

## Energy changes in chemical reactions

### Introduction

- ❖ Energy is defined as the capacity/ability to do work.
- ❖ There are several forms of energy but the most important of interest in this case is **chemical energy** stored in chemical substances.
- ❖ Chemical reactions occur with a change in energy which leads to
  - (i) either **rise** (increase) in temperature.
  - (ii) or **fall** (decrease) in temperature.
- ❖ The rise or fall in temperature can be detected by the use of a **thermometer**.

**Note:**

Chemical energy can manifest itself during chemical reactions in several other several forms apart from heat. For example; as light, sound, electricity etc.

### Types of chemical reactions

- ❖ There are **two** types of chemical reactions in relation to heat changes namely:
  - (i) Exothermic reactions
    - In this case, heat is liberated (given out) to the surroundings and thus, there is a rise (increase) in temperature.
    - Thus, an **exothermic reaction** is one during which heat is liberated to the surroundings.
    - Common examples of exothermic reactions are; combustion, neutralization, dissolution of acids and bases in water etc.
  - (ii) Endothermic reactions
    - In endothermic reactions, heat is absorbed from the surroundings and thus, there is a fall (decrease) in temperature.
    - Thus, an **endothermic reaction** is one during which heat is absorbed from the surroundings.
    - Examples of some endothermic reactions are; dissolution of sodium chloride in water, sodium thiosulphate in water, ammonium chloride in water, decomposition of copper(II) carbonate, etc.

### Units of heat change

- ❖ The internationally accepted unit for heat change in chemical reactions is **kJ** (kilo joules); which means 1000 joules.  
Thus,  $1\text{kJ} = 1000\text{ J}$
- ❖ The used of kJ changes vary large values to much smaller values which can easily be handled and appreciated. For example  $20\text{ kJ} = 20,000\text{ J}$ .

## The $\Delta H$ notation

- ❖ The heat content of a chemical substance is known as **enthalpy** and is denoted by **H**.
- ❖ Since it is not easy to determine the heat content a chemical substance possess (*i.e. the energy possessed by any chemical substance is difficult to measure*), we shall focus on the determination of the **heat change** also called **enthalpy change**.
- ❖ The symbol for the heat change is  $\Delta H$  ( $\Delta$  means change in) and is defined as;  
$$\Delta H = H(\text{products}) - H(\text{reactants})$$
- ❖ For **exothermic reactions**,  $\Delta H$  values are **negative**.

For example;

- (i)  $C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -390 \text{ kJ mol}^{-1}$   
This means that when **one mole** of solid carbon burns **completely** in oxygen to form **one mole** of gaseous carbon dioxide, **390 kJ** of heat is **evolved**/liberated/given out to the surroundings.
- (ii)  $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H = -286 \text{ kJ mol}^{-1}$   
This means that when **one mole** of gaseous hydrogen burns **completely** in oxygen to form **one mole** of liquid water, **286 kJ** of heat is **evolved**/liberated/given out to the surroundings.

- ❖ For endothermic reactions,  $\Delta H$  values are **positive**.

For example;  $C(s) + 2S(s) \rightarrow CS_2(l);$

$$\Delta H = +117 \text{ kJ mol}^{-1}$$

This means that when **one mole** of solid carbon reacts with two moles of sulphur to form one mole of liquid carbon disulphide, **117 kJ** of heat is **absorbed** from the surroundings.

### Trial question

Under suitable conditions, nitrogen and hydrogen separately react with oxygen according to the following equations.



State what each of the equations means.

## Types of heat (enthalpy) change

- ❖ The types of heat changes in chemical reactions depend on the type of reaction taking place.
- ❖ Some important heat changes are;

### A. Heat of combustion

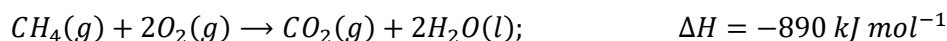
- ❖ **Definition:** Heat of combustion is the heat evolved when one mole of a substance is burnt completely in oxygen.
- ❖ The values of heats of combustion of substances are always **negative**. This is because heat is always evolved when substances are burnt in oxygen.

❖ The values for heats of combustion for some common substances are:

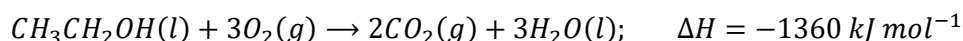
Carbon:



Methane:



Ethanol:



**Note:**

The above substances are used as **fuels**. This is because the substances produce a lot of heat when burnt.

**Questions**

1. Carbon burns in oxygen according to the following equation:



(a) Calculate the:

(i) amount of heat evolved when 3.6 g of carbon is burnt completely in oxygen.

**Solution**

$$\text{No. of moles of carbon burnt} = \frac{3.6}{12} = 0.3$$

1 mole of carbon burns to produce 390 kJ of heat

$$0.3 \text{ moles of carbon burns to produce } (0.3 \times 390) \text{ kJ of heat} \\ = 117 \text{ kJ of heat}$$

(ii) volume of oxygen at s.t.p that would be required to produce 78.6 kJ of heat.  
(C=12; 1 mole of gas occupies 22.4 dm<sup>3</sup> at s.t.p)

**Solution**

$$\text{No. of moles of carbon burnt} = \frac{3.6}{12} = 0.3$$

1 mole of carbon reacts with 1 mole of oxygen.

No. of moles of oxygen used = 0.3

1 mole of oxygen occupies 22.4 dm<sup>3</sup>

$$0.3 \text{ moles of oxygen occupies } (0.3 \times 22.4) \text{ dm}^3 = 6.72 \text{ dm}^3$$

(b) 80 kg of charcoal costs Shs.40,000. Calculate the cost of charcoal required to produce 227,500 kJ of heat.

**Solution**

390 kJ of heat is produced by 1 mole of carbon.

