Joules}}{\text{Mass of base + acid} \times \Delta T}$$

$$\Rightarrow \frac{5540}{(50+50) \times 13.25} = \mathbf{4.1811 \text{ J}^{-1} \text{ g}^{-1} \text{ K}^{-1}}$$

Graphically ΔH_n can be determined as in the example below:

Procedure

Place 8 test tubes in a test tube rack .Put 5cm³ of 2M sodium hydroxide solution into each test tube.

Measure 25cm³ of 1M hydrochloric acid into 100cm³ plastic beaker.

Record its initial temperature at volume of base =0. Put one portion of the base into the beaker containing the acid.

Stir carefully with the thermometer and record the highest temperature change to the nearest 0.5°C.

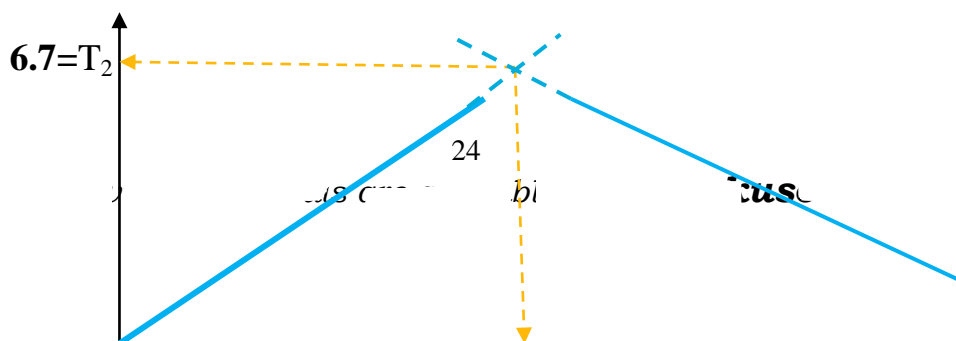
Repeat the procedure above with other portions of the base to complete table 1 below

Table 1:Sample results.

Volume of acid(cm ³)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Volume of alkali(cm ³)	0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
Final temperature(°C)	22.0	24.0	26.0	28.0	28.0	27.0	26.0	25.0	24.0
Initial temperature(°C)	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Change in temperature	0.0	2.0	4.0	6.0	6.0	5.0	4.0	3.0	2.0

(a)Complete the table to determine the change in temperature.

(b)Plot a graph of volume of sodium hydroxide against temperature change.



$$0 = T_1$$

From the graph show and determine :

(i) the highest temperature change ΔT

$\Delta T = T_2 - T_1 \Rightarrow$ highest temperature - T_2 (from extrapolating a correctly plotted graph) less lowest temperature at volume of base = 0 : T_1

$$\Rightarrow \Delta T = 6.7 - 0.0 = \mathbf{6.7^{\circ}\text{C}}$$

(ii) the volume of sodium hydroxide used for complete neutralization

From a correctly plotted graph – **16.75 cm³**

(c) Calculate the number of moles of the alkali used

$$\text{Moles NaOH} = \frac{\text{molarity} \times \text{volume}}{1000} \Rightarrow \frac{2\text{M} \times 16.75\text{cm}^3}{1000} = \mathbf{0.0335 \text{ moles}}$$

(d) Calculate ΔH for the reaction

$$\Delta H = \text{mass of solution (acid+base)} \times c \times \Delta T$$

$$\Rightarrow (25.0 + 16.75) \times 4.2 \times 6.7 = \frac{1174.845 \text{ J}}{1000} = \mathbf{1.174845 \text{ kJ}}$$

(e) Calculate the molar enthalpy of neutralization of the alkali.

$$\Delta H_n = \frac{\Delta H_n}{\text{Number of moles}} = \frac{1.174845 \text{ kJ}}{0.0335} = \mathbf{35.0701 \text{ kJ}}$$

(d) Standard enthalpy/heat of solution ΔH°_s

The standard enthalpy of solution ΔH°_s is defined as the energy change when one mole of a substance is dissolved in excess distilled water to form an infinite dilute solution. An infinite dilute solution is one which is **too** dilute to be diluted further.

Dissolving a solid involves two processes:

(i) **breaking** the **crystal** of the solid into **free ions** (cations and anion). This process is the **opposite** of the **formation** of the crystal itself. The energy required to form one mole of a crystal structure from its **gaseous ions** is called **Lattice energy/heat/enthalpy of lattice (ΔH_l)**. Lattice energy/heat/enthalpy of lattice (ΔH_l) is an endothermic process ($+\Delta H_l$).

The table below shows some ΔH_1 in kJ for the process $\text{MX}(s) \rightarrow \text{M}^+(g) + \text{X}^-(g)$

	Li	Na	K	Ca	Mg
F	+1022	+900	+800	+760	+631
Cl	+846	+771	+690	+2237	+2493
Br	+800	+733	+670	+2173	+2226

(ii) **surrounding** the free ions by polar **water** molecules. This process is called **hydration**. The energy produced when one mole of ions are completely hydrated is called **hydration energy**/ heat/enthalpy of hydration (ΔH_h). Hydration energy /enthalpy of hydration (ΔH_h) is an **exothermic** process (ΔH_h).

The table below shows some ΔH_h in kJ for some ions;

ion	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	Br^-
ΔH_h	-1091	-406	-322	-1920	-1650	-506	-364	-335

The **sum** of the **lattice** energy $+\Delta H_1$ (endothermic) and **hydration** energy $-\Delta H_h$ (exothermic) gives the heat of solution $-\Delta H_s$

$$\Delta H_s = \Delta H_1 + \Delta H_h$$

Note

Since ΔH_1 is an endothermic process and ΔH_h is an exothermic process then ΔH_s is:

(i) **exothermic** if ΔH_1 is **less** than ΔH_h and hence a solid **dissolve** easily in water.

(ii) **endothermic** if ΔH_1 is **more** than ΔH_h and hence a solid does not **dissolve** easily in water.

(a) Dissolving sodium chloride crystal/s:

(i) NaCl ----breaking the crystal into free ions---> $\text{Na}^+(g) + \text{Cl}^-(g)$ $\Delta H_1 = +771 \text{ kJ}$

(ii) Hydrating the ions;



$$\Delta H_s = \Delta H_1 + \Delta H_h \rightarrow (-406 \text{ kJ} + -364 \text{ kJ}) + 771 \text{ kJ} = \underline{\underline{+1.0 \text{ kJmole}^{-1}}}$$

NaCl does not **dissolve** easily in water because overall ΔH_s is **endothermic**

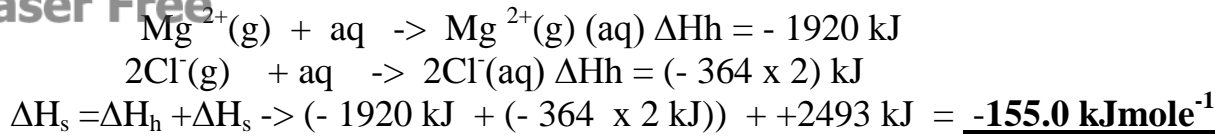
Solubility of NaCl therefore increases with increase in temperature.