390 kJ of heat is produced by 12 g of carbon.

$$227,500 \text{ kJ of heat are produced by } \left( \frac{12 \times 227500}{390} \right) \text{ g of carbon} \\ = 7,000 \text{ g of carbon}$$

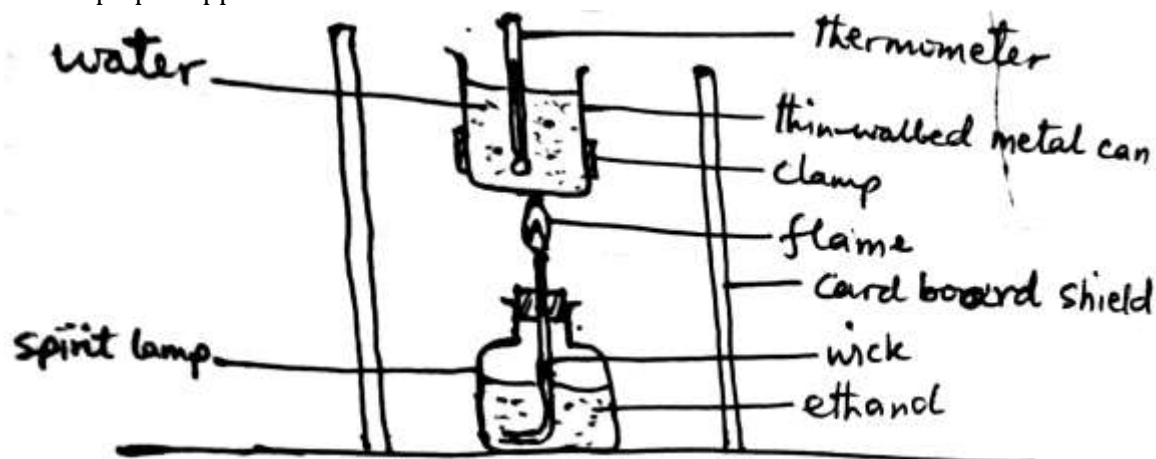
80,000 g (80 kg) of charcoal cost Shs 4000

$$7,000 \text{ g (7 kg) g of charcoal cost Shs. } \left( \frac{7000 \times 4000}{80000} \right) = \text{Shs.350}$$

2. The enthalpy of combustion of methane is  $-890 \text{ kJ mol}^{-1}$ .
- Write equation for the complete combustion of methane.
  - Calculate the:
    - amount of heat that can be produced by when  $12 \text{ dm}^3$  of methane is completely burnt in oxygen at room temperature and pressure.
    - volume of methane at s.t.p that will burn in excess oxygen to produce  $2670 \text{ kJ}$  of heat.
3. Octane burns in excess air according to the following equation:  
 $2\text{C}_8\text{H}_{18}(\text{l}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{l}); \quad \Delta H = -12,250 \text{ kJ}$
- Given that  $5.7 \text{ g}$  of octane were burnt, determine the:
    - amount of heat produced.
    - volume of carbon dioxide produced at s.t.p.
  - Calculate the:
    - molar heat of combustion of octane.
    - mass of octane that would be burnt in order to produce  $13.20 \text{ kJ}$  of heat.  
 (C=12; H=1; 1 mole of gas occupies  $22.4 \text{ dm}^3$  at s.t.p)
4. Compound **Z** has a molecular formula,  $\text{C}_3\text{H}_8$ . The enthalpy of combustion of **Z** is  $2220 \text{ kJ mol}^{-1}$ . Calculate the enthalpy change which occurs when  $3.96 \text{ g}$  of **Z** is completely burnt in oxygen. (C=12; H=1)

**An experiment to determine the heat of combustion of a liquid fuel (e.g. methanol, ethanol or propanol) in the laboratory.**

The step up of apparatus is as follows:



**Experimental procedure**

- A improvised lamp containing some ethanol is weighed and mass recorded say,  $x \text{ g}$ .
- A known volume,  $v \text{ cm}^3$  of water is placed in a thin-walled tin can and a thermometer inserted.
- The water is stirred and its initial temperature  $t_i^\circ\text{C}$  is noted.
- The can having water is placed directly over the lamp protected with cardboard shields.
- The lamp is lit and the flame produced is used to heat the water in the can.
- The water is frequently stirred until its temperature rises appreciatively.

- The flame is put off and the final temperature  $t_f$  °C of water is noted
- The lamp is allowed to cool and reweighed with its contents and the mass recorded say  $y$  g.

### Treatment of results

- Density of water  $1 \text{ g cm}^{-3}$ ; mass of water  $= v \times 1 = v \text{ g}$
- Specific heat capacity of water  $= 4.2 \text{ J g}^{-1} \text{ °C}^{-1}$
- Temperature rise,  $\Delta t = (t_f - t_i) \text{ °C}$
- Mass of ethanol burnt  $= \left( \text{mass of improvised lamp before burning} \right) - \left( \text{mass of improvised lamp after burning} \right) = (x - y) \text{ g}$
- Assuming no heat loss to the surroundings and the can has a negligible heat capacity;
- Heat supplied by ethanol burnt  $=$  heat absorbed by water.  

$$= \left( \frac{\text{mass of water}}{\text{of water}} \right) \times \left( \frac{\text{S.H.C}}{\text{of water}} \right) \times \left( \frac{\text{temp}}{\text{rise}} \right)$$

$$= v \times 4.2 \times \Delta t$$

$$= (4.2v\Delta t) \text{ J}$$
- R.f.m of ethanol,  $\text{C}_2\text{H}_5\text{OH} = 24 + 6 + 16 = 46$   
 No of moles of ethanol burnt  $= \frac{x-y}{46}$   
 $\frac{x-y}{46}$  moles of ethanol produce  $(4.2v\Delta t) \text{ J}$  of heat  
 1 mole of ethanol produces  $\left( \frac{4.2v\Delta t}{\frac{x-y}{46}} \right) \text{ J}$  of heat
- Thus, heat of combustion of ethanol  $= - \left( \frac{4.2v\Delta t}{\frac{x-y}{46}} \right) \text{ J mol}^{-1}$  **or**  $- \left( \frac{4.2v\Delta t}{\frac{x-y}{46} \times 1000} \right) \text{ kJ mol}^{-1}$

#### Note:

- (i) The experimental results/values are usually much lower than the actual values.  
 This is because some of the heat produced is lost to the surroundings (e.g. warming the tin can and air) and does not pass into the water.
- (ii) In order to minimize heat losses to the surroundings;
  - Cover the tin can to minimize heat loss due to evaporation.
  - Use a thin copper can because it retains very little heat and is a very good conductor of heat.
  - Use cardboard shields so that the flame remains steady.
  - No wire gauze should be used since it also absorbs heat.
- (iii) Applications of heat of heats of combustion values
  - To determine the best fuel depending on the heat energy given out.
  - Since food is a biological fuel, the values are used in choosing food samples to be taken by people on a diet. This is in accordance with the amount of energy the food sample liberates when the biological combustion takes place in the body.

### Trial Questions

1. The following results were obtained during an experiment to determine the heat of combustion of ethanol.

• Initial temperature of water	= 17.7°C
• Final temperature of water	= 41.2°C
• Volume of water in the thin can	= 101 cm <sup>3</sup>
• Mass of (lamp+ethanol) before burning	= 29.974 g
• Mass of (lamp+ethanol) after burning	= 29.592 g
• Density of water	= 1.0 g cm <sup>-3</sup>
• Specific heat capacity of water	= 4.2 Jg <sup>-1</sup> °C <sup>-1</sup>

(a) Using the data, determine the heat of combustion of ethanol. (H=1; C=12)

(b) The actual/expected heat of combustion of ethanol is  $-1367 \text{ kJ mol}^{-1}$ .

(i) State whether the value obtained in (a) is less than, equal to or more than the actual value of heat of combustion of ethanol.

(ii) Give a reason for your answer in (b)(i).

2. (a) Define the term **enthalpy of combustion**.

(b) With the aid of a well-labeled diagram, describe an experiment you would carry out in the laboratory to determine the enthalpy of combustion of methanol.

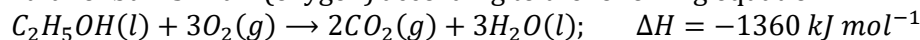
(c) (i) In an experiment to determine the enthalpy of combustion of methanol, 3.2 g of methanol was burnt and heat evolved caused the temperature of 300 cm<sup>3</sup> of water to rise by 56.0°C.

Calculate the experimental value of the enthalpy of combustion of methanol.

(molar mass of methanol = 32; density of water = 1 g cm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>°C<sup>-1</sup>)

(ii) The standard enthalpy of methanol is  $-726 \text{ kJ mol}^{-1}$ . Compare the experimental value obtained in (c)(i) with the standard value. Explain your answer.

(d) Ethanol burns in air (oxygen) according to the following equation.



(i) What does  $-1360 \text{ kJ mol}^{-1}$  mean?

(ii) Calculate the mass of ethanol required to produce  $-1360 \text{ kJ}$  of heat.

(iii) Determine the mass of ethanol that is required to rise the temperature of 1000 cm<sup>3</sup> of water by 100°C.

(O=16; C=12; H=1; density of water = 1 g cm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>°C<sup>-1</sup>)

(e) When 23.6 g of butane (C<sub>4</sub>H<sub>10</sub>) was burnt, the heat evolved raised the temperature of 100 g of water from 30°C to 40°C. Calculate the molar heat of combustion of butane.

(C=12; H=1; density of water = 1 g cm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>°C<sup>-1</sup>)

(f) Calculate the volume of methane which when burnt at s.t.p will raise the temperature of 160 g of water by 15°C.

(C=12; H=1; 1 mole of gas occupies 22.4 dm<sup>3</sup> at s.t.p; density of water = 1 g cm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>°C<sup>-1</sup>)

(g) The standard heats of combustion of straight chain alkanes are given below.

Alkane	Methane	Ethane	Propane	Butane	Heptane
Molecular formula	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>7</sub> H <sub>16</sub>
Heat of combustion (kJ mol <sup>-1</sup> )	890	1560	2220	2877	4800

(i) Define the **term heat of combustion**. Illustrate your answer using ethane.

- (ii) Plot a graph of heat of combustion (vertical axis) against the number of carbon atoms (horizontal axis).
- (iii) From the graph, determine the heat of combustion of a straight chain alkane with six carbon atoms.
- (iv) What is the shape of your graph?
- (v) State the relationship between the heat of combustion of an alkane and the number of carbon atoms in an alkane.
- (vi) A litre of methane gas costs 600/=. Calculate the cost of methane required to produce  $1.746 \times 10^6$  J of heat at room temperature.  
(1 mole of gas occupies 24 litres at room temperature)
- (h) The enthalpy of combustion of some straight chain alcohols are shown in the table below.

Alcohol	$CH_3OH$	$C_2H_5OH$	$C_3H_7OH$	$C_4H_9OH$	$C_5H_{11}OH$	$C_6H_{13}OH$
Formula mass						
Enthalpy of combustion ( $kJ\ mol^{-1}$ )	726	1371	2017	2673	3331	3984

- (i) Copy the table and fill in the values for the formula masses of the alcohols.  
( $H = 1$ ;  $C = 12$ ;  $O = 16$ )
- (ii) Plot a graph of enthalpy of combustion (vertical axis) against formula mass (horizontal axis).
- (iii) State how the enthalpies of the straight chain alcohols vary with their formula masses.
- (iv) Use your graph to determine the enthalpy of combustion of a straight chain alcohol of formula mass 116.

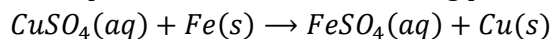
## B. Heat of displacement

- ❖ **Definition:** Heat of displacement is the heat change that occurs when one mole of aqueous ions is displaced from its aqueous solution.
- ❖ Examples of some displacement reactions are:

- (i) When iron filings/dust/wire is added to an aqueous solution of copper(II) sulphate; the mixture becomes **warm**. The **blue solution** turns to a pale **green solution** and a **brown solid** is formed/deposited.