Increase in temperature increases the energy to break the crystal lattice of NaCl to free $\text{Na}^+(g) + \text{Cl}^-(g)$

(b) **Dissolving magnesium chloride crystal/s//** $\text{MgCl}_2(s) \rightarrow \text{MgCl}_2(aq)$

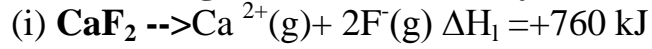
(i) MgCl_2 --breaking the crystal into free ions--> $\text{Mg}^{2+}(g) + 2\text{Cl}^-(g)$ $\Delta H_1 = +2493 \text{ kJ}$

(ii) Hydrating the ions;

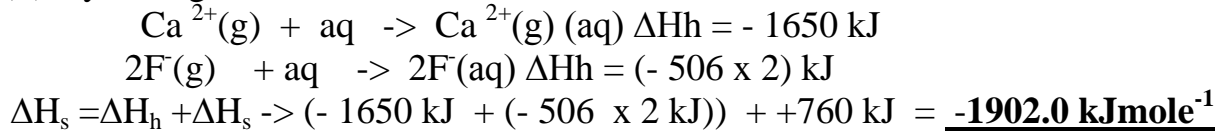


MgCl₂ (s) **dissolve** easily in water because overall ΔH_s is **exothermic** .
Solubility of MgCl₂ (s) therefore decreases with increase in temperature.

(c) Dissolving Calcium fluoride crystal/s// CaF₂ (s) -> CaF₂ (aq)

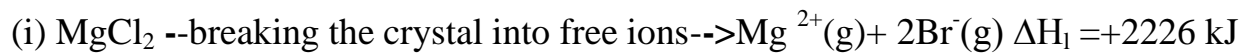


(ii) Hydrating the ions;

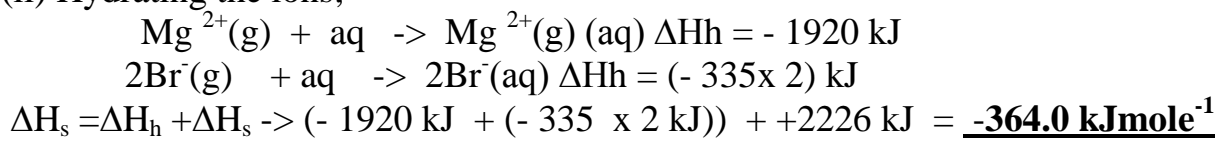


CaF₂ (s) **dissolve** easily in water because overall ΔH_s is **exothermic** .
Solubility of CaF₂ (s) therefore decreases with increase in temperature.

(d) Dissolving magnesium bromide crystal/s// MgBr₂ (s) -> MgBr₂ (aq)



(ii) Hydrating the ions;



MgBr₂ (s) **dissolve** easily in water because overall ΔH_s is **exothermic** .
Solubility of MgBr₂(s) therefore decreases with increase in temperature.

Practically the heat of solution can be determined from dissolving known amount /mass/volume of solute in known mass /volume of water/solvent.

From the temperature of solvent **before** and **after** dissolving the change in temperature (ΔT) during dissolution is determined.

To determine the ΔH_s ammonium nitrate

Place 100cm³ of distilled water into a plastic beaker/calorimeter. Determine its temperature and record it at time =0 in table I below.

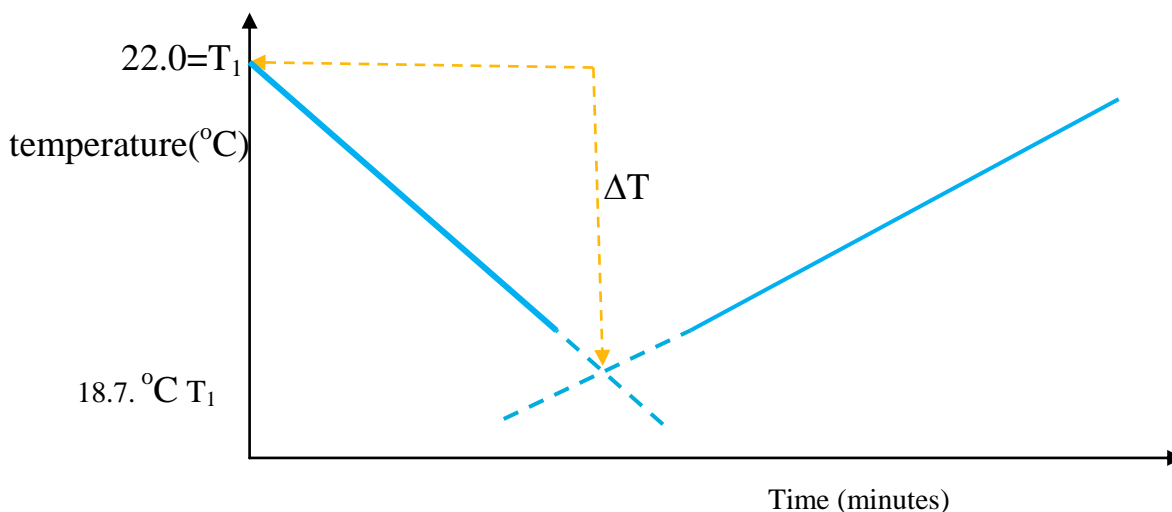
Put all the 5.0g of ammonium nitrate (potassium nitrate/ammonium chloride can also be used) provided into the plastic beaker/calorimeter, stir using a thermometer and record the highest temperature change to the nearest 0.5°C after every ½ minute to complete table I.

Continue stirring the mixture throughout the experiment.

Sample results: Table I

Time (minutes)	0.0	½	1	1 ½	2	2 ½	3	3 ½
Temperature(°C)	22.0	21.0	20.0	19.0	19.0	19.5	20.0	20.5

(a) Plot a graph of temperature against time(x-axis)



(b) From the graph show and determine the highest temperature change ΔT

$$\Delta T = T_2 - T_1 \Rightarrow \text{lowest temperature} - T_2 \text{ (from extrapolating a correctly plotted graph)} - \text{highest temperature at volume of base} = 0 : T_1$$

$$\Rightarrow \Delta T = 18.7 - 22.0 = \mathbf{3.3^\circ C}$$

(c) Calculate the number of moles of ammonium nitrate(V) used

$$\text{Moles } \text{NH}_4\text{NO}_3 = \frac{\text{mass used}}{\text{Molar mass}} \Rightarrow \frac{5.0}{80} = \mathbf{0.0625 \text{ moles}}$$