The pale green solution is due to the formation of iron(II) sulphate and the brown solid is copper.

The equation for the reaction taking place is:



**Or** ionic equation is:  $Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$

### Explanation:

Iron is **higher** in the **reactivity series** than copper. Thus, iron is **more reactive** than copper. It therefore **displaces** copper from solution. The reaction mixture becomes warm because the reaction is **exothermic**.

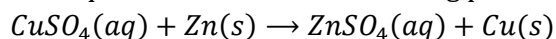
**Note:**

In the above reaction,  $Cu^{2+}$  ions have been **reduced** to  $Cu$  and  $Fe$  has been **oxidized** to  $Fe^{2+}$ . Thus, the above reaction is called a **redox reaction**.

- (ii) When zinc dust/powder/granules is added to an aqueous solution of copper(II) sulphate; the mixture becomes **warm**. The **blue solution** turns to a **colourless solution** and a **brown solid** is formed/deposited.

The colourless solution is due to the formation of zinc sulphate and the brown solid is copper.

The equation for the reaction taking place is:



**Or** ionic equation is:  $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

**Explanation:**

Zinc is **higher** in the **reactivity series** than copper. Thus, zinc is **more reactive** than copper. It therefore **displaces** copper from solution. The reaction mixture becomes warm because the reaction is **exothermic**.

**Note:**

In the above reaction,  $Cu^{2+}$  ions have been **reduced** to  $Cu$  and  $Zn$  has been **oxidized** to  $Zn^{2+}$ . Thus, the above reaction is called a **redox reaction**.

**Trial Questions**

- Magnesium powder was added to copper(II) sulphate, the mixture was shaken and allowed to stand.
  - State what was observed.
  - Write an ionic equation for the reaction that took place.
  - The experiment was repeated using silver.
    - State what was observed
    - Explain your answers in (a) and (c)(i).
- In order to illustrate a redox reaction, zinc was added to copper(II) sulphate solution and the setup left to stand for some time.
  - State what was observed.
  - State the substance that was:
    - oxidised .....
    - reduced.....
  - Write equation for the redox reaction that took place.
  - Name one other substance that would react with copper(II) sulphate in a similar way like zinc.

- ❖ Just like the heat of combustion, the heat of displacement can be experimentally determined. In the experimental determination of the heat of displacement, the container/beaker used must be **plastic** (since it is a poor conductor of heat) or **well-lagged** (to minimize heat loss to the surroundings).



### Questions

- When excess zinc dust was added to 100 cm<sup>3</sup> of a 0.2 M copper(II) sulphate solution in a well-lagged container, the temperature of the mixture changed from 20.0°C to 30.4°C.
  - Give a reason why:
    - there was a temperature rise.
    - the container was well-lagged.
  - Write an ionic equation for the reaction that took place.
  - Calculate the molar heat of reaction. State the necessary assumptions made. (density of water = 1 g cm<sup>-3</sup>; S.H.C of water = 4.2 J g<sup>-1</sup>°C<sup>-1</sup>)
  - The experiment was repeated using a metallic cup instead of a well-lagged container.
    - State whether the heat of the reaction was equal to, less or more than that obtained in (c).
    - Give a reason for your answer in (d)(i).
  - In another experiment, excess silver was added to 100 cm<sup>3</sup> of a 0.2 M copper(II) sulphate solution maintained at 20.0°C in a well-lagged container. The final temperature of the mixture was noted and recorded.
    - State whether the temperature of the resultant mixture decreased, increased or remained constant.
    - Give a reason for your answer in (e)(i).

### Solution:

- The reaction produced heat (or an exothermic reaction occurred)
  - To minimize heat loss to the surroundings.
- $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$
- Assuming the solution is dilute; both its density of and SHC are equal to that of water.  
Mass of solution = (100 × 1) = 100 g  
Assuming no heat loss to the surroundings; heat produced/lost = heat gained  
Heat produced =  $mc\theta = 100 \times 4.2 \times (30.4 - 20.0) = 4368 J$   
No. of moles of  $Cu^{2+}$  ions that reacted =  $\left(\frac{100 \times 0.2}{1000}\right) = 0.02$   
0.02 moles of  $Cu^{2+}$  ions produce 4368 J of heat.  
1 mole of  $Cu^{2+}$  ions produce  $\left(\frac{4368}{0.02}\right) J$  of heat.  
 $= 218,400 J$  of heat = 218.4 kJ of heat

∴ molar heat of reaction =  $-218.4 kJ mol^{-1}$

### Other assumptions:

No significant increase in mass occurred on addition of zinc dust to the solution.

- Less
    - Some heat produced was absorbed by the metallic cup.
  - Remained constant.
    - No reaction occurred. This is because silver is less reactive than copper (Silver is below copper in the reactivity series)
- When excess filings were added to 200 cm<sup>3</sup> of a 0.5 M copper(II) sulphate solution in a plastic cup, the temperature of the solution rose by 17.9°C.
    - Write equation for the reaction that took place.
    - Suggest a reason why a plastic cup was used instead of a metallic cup.
    - Calculate the enthalpy change for the reaction.

( $O = 16$ ;  $S = 32$ ;  $Fe = 56$ ;  $Cu = 64$ ; density of water =  $1 \text{ g cm}^{-3}$ ; S.H.C of water =  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ )

(d) State any assumption(s) you have made in the calculations in (c).

3. When 1.6 g of zinc powder was added to  $250 \text{ cm}^3$  of a 0.05 M copper(II) sulphate solution in a plastic cup and the mixture shaken, 5.45 kJ of heat was evolved.

(a) State:

- (i) why a plastic cup was used instead of a metallic cup.
- (ii) why zinc powder was in excess.
- (iii) what would be observed in plastic cup at the end of the reaction.

(b) Write an ionic equation for the reaction that took place.

(c) Calculate the:

- (i) number of moles of zinc powder used.
- (ii) number of moles of copper(II) sulphate used.
- (iii) heat of displacement of copper.

### C. Heat of solution

- ❖ When a solute is added into water, it dissolves to form a **solution**.

The formation of the solution occurs with either **evolution** or **absorption** of heat.

Thus, the **heat of solution** (of a solute) is the heat change when **one mole** of a solute dissolves in a large volume of water.

#### Note:

Heat evolved/absorbed during the formation of a solution depends on the amount of water used.

- ❖ The heat of solution can be

- either **negative**. In this case, the process is **exothermic**.
- or positive. In this case, the process is **endothermic**.

- ❖ For example:

- (i) Concentrated sulphuric acid, sodium hydroxide pellets and solid potassium hydroxide dissolve in water with **evolution** of heat (i.e. mixture become becomes **hot**/warm) and thus, their values of heat of solution are **negative**.
- (ii) Ammonium nitrate and sodium thiosulphate dissolve in water with **absorption** of heat (i.e. mixture become becomes **cold**) and thus, their values of heat of solution are **positive**.

#### Questions

1. When 4.0 g of ammonium nitrate was dissolved in  $96 \text{ cm}^3$  of water at  $20.0^\circ\text{C}$  in a plastic cup, the final temperature of the resultant solution was  $14.0^\circ\text{C}$ .

(a) What does the change in the temperature from  $20.0^\circ\text{C}$  to  $14.0^\circ\text{C}$  indicate about the process that occurred?

(b) Calculate the heat of solution of ammonium nitrate.

( $O = 16$ ;  $N = 14$ ;  $H = 1$ ; density of water =  $1 \text{ g cm}^{-3}$ ; S.H.C of water =  $4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ )

#### Solution:

(a) Ammonium nitrate dissolves **endothermically** by **absorbing heat from water**.

(b) Mass of solution = mass of solvent + mass of solute =  $(96 \times 1) + 4.0 = 100.0 \text{ g}$

Assuming the solution formed is dilute; its SHC is equal to that of water.

For no heat loss to the surroundings; heat evolved/lost = heat gained/absorbed

$$\text{Heat solution} = mc\theta = 100.0 \times 4.2 \times (20.0 - 14.0) = 2520 \text{ J}$$

$$\text{R.f.m of NH}_4\text{NO}_3 = 14 + (4 \times 1) + 14 + (16 \times 3) = 80$$

$$\text{No. of moles of NH}_4\text{NO}_3 \text{ used} = \frac{4.0}{80} = 0.05$$

0.05 moles of  $\text{NH}_4\text{NO}_3$  absorbs 2520 J of heat

$$1 \text{ mole of NH}_4\text{NO}_3 \text{ absorbs } \left(\frac{2520}{0.05}\right) \text{ J of heat} = 50,400 \text{ J of heat} = 50.4 \text{ kJ of heat}$$

$$\therefore \text{Heat of solution} = +50.4 \text{ kJ mol}^{-1}$$

2. When 20.0 g of sodium hydroxide pellets were added to 980 cm<sup>3</sup> of distilled water in a plastic cup and the mixture stirred, the temperature of the resultant mixture rose by 5.2°C. Determine the heat of solution of sodium hydroxide.

( $Na = 23$ ;  $O = 16$ ;  $H = 1$ ; density of water = 1 gcm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>K<sup>-1</sup>)

(Answer: -42.68 kJ mol<sup>-1</sup>)

3. When 31.0 g of powdered sodium chloride was dissolved in sufficient amount of water in a plastic beaker to form 131 cm<sup>3</sup> of solution, the temperature of the resultant solution dropped by 4.7°C. Calculate the heat of solution of sodium chloride.

( $Na = 23$ ;  $O = 16$ ;  $Cl = 35.5$ ; density of water = 1 gcm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>K<sup>-1</sup>)

(Answer: +4.89 kJ mol<sup>-1</sup>)

4. When concentrated sulphuric acid was added to a sufficient volume of water, the volume of the resultant solution was 1000 cm<sup>3</sup>. If the heat of the solution of sulphuric acid is -71.0 kJ mol<sup>-1</sup>, determine the temperature change that occurred.

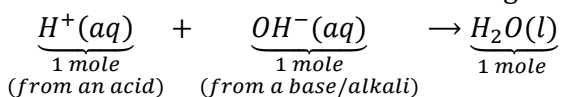
( $S = 32$ ;  $O = 16$ ;  $H = 1$ ; density of water = 1 gcm<sup>-3</sup>; S.H.C of water = 4.2 Jg<sup>-1</sup>K<sup>-1</sup>)

(Answer: 16.9°C)

#### D. Heats of neutralization

❖ Neutralization is the reaction between a **base** and an **acid** to form a **salt** and **water** only.

❖ The essential reaction that occurs during neutralization of interest is:



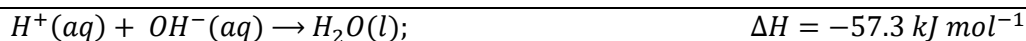
❖ Thus, the **enthalpy (heat) of neutralization** refers to the heat change when one mole of aqueous hydrogen ions from an acid reacts with one mole of aqueous hydroxide ions from an alkali (a base) to form one mole of water.

##### Note:

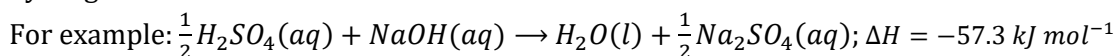
- When strong acids (e.g. HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) react with strong alkalis/bases (e.g. NaOH, KOH, Ca(OH)<sub>2</sub>), the heats of neutralization are approximately constant (i.e. about the same value) and higher; being -57.3 kJ mol<sup>-1</sup>.

##### Reason:

Both the acid and the base/alkali are **fully ionized** in their dilute aqueous solutions. Thus, the only reaction that occurs is between aqueous hydrogen ions and aqueous hydroxide ions to form water.



- For sulphuric acid, we always quote half a mole (i.e.  $\frac{1}{2}H_2SO_4$ ). This is because the acid is **dibasic** and thus, each mole of the acid produces two moles of hydrogen ions on ionization. Therefore, a half mole of the acid will produce the necessary one mole of hydrogen ions on ionization.