(d) Calculate ΔH for the reaction

$$\Delta H = \text{mass of water} \times c \times \Delta T$$

$$\rightarrow 100 \times 4.2 \times 3.3 = \frac{+1386 \text{ J}}{1000} = \mathbf{+1.386 \text{ kJ}}$$

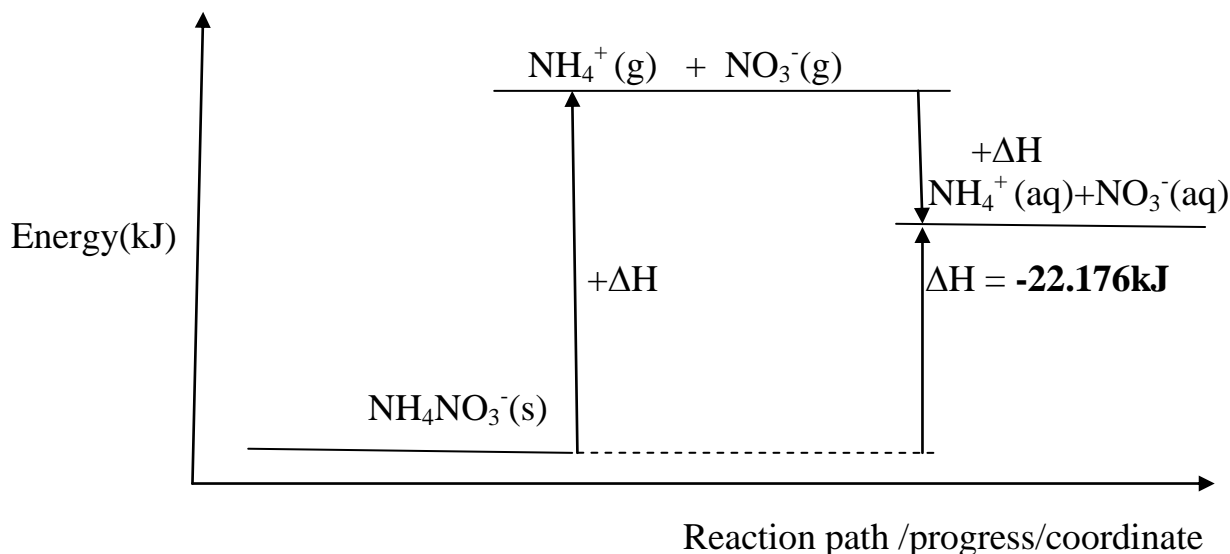
(e) Calculate the molar enthalpy of dissolution of ammonium nitrate(V).

$$\Delta H_s = \frac{\Delta H}{\text{Number of moles}} = \frac{+1.386 \text{ kJ}}{0.0625 \text{ moles}} = \mathbf{+22.176 \text{ kJ mole}^{-1}}$$

(f) What would happen if the distilled water was heated before the experiment was performed.

The ammonium nitrate(V) would take less time to dissolve. Increase in temperature reduces lattice energy causing endothermic dissolution to be faster

(g) Illustrate the process above in an energy level diagram



(h) 100cm³ of distilled water at 25°C was added carefully 3cm³ concentrated sulphuric(VI) acid of density 1.84gcm⁻³. The temperature of the mixture rose from 25°C to 38°C. Calculate the molar heat of solution of sulphuric(VI) acid (S=32.0, H=1.0, O=16.0)

Working

Molar mass of H₂SO₄ = 98g

Mass of H₂SO₄ = Density x volume => 1.84gcm⁻³ x 3cm³ = **5.52 g**

Mass of H₂O = Density x volume => 1.00gcm⁻³ x 100cm³ = **100 g**

Moles of H₂SO₄ = $\frac{\text{mass}}{\text{Molar mass of H}_2\text{SO}_4}$ => $\frac{5.52 \text{ g}}{98\text{g}}$ = **0.0563 moles**

Enthalpy change $\Delta H = (\text{mass of acid} + \text{water}) \times \text{specific heat capacity of water} \times \Delta T$
 => $(100 + 5.52 \text{ g}) \times 4.2 \times 13^\circ\text{C} = \frac{5761.392 \text{ J}}{1000} = \mathbf{5.761392 \text{ kJ}}$

ΔH_s of H₂SO₄ = $\frac{\Delta H}{\text{Moles of H}_2\text{SO}_4}$ => $\frac{5.761392 \text{ kJ}}{0.0563 \text{ moles}} = \mathbf{-102.33378 \text{ kJ moles}^{-1}}$

(e) Standard enthalpy/heat of formation ΔH_f°

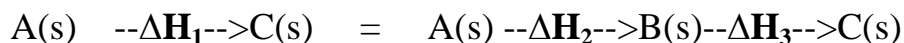
The molar enthalpy of formation ΔH_f° is defined as the energy change when one mole of a compound is formed from its elements at 298K(25°C) and 101325Pa(one atmosphere)pressure. ΔH_f° is practically difficult to determine in a school laboratory.

It is normally determined by applying Hess' law of constant heat summation.

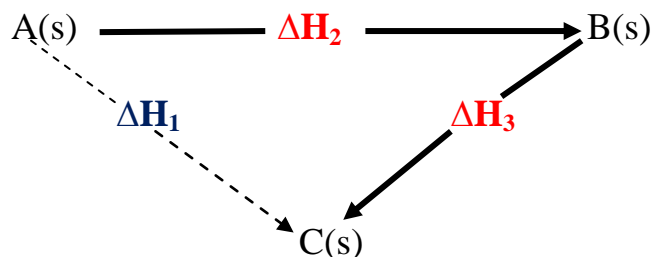
Hess' law of constant heat summation states that **“the total enthalpy/heat/energy change of a reaction is the same regardless of the route taken from reactants to products at the same temperature and pressure”**.

Hess' law of constant heat summation is as a result of a series of experiments done by the German Scientist Henri Hess(1802-1850).

He found that the total energy change from the reactants to products was the same irrespective of the intermediate products between. i.e.