- For neutralization reactions involving weak acids (e.g. ethanoic acid) or weak bases/alkalis (e.g. aqueous ammonia), the heats of neutralisation are **not constant** and can be more or less than  $-57.3 \text{ kJ mol}^{-1}$ .

**Reason:**

Weak acids or bases/alkalis are only **slightly ionized** in dilute aqueous solutions. Thus, part of heat to be evolved is used to first ionize the molecules of the weak acids or bases (into the respective ions) before neutralisation reaction takes place. The heat of ionization affects the total heat change.

- Consider the following sets/pairs of acids and alkalis:

<b>Pair A</b>	200 cm <sup>3</sup> of 2 M KOH and 200 cm <sup>3</sup> of 2M HCl
<b>Pair B</b>	200 cm <sup>3</sup> of 2 M NaOH and 200 cm <sup>3</sup> of 1M H <sub>2</sub> SO <sub>4</sub>
<b>Pair C</b>	200 cm <sup>3</sup> of 2 M NH <sub>4</sub> OH and 200 cm <sup>3</sup> of 2M CH <sub>3</sub> COOH
<b>Pair D</b>	200 cm <sup>3</sup> of 2 M NaOH and 200 cm <sup>3</sup> of 2M CH <sub>3</sub> COOH

From the above pairs/sets, we can conclude that:

- Pairs A and B will register the highest temperature rise (since both the acid and base are strong and are fully ionized in a dilute aqueous solution) followed by pair D (since only the acid is weak and is only slightly ionized in dilute aqueous solution).
- Pair C will register the least/lowest temperature rise. This is because both the acid and the base are weak and are only slightly/partially ionized in dilute aqueous solution. Thus, a lot of heat is required to first ionize each of them before neutralisation reaction occurs.

**An experiment to determine the heat of neutralisation of hydrochloric acid by sodium hydroxide solution in a laboratory.**

**Experimental procedure are:**

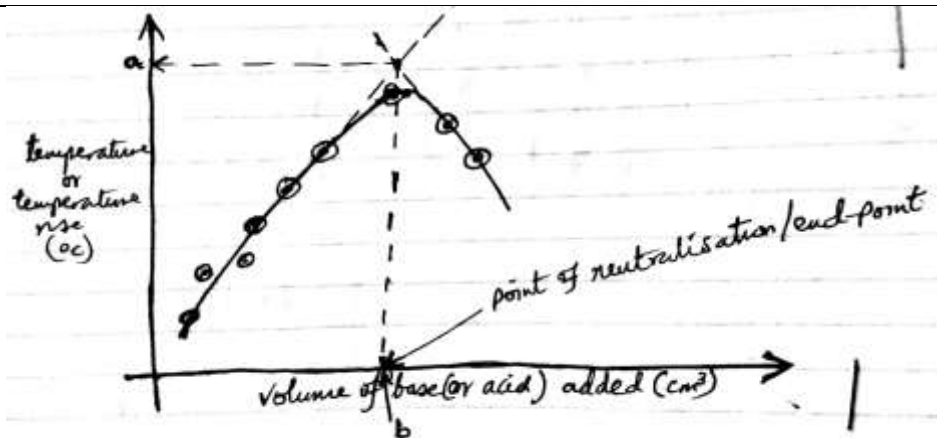
- A known volume ( $v \text{ cm}^3$ ) of hydrochloric acid solution of known molarity ( $a \text{ mol dm}^{-3}$ ) is placed in a plastic cup/beaker/bottle and its initial temperature ( $t_1^\circ\text{C}$ ) noted and recorded.
- The thermometer is washed with distilled water and dried.
- An equal volume ( $v \text{ cm}^3$ ) of sodium hydroxide solution of the same molarity is measured into another clean plastic beaker and its initial temperature ( $t_2^\circ\text{C}$ ) noted and recorded.
- The sodium hydroxide solution is at once quickly poured into the measured acid solution in a plastic beaker.
- The mixture is gently stirred well using a thermometer and its highest/maximum steady temperature ( $t_3^\circ\text{C}$ ) is noted and recorded.

### Treatment of results

- Total volume of solution formed =  $2v \text{ cm}^3 \therefore$  mass of water =  $2v \times 1 = 2v \text{ g}$
- Assuming the solution formed is **dilute**;  
density of solution formed = density of water =  $1 \text{ g cm}^{-3}$   
specific heat capacity of solution formed = specific heat capacity of water =  $4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$
- Average initial temperature =  $\left(\frac{t_1+t_2}{2}\right)^\circ\text{C}$
- Temperature rise/change for the solution,  $\Delta t = \left[t_3 - \left(\frac{t_1+t_2}{2}\right)\right]^\circ\text{C}$
- Assuming no heat losses to the surroundings and the can has a negligible heat capacity;  
Heat evolved = heat gained by water.  
Heat evolved,  $\Delta H = \left(\text{mass of solution}\right) \times \left(\text{S.H.C of solution}\right) \times \left(\text{temp rise}\right)$   
 $= 2v \times 4.2 \times \Delta t = (8.2v\Delta t) \text{ J}$
- No of moles of acid used = No of moles of base used =  $\frac{av}{1000}$
- The equation for the reaction is  $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$   
1 mole of acid reacts with 1 mole of base to form 1 mole of water  
Thus, moles of water formed =  $\frac{av}{1000}$   
 $\therefore \frac{av}{1000}$  moles water formed causes evolution of  $\Delta H \text{ J}$  of heat  
1 mole of water formed causes evolution of  $\left(\frac{\Delta t}{\frac{av}{1000}}\right) \text{ J}$  of heat
- Thus, heat of neutralisation =  $-\left(\frac{\Delta t}{\frac{av}{1000}}\right) \text{ J mol}^{-1}$  or  $-\left(\frac{\Delta t}{av}\right) \text{ kJ mol}^{-1}$

#### Note:

- (i) The experimental values of heats of neutralisation are usually lower than the expected/theoretical values. This is because heat is lost to the surroundings.
- (ii) A plastic cup/beaker/bottle is preferred to a glass (or metallic) cup/beaker/beaker because a plastic is a bad conductor of heat.
- (iii) For more accurate results, the acid and the base (alkali) solutions should be mixed in a vacuum flask or a plastic cup (or beaker) lagged with a cotton wool (or tissue). The cotton wool or tissue helps to minimize heat loss to the surroundings.
- (iv) Better experimental results can also be obtained:
  - (a) either when the temperatures of the well stirred mixture are read off and recorded at regular time intervals.
  - (b) or when fixed amounts of base (or acid) solution are added to a fixed amount of acid (or base) solution in a plastic (or polythene) beaker surrounded by lagging. The mixture is carefully well stirred after each additions using a thermometer. The temperatures of the well stirred mixture are noted and recorded.
- (v) In both cases in (vi), a graph of temperature of the resultant solution (or temperature rise/change) **against** volumes of acid (base) solution added is plotted.  
The general shape of the expected graph is as follows:



- ✓ **a** is the highest temperature (or the highest temperature rise/change) attained by the solution.
- ✓ **b** is the volume of acid (or base) solution required at end-point (or required for neutralisation to be complete).
- ✓ At end-point (point of neutralisation), the highest temperature (or temperature rise) is reached.
- ✓ After the neutralisation reaction is complete or end-point is reached, **no more rise in temperature** occurs because there is **no reaction taking place**. This is because all the acid (or base) in the **beaker** is used up by the base (or acid) being added. The temperature of the mixture remains constant or reduces.

### Specimen Results:

Volume of 2 M hydrochloric acid solution	= 20.0 cm <sup>3</sup>
Volume of 2 M sodium hydroxide solution	= 20.0 cm <sup>3</sup>
Initial temperature of sodium hydroxide solution	= 15.0°C
Initial temperature of hydrochloric acid solution	= 15.4°C
Final/maximum temperature of the mixture	= 28.2°C

### Questions:

- (a) Write an ionic equation for the reaction that took place.
- (b) Determine the heat of neutralisation. (density of water = 1 gcm<sup>-3</sup> and S.H.C of water = 4.2 Jg<sup>-1</sup>°C<sup>-1</sup>)
- (c) State whether the value obtained in (b) is equal to, less than or above 57.3 kJ mol<sup>-1</sup>.
- (d) Explain your answer in (c).

### Trial Questions

1. The heats of neutralisation for some pairs of acids and bases (alkalis) are given in the table below.

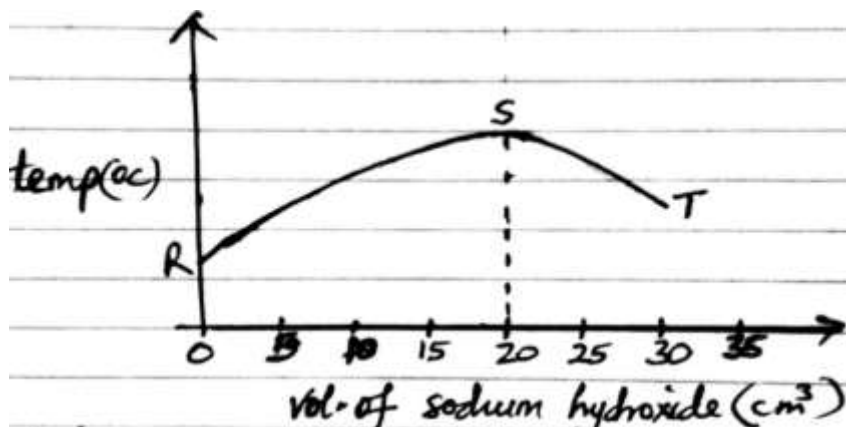
Pair	Reactants	Heat of neutralisation ( $\text{kJ mol}^{-1}$ )
I	NaOH(aq) and HCl(aq)	-57.3
II	NaOH (aq) and $\text{CH}_3\text{COOH}$ (aq)	-55.0
III	KOH(aq) and $\text{HNO}_3$ (aq)	-57.3
IV	$\text{NH}_4\text{OH}$ (aq) and HCl(aq)	-51.5

- (a) Briefly explain why:
- the values of heats of neutralisation are negative.
  - the heats of neutralisation in pairs I and III are high and the same.
  - the heats of neutralisation in pairs II and IV are lower than the expected value of about  $-57.3 \text{ kJ mol}^{-1}$ .
- (b) When hydrogen chloride gas is bubbled into water in a plastic cup, an appreciable rise in temperature occurred whereas bubbling the same amount of the gas into the same volume of trichloromethane in a plastic cup caused no apparent change in temperature. Explain this observation.
2. (a)  $50 \text{ cm}^3$  of 2 M nitric acid at  $21^\circ\text{C}$  and the same volume of 2 M sodium hydroxide at  $23^\circ\text{C}$  were mixed in a plastic cup. The mixture was stirred and its maximum temperature recorded as  $35^\circ\text{C}$ . Calculate the heat change for the reaction and hence, work out the molar heat of neutralisation of the acid. (density of water =  $1 \text{ g cm}^{-3}$  and S.H.C of water =  $4.2 \text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$ )
- (b) In another experiment,  $50 \text{ cm}^3$  of 2 M ammonia solution was used in place of sodium hydroxide solution.
- State whether the molar heat of neutralisation value was less than, equal to or greater than the value obtained in (a).
  - Explain your answer in (b)(i).
3. The table below shows the calculated values of heats evolved when  $100 \text{ cm}^3$  of aqueous solution containing 8.0 g of sodium hydroxide was added to various volumes of aqueous nitric acid solution.