Applying Hess' law of constant heat summation then:



The above is called an **energy cycle diagram**. It can be used to calculate any of the missing energy changes since:

- (i) $\Delta H_1 = \Delta H_2 + \Delta H_3$
- (ii) $\Delta H_2 = \Delta H_1 + -\Delta H_3$
- (iii) $\Delta H_3 = -\Delta H_1 + \Delta H_2$

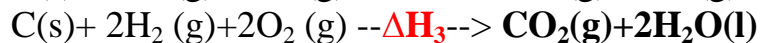
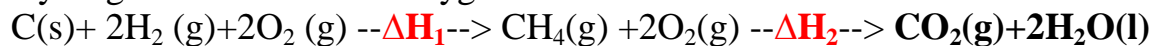
Examples of applying Hess' law of constant heat summation

1. Calculate the molar enthalpy of formation of methane (CH_4) given that ΔH_c° of carbon-graphite is $-393.5 \text{ kJ mole}^{-1}$, Hydrogen is $-285.7 \text{ kJ mole}^{-1}$ and that of

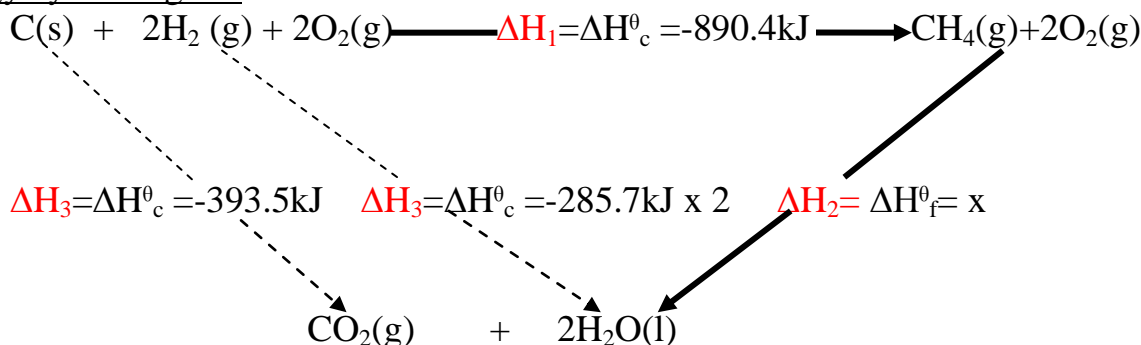
methane is 890 kJmole^{-1}

Working

Carbon-graphite ,hydrogen and oxygen can react to first form methane.
Methane will then burn in the oxygen present to form carbon(IV)oxide and water.
Carbon-graphite can burn in the oxygen to form carbon(IV)oxide.
Hydrogen can burn in the oxygen to form water.



Energy cycle diagram



Substituting:

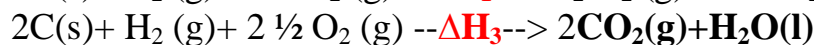
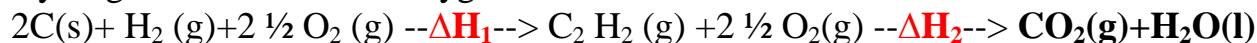
$$\begin{aligned} \Delta H_3 &= \Delta H_1 + \Delta H_2 \\ -393.5 + (-285.7 \times 2) &= -890.4 \text{ kJ} + x \\ x &= -74.5 \text{ kJ} \\ \text{Heat of formation } \Delta H_f^\circ \text{ CH}_4 &= -74.5 \text{ kJmole}^{-1} \end{aligned}$$

2. Calculate the molar enthalpy of formation of ethyne (C_2H_2) given : ΔH_c° of carbon-graphite = -394 kJmole^{-1} , Hydrogen = -286 kJmole^{-1} , (C_2H_2) = $-1300 \text{ kJmole}^{-1}$

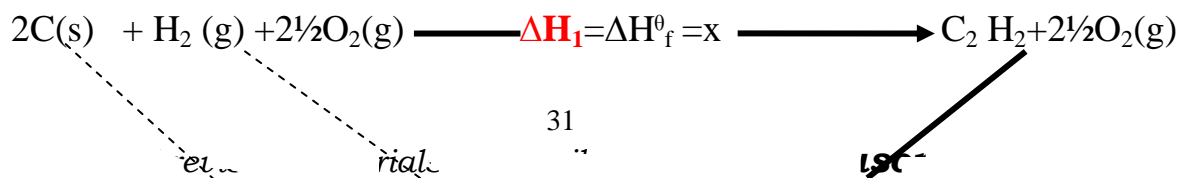
Working

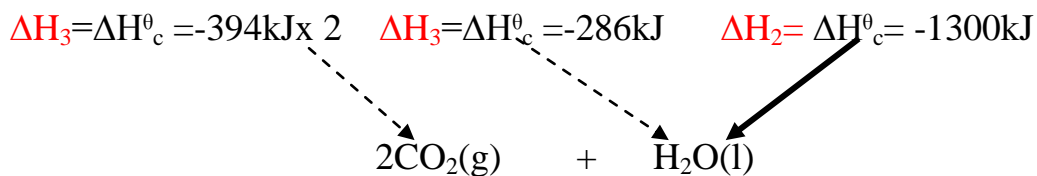
Carbon-graphite ,hydrogen and oxygen can react to first form ethyne.
Ethyne will then burn in the oxygen present to form carbon(IV)oxide and water.
Carbon-graphite can burn in the oxygen to form carbon(IV)oxide.

Hydrogen can burn in the oxygen to form water.



Energy cycle diagram





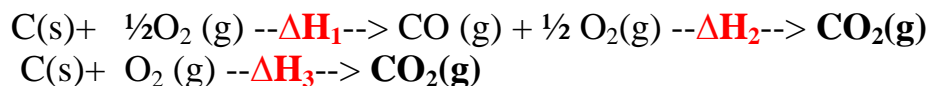
Substituting:

$$\begin{aligned} \Delta H_3 &= \Delta H_1 + \Delta H_2 \\ (-394 \times 2) + -286 &= -1300 \text{ kJ} + x \\ x &= +244 \text{ kJ} \\ \text{Heat of formation } \Delta H_f^\theta \text{ CH}_4 &= +244 \text{ kJmole}^{-1} \end{aligned}$$

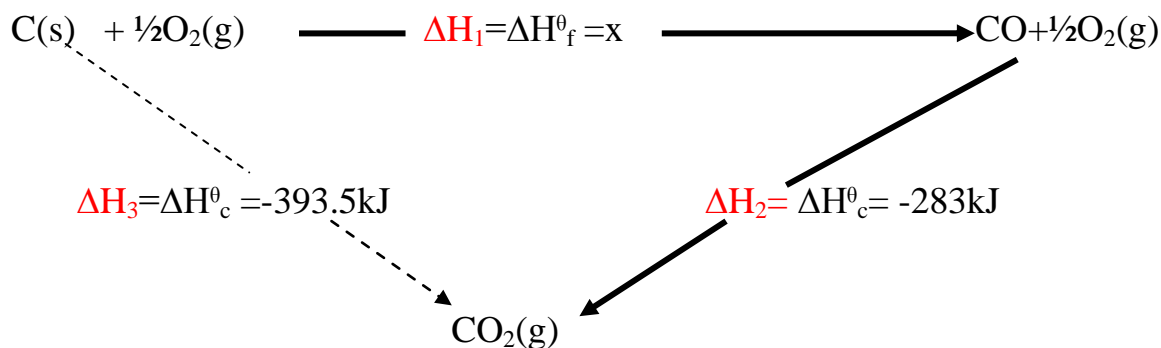
3. Calculate the molar enthalpy of formation of carbon(II)oxide (CO) given : ΔH_c^θ of carbon-graphite = $-393.5 \text{ kJmole}^{-1}$, ΔH_c^θ of carbon(II)oxide (CO) = -283 kJmole^{-1}

Working

Carbon-graphite reacts with oxygen first to form carbon (II)oxide (CO).
Carbon(II)oxide (CO) then burn in the excess oxygen to form carbon(IV)oxide.
Carbon-graphite can burn in excess oxygen to form carbon (IV) oxide.



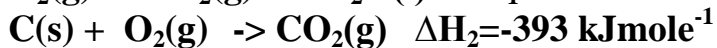
Energy cycle diagram



Substituting:

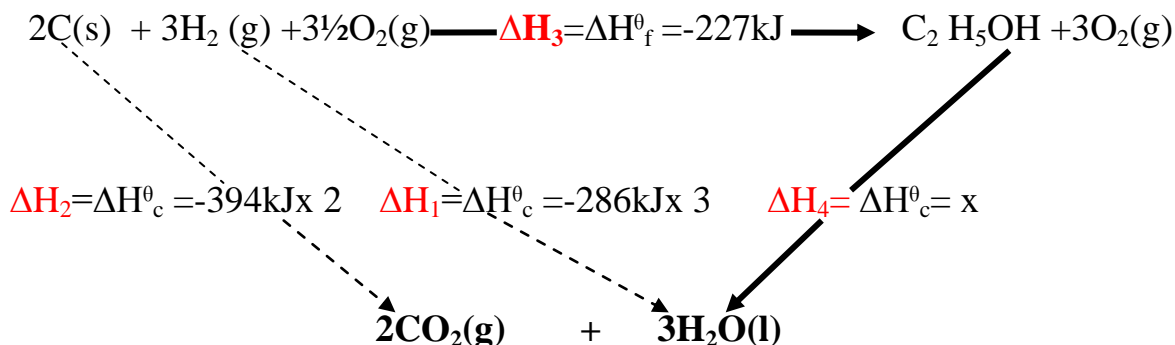
$$\begin{aligned} \Delta H_3 &= \Delta H_1 + \Delta H_2 \\ -393.5 \text{ kJ} &= -283 \text{ kJ} + x \\ x &= -110 \text{ kJ} \\ \text{Heat of formation } \Delta H_f^\theta \text{ CO} &= -110 \text{ kJmole}^{-1} \end{aligned}$$

4. Study the information below:



Use the information to calculate the molar enthalpy of combustion ΔH_4 of ethanol

Energy cycle diagram



Substituting:

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

$$(-394 \times 2) + (-286 \times 3) = -277 + x$$

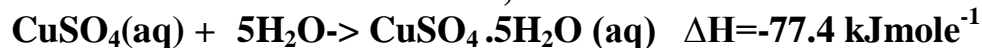
$$\Delta H_4 = -1369 \text{ kJ}$$

$$\text{Heat of combustion } \Delta H_c^\circ \text{ C}_2\text{H}_5\text{OH} = -1369 \text{ kJmole}^{-1}$$

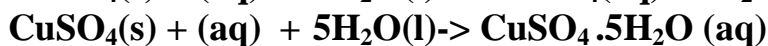
5. Given the following information below:



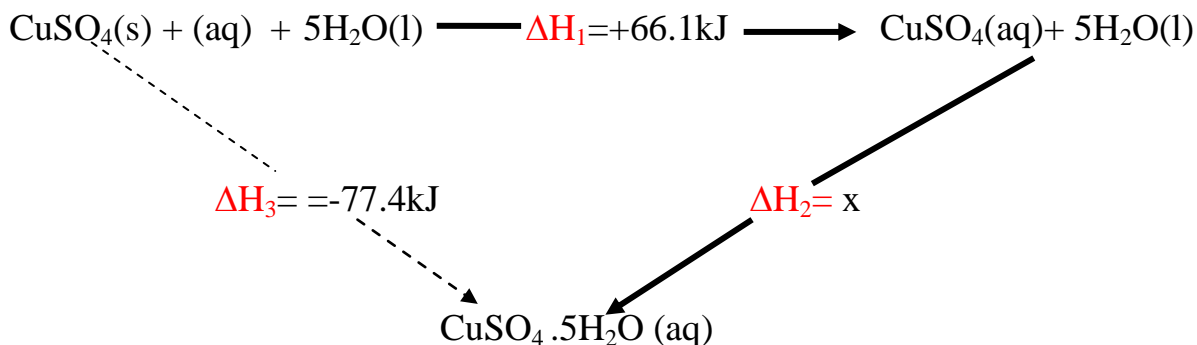
Calculate ΔH for the reaction;



Working



Energy cycle diagram



Substituting:

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

$$(-77.4\text{kJ} = x + +66.1\text{kJ})$$

$$\Delta H_4 = -10.9 \text{ kJ}$$

Heat of dissolution of $\text{CuSO}_4 = -10.9\text{kJmole}^{-1}$

Practically, Hess' law can be applied practically as in the following examples

a) Practical example 1

Determination of the enthalpy of formation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Experiment I

Weigh accurately 12.5 g of copper(II)sulphate(VI)pentahydrate. Measure 100cm³ of distilled water into a beaker. Determine its temperature T_1 .Put all the crystals of the copper(II)sulphate(VI)pentahydrate carefully into the beaker. Stir using a thermometer and determine the highest temperature change T_2 Repeat the procedure again to complete table 1.

Table 1:Sample results

Experiment	I	II
Highest /lowest temperature T_2	27.0	29.0
Initial temperature T_1	24.0	25.0
Change in temperature ΔT	3.0	4.0

Experiment II

Weigh accurately 8.0g of anhydrous copper(II)sulphate(VI). Measure 100cm³ of distilled water into a beaker. Determine its temperature T_1 .Put all the crystals of the copper(II)sulphate(VI)pentahydrate carefully into the beaker. Stir using a thermometer and determine the highest temperature change T_2 Repeat the procedure again to complete table II.

Table II :Sample results

Experiment	I	II
Highest /lowest temperature T_2	26.0	27.0
Initial temperature T_1	25.0	25.0
Change in temperature ΔT	1.0	2.0

Questions

(a)Calculate the average ΔT in

(i)Table I

$$\Delta T = T_2 - T_1 \Rightarrow \frac{3.0 + 4.0}{2} = 3.5^\circ\text{C}$$

(ii) Table II

$$\Delta T = T_2 - T_1 \Rightarrow \frac{1.0 + 2.0}{2} = 1.5^\circ\text{C}$$

(b) Calculate the number of moles of solid used in:

(i) Experiment I

$$\text{Moles of CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{\text{Mass}}{\text{Molar mass}} \Rightarrow \frac{12.5}{250} = 0.05 \text{ moles}$$

(ii) Experiment II

$$\text{Moles of CuSO}_4 = \frac{\text{Mass}}{\text{Molar mass}} \Rightarrow \frac{8.0}{160} = 0.05 \text{ moles}$$

(c) Calculate the enthalpy change for the reaction in:

(i) Experiment I

$$\begin{aligned} \text{Enthalpy change of CuSO}_4 \cdot 5\text{H}_2\text{O} &= \text{mass of Water (m)} \times c \times \Delta T \\ &\Rightarrow \frac{100\text{cm}^3 \times 4.2 \times 3.5^\circ\text{C}}{1000} = -1.47\text{kJ} \end{aligned}$$

(ii) Experiment II

$$\begin{aligned} \text{Enthalpy change of CuSO}_4 &= \text{mass of water (m)} \times c \times \Delta T \\ &\Rightarrow \frac{100\text{cm}^3 \times 4.2 \times 1.5^\circ\text{C}}{1000} = -0.63\text{kJ} \end{aligned}$$

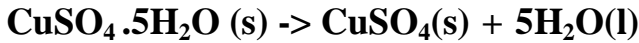
(c) Calculate the molar enthalpy of solution CuSO₄·5H₂O (s) from the results in (i) experiment I.

$$\Delta H_s = \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{\Delta H}{\text{Number of Moles}} \Rightarrow \frac{-1.47\text{kJ}}{0.05 \text{ moles}} = 29.4\text{kJ}$$

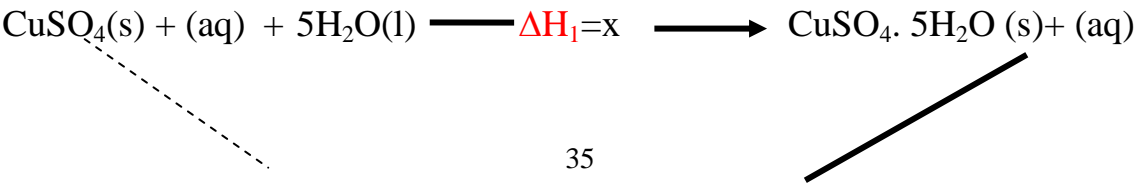
(ii) experiment II.

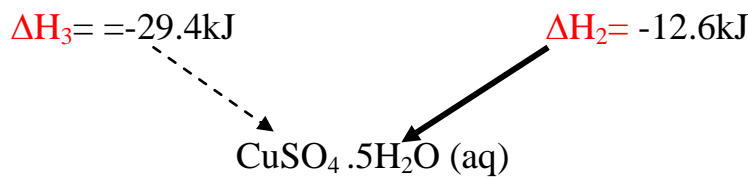
$$\Delta H_s = \text{CuSO}_4 = \frac{\Delta H}{\text{Number of Moles}} \Rightarrow \frac{-0.63\text{kJ}}{0.05 \text{ moles}} = 12.6\text{kJ}$$

(d) Using an energy level diagram, calculate the molar enthalpy change for the reaction:



Energy cycle diagram





$$\begin{aligned} \Delta H_3 &= \Delta H_1 + \Delta H_2 \\ \Rightarrow -29.4\text{kJ} &= -12.6\text{kJ} + x \\ \Rightarrow -29.4\text{kJ} - (-12.6\text{kJ}) &= x \\ \mathbf{x} &= \mathbf{16.8\text{kJ}} \end{aligned}$$

b) Practical example II

Determination of enthalpy of solution of ammonium chloride

Theoretical information.

Ammonium chloride dissolves in water to form ammonium chloride solution. Aqueous ammonia can react with excess dilute hydrochloric acid to form ammonium chloride solution. The heat change taking place can be calculated from the heat of reactions:

- (i) $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
- (ii) $\text{NH}_4\text{Cl}(\text{s}) + (\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq})$
- (iii) $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq})$

Experiment procedure I

Measure 50cm³ of water into a 100cm³ beaker. Record its temperature T_1 as initial temperature to the nearest 0.5°C in table I. Add exactly 5.0g of ammonium chloride crystals weighed carefully into the water. Stir and record the highest temperature change T_2 as the final temperature change. Repeat the above procedure to complete table I.

Sample results Table I

Experiment	I	II
final temperature(°C)	19.0	20.0
initial temperature(°C)	22.0	22.0
temperature change ΔT (°C)	3.0	2.0

Experiment procedure II

Measure 25cm³ of 2M aqueous ammonia into a 100cm³ beaker. Record its temperature T_1 as initial temperature to the nearest 0.5°C in table II. Measure 25cm³ of 2M hydrochloric acid solution. Add the acid into the beaker containing

aqueous ammonia. Stir and record the highest temperature change T_2 as the final temperature change. Repeat the above procedure to complete table II.

Sample results: Table II

Experiment	I	II
final temperature($^{\circ}\text{C}$)	29.0	29.0
initial temperature($^{\circ}\text{C}$)	22.0	22.0
temperature change $\Delta T(^{\circ}\text{C})$	7.0	7.0

Sample Calculations:

(a) Calculate the average ΔT in

(i) Table I

$$\Delta T = T_2 - T_1 \Rightarrow \frac{-3.0 + -2.0}{2} = 2.5^{\circ}\text{C}$$

(ii) Table II

$$\Delta T = T_2 - T_1 \Rightarrow \frac{7.0 + 7.0}{2} = 7.0^{\circ}\text{C}$$

(b) Calculate the enthalpy change for the reaction in:

(i) Experiment I

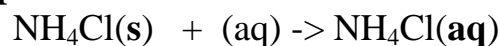
$$\begin{aligned} \text{Enthalpy change } \Delta H &= \text{mass of Water(m)} \times c \times \Delta T \\ & \Rightarrow \frac{50\text{cm}^3 \times 4.2 \times 2.5^{\circ}\text{C}}{1000} = +0.525\text{kJ} \end{aligned}$$

(ii) Experiment II

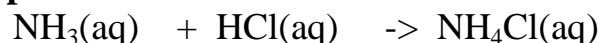
$$\begin{aligned} \text{Enthalpy change of CuSO}_4 &= \text{mass of water(m)} \times c \times \Delta T \\ & \Rightarrow \frac{25+25\text{cm}^3 \times 4.2 \times 7^{\circ}\text{C}}{1000} = +1.47\text{kJ} \end{aligned}$$

(c) Write the equation for the reaction taking place in:

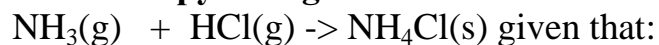
(i) Experiment I



(ii) Experiment I

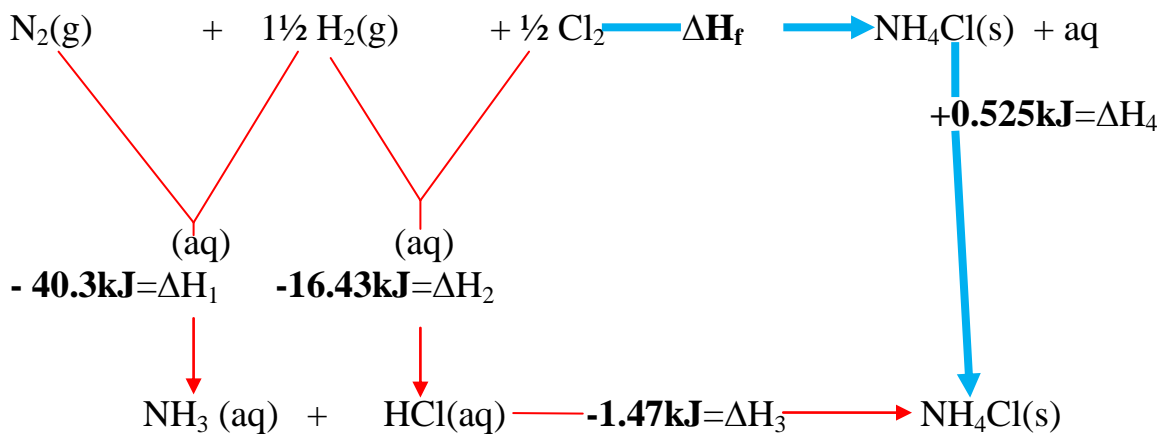


(d) Calculate the enthalpy change ΔH for the reaction:



(e) Applying Hess' Law of constant heat summation:

Energy level diagram



$$\begin{aligned} \Delta H_1 + \Delta H_2 + \Delta H_3 &= \Delta H_4 + \Delta H_f \\ -40.3\text{kJ} + -16.43\text{kJ} + -1.47\text{kJ} &= +0.525\text{kJ} + \Delta H_f \\ \Rightarrow \Delta H_f &= -58.865\text{kJ} \end{aligned}$$

Practice theoretical examples:

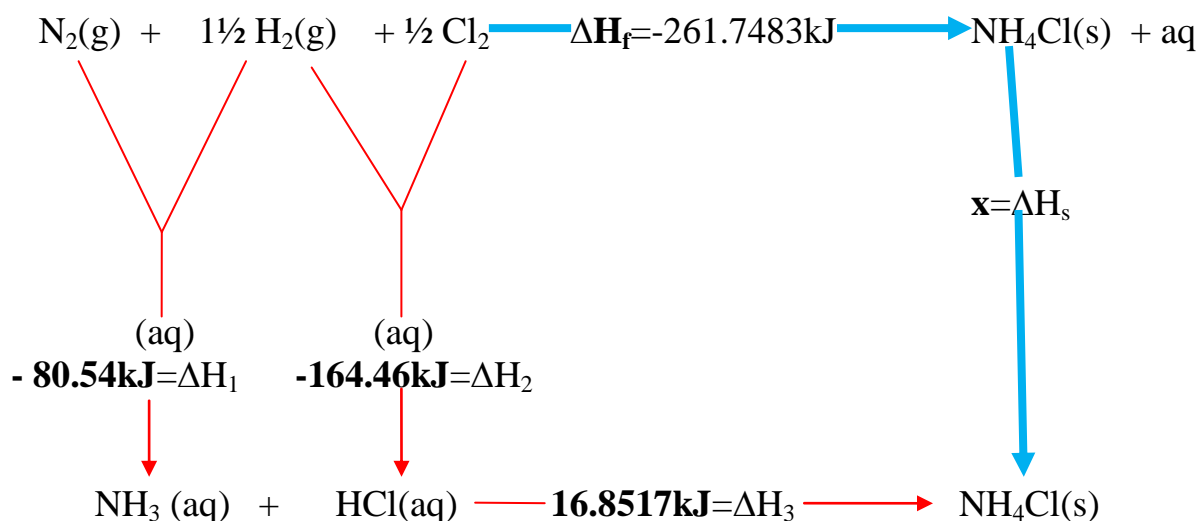
1. Using an energy level diagram calculate the ΔH_s of ammonium chloride crystals given that.

$$\Delta H_f \text{ of } \text{NH}_3(\text{aq}) = -80.54\text{kJ mole}^{-1}$$

$$\Delta H_f \text{ of } \text{HCl}(\text{aq}) = -164.46\text{kJ mole}^{-1}$$

$$\Delta H_f \text{ of } \text{NH}_4\text{Cl}(\text{aq}) = -261.7483\text{kJ mole}^{-1}$$

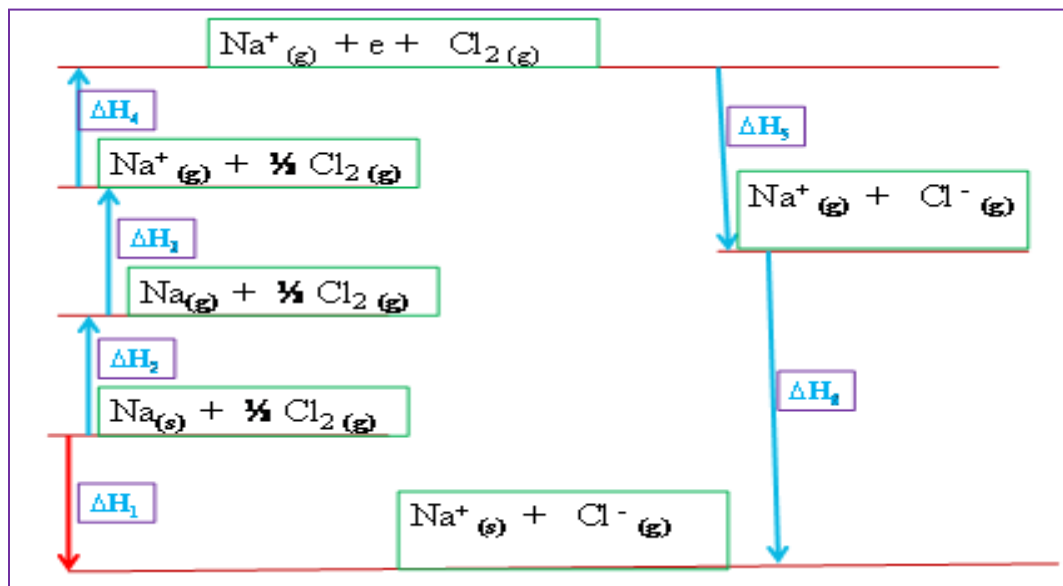
$$\Delta H_s \text{ of } \text{NH}_4\text{Cl}(\text{aq}) = -16.8517\text{kJ mole}^{-1}$$



$$\begin{aligned} \Delta H_1 + \Delta H_2 + \Delta H_3 &= \Delta H_4 + \Delta H_f \\ -80.54\text{kJ} + -164.46\text{kJ} + 16.8517\text{kJ} &= -261.7483\text{kJ} + \Delta H_f \\ \Rightarrow \Delta H_f &= -33.6\text{kJmole}^{-1} \end{aligned}$$

Study the energy cycle diagram below and use it to:

(a) Identify the energy changes ΔH_1 ΔH_2 ΔH_3 ΔH_4 ΔH_5 ΔH_6



ΔH_1 - enthalpy/heat of formation of sodium chloride (ΔH_f)

ΔH_2 - enthalpy/heat of atomization of sodium (ΔH_{at})

ΔH_3 - enthalpy/heat of ionization/ionization energy of sodium (ΔH_i)

ΔH_4 - enthalpy/heat of atomization of chlorine (ΔH_{at})

ΔH_5 - enthalpy/heat of electron affinity of chlorine (ΔH_e)

ΔH_6 enthalpy/heat of lattice/Lattice energy of sodium chloride (ΔH_l)

(b) Calculate ΔH_1 given that $\Delta H_2 = +108 \text{ kJ}$, $\Delta H_3 = +500 \text{ kJ}$, $\Delta H_4 = +121 \text{ kJ}$, $\Delta H_5 = -364 \text{ kJ}$ and $\Delta H_6 = -766 \text{ kJ}$

Working:

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

Substituting:

$$\Delta H_1 = +108 \text{ kJ} + +500 \text{ kJ} + +121 \text{ kJ} + -364 \text{ kJ} + -766 \text{ kJ}$$

$$\Delta H_1 = \underline{\underline{-401 \text{ kJmole}^{-1}}}$$

(c) Given the that:

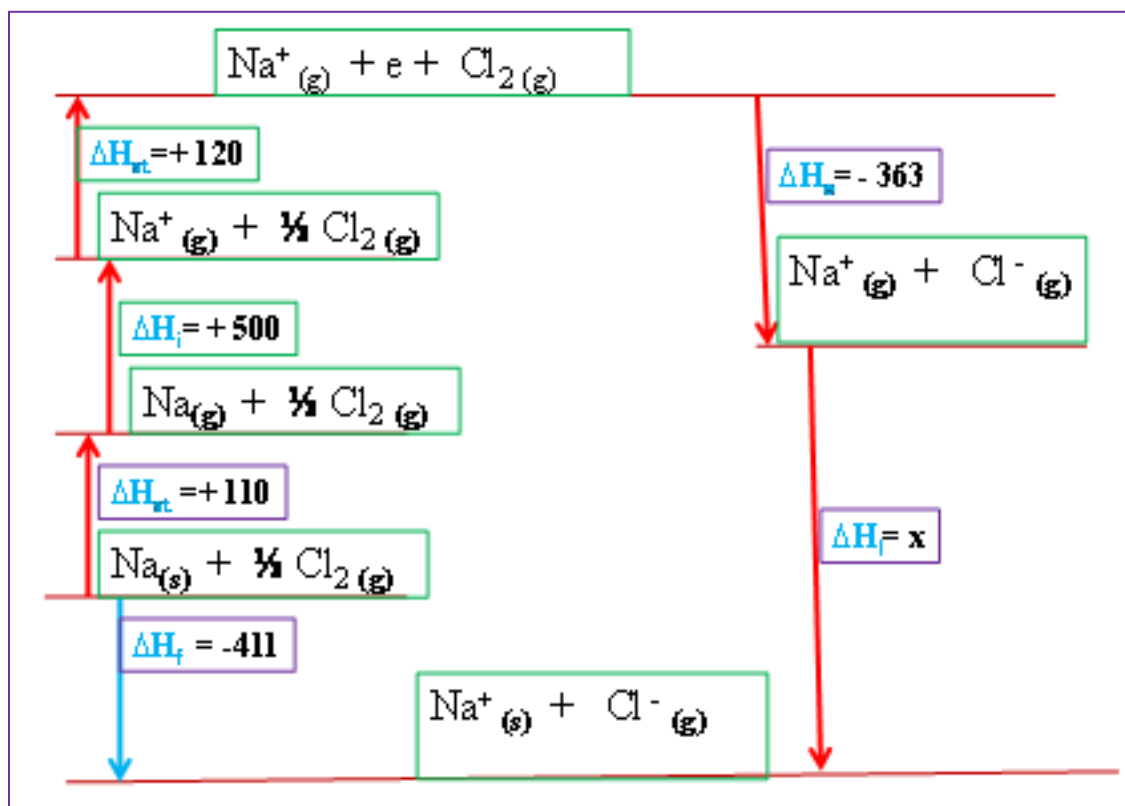
(i) Ionization energy of sodium = $+ 500 \text{ kJmole}^{-1}$

(ii) ΔH_{at} of sodium = $+ 110 \text{ kJmole}^{-1}$

(iii) Electron affinity of chlorine = $- 363 \text{ kJmole}^{-1}$

(iv) ΔH_{at} of chlorine = $+ 120 \text{ kJmole}^{-1}$

(v) ΔH_f of sodium chloride = -411kJ , calculate the lattice energy of sodium chloride using an energy cycle diagram.



Working:

Applying Hess law then:

$$\Delta H_f = \Delta H_a + \Delta H_i + \Delta H_a + \Delta H_e + \Delta H_l$$

Substituting:

$$-411 = +108\text{kJ} + +500\text{kJ} + +121\text{kJ} + -364\text{kJ} + x$$

$$-411 + -108\text{kJ} + -500\text{kJ} + -121\text{kJ} + +364\text{kJ} = x$$

$$x = \underline{\underline{-776\text{kJmole}^{-1}}}$$

When 0.6g of element M was completely burnt in Oxygen, the heat evolved raised the temperature of 500cm³ of water from 28 °C to 37 °C. Calculate the relative molecular mass of M given the molar heat of combustion of M is 380kJmole⁻¹. Specific heat capacity of water is 4.2kJ⁻¹K⁻¹Kg⁻¹g.

Working

$$\text{Heat evolved } \Delta H = \text{Mass of water} \times c \times \Delta T$$

$$\Rightarrow 500 \times 4.2 \times 9 = \frac{18900\text{J}}{1000} = \underline{18.9\text{kJ}}$$

$$\text{Moles of M} = \frac{\text{Heat evolved } \Delta H}{\text{Molar heat of combustion}} \Rightarrow \frac{18.9 \text{ kJ}}{380 \text{ kJ}} = \underline{0.0497 \text{ moles}}$$

$$\text{Relative atomic mass} = \frac{\text{Mass}}{\text{Moles}} \Rightarrow \frac{0.6 \text{ g}}{0.0497 \text{ moles}} = \underline{12.0724} \text{ (No units)}$$

*******END*******

- ❖ All secondary school schemes of work.
- ❖ Form 1-form 4 revision papers in all subjects.
- ❖ Marking schemes to most of the revision papers.
- ❖ K.C.S.E past papers.
- ❖ University past papers.
- ❖ K.A.S.N.E.B past papers e.g. C.P.A
- ❖ Primary school schemes of work.

- ❖ *Primary school revision papers to all classes.*
- ❖ *Marking schemes to primary school past papers.*
- ❖ *K.C.P.E past papers.*