Volume of acid used ( $\text{cm}^3$ )	60	80	90	100	120	140
Heat evolved (kJ)	6.6	8.9	9.9	11.0	11.1	10.9

- (a) Define the term **heat (enthalpy) of neutralisation**.
- (b) Write an ionic equation for the reaction that took place.
- (c) Determine the molarity of sodium hydroxide solution. (Na=23; O=16; H=1)
- (d) Plot a graph of heat evolved (vertical axis) against the volume of acid used (horizontal axis).
- (e) Use your graph to obtain the heat evolved when:
- $70 \text{ cm}^3$  of the acid is used.
  - $110 \text{ cm}^3$  of the acid is used
4. When  $50.0 \text{ cm}^3$  of 0.5 M hydrochloric acid was added to  $50.0 \text{ cm}^3$  of potassium hydroxide in a calorimeter, there was a temperature rise from  $27.5^\circ\text{C}$  to  $30.8^\circ\text{C}$ . Calculate the enthalpy change for the reaction. (density of water =  $1 \text{ g cm}^{-3}$  and S.H.C of water =  $4.2 \text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$ )
5. When  $50.0 \text{ cm}^3$  of 1.0 M sulphuric acid was added to  $50.0 \text{ cm}^3$  of 2.0 M sodium hydroxide in a plastic cup, the temperature of the mixture rose by  $13.6^\circ\text{C}$ .

- (a) Write an ionic equation for the reaction that occurred.
- (b) Calculate the enthalpy of neutralisation of sodium hydroxide. (density of water =  $1 \text{ g cm}^{-3}$  and S.H.C of water =  $4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ )
6. When  $20.0 \text{ cm}^3$  of  $2.0 \text{ M}$  hydrochloric acid was added to  $20.0 \text{ cm}^3$  of  $2.0 \text{ M}$  sodium hydroxide in a calorimeter, the temperature of the mixture rose by  $\theta^{\circ}\text{C}$ . If the heat of neutralisation of the reaction is  $-54.6 \text{ kJ mol}^{-1}$ , determine the value of  $\theta$ . (density of water =  $1 \text{ g cm}^{-3}$  and S.H.C of water =  $4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ )
7. When  $2.4 \text{ g}$  of magnesium was reacted with  $200 \text{ cm}^3$  of  $2.0 \text{ M}$  hydrochloric acid,  $13.6 \text{ kJ}$  of heat was evolved. Calculate the molar heat of reaction of magnesium with the acid. ( $\text{Mg}=24$ )
8. (a) The graph below shows the change in temperature when  $0.49 \text{ M}$  sodium hydroxide solution was added to  $20 \text{ cm}^3$  of a monobasic acid.



- (i) What does point S represent?
- (ii) Determine the:
- volume of sodium hydroxide required to neutralize the acid.
  - molarity of the hydrochloric acid.
- (iii) State why there is temperature rise from R to S.
- (b) The experiment was repeated using  $0.5 \text{ M}$  ammonia solution instead of  $0.5 \text{ M}$  sodium hydroxide solution. State whether the maximum temperature was greater than, less than or equal to that in (a). Give a reason for your answer.
9. In an experiment,  $25 \text{ cm}^3$  of  $1.0 \text{ M}$  sodium hydroxide solution was pipetted into a plastic beaker wrapped with a tissue. To the alkali in the beaker was added  $1.0 \text{ M}$  sulphuric acid at regular intervals of  $5.0 \text{ cm}^3$ . After each addition of the acid, the mixture was stirred using a thermometer and the maximum temperature of mixture noted and recorded.

The table below gives the results of the experiment.

Volume of acid added ( $\text{cm}^3$ )	5.0	10.0	15.0	20.0	25.0
Maximum temperature of mixture ( $^{\circ}\text{C}$ )	28.0	31.0	30.5	29.0	28.0
Temperature rise ( $^{\circ}\text{C}$ )					

- (a) Write equation for the reaction that took place.
- (b) Given that both the acid solution and alkali solution were kept at  $23.0^{\circ}\text{C}$ , determine the temperature rise after each addition of the acid, copy the table and enter your answers in the spaces provided in the table.



- (c) Plot a graph of temperature rise (vertical axis) against volume of acid added (horizontal axis).
- (d) Determine from graph:
- the maximum volume of acid required to completely react with the alkali.
  - the temperature at end-point.
- (e) Work out the enthalpy of neutralisation of sodium hydroxide. State any necessary assumptions made. (density of water =  $1 \text{ g cm}^{-3}$  and S.H.C of water =  $4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ )
- (f) Give a reason for each of the following in the experiment.
- Use of a plastic cup.
  - Wrapping the plastic beaker using tissue.

10. In an experiment to compare the enthalpies of neutralization of alkali **W** and alkali **Z** with hydrochloric acid,  $20 \text{ cm}^3$  of each alkali solution was pipetted into separate plastic beakers. To each alkali in the beaker was added hydrochloric acid at regular intervals of  $5.0 \text{ cm}^3$ . After each addition of the acid, the mixture was stirred using a thermometer and the maximum temperature of mixture noted and recorded.

The table below gives the results of the experiment.

Volume of acid added ( $\text{cm}^3$ )		0.0	5.0	10.0	15.0	20.0	25.0	30.0
Maximum temperature attained by mixture ( $^{\circ}\text{C}$ )	Mixture of <b>W</b> and acid	27.0	32.0	34.5	37.0	38.0	37.0	36.0
	Mixture of <b>Z</b> and acid	26.5	30.5	33.0	34.0	33.0	32.0	31.0

- (a) Plot on the same axes, graphs of maximum temperature attained by mixture (vertical axis) against volume of acid added (horizontal axis).
- (b) Using the graphs you have plotted, determine the highest temperature for the reaction between hydrochloric acid and
- W**
  - Z**
- (c) Determine the maximum temperature change for each of the reactions.
- (d) Which one of the alkalis **W** and **Z** has a higher enthalpy of neutralization with hydrochloric acid?
- (e) Give a reason for your answer in (d).

## FUELS

- ❖ Fuels are substances that burn in oxygen to produce heat.
- ❖ Most fuels contain carbon and hydrogen, and they include:
  - Solid fuels; coal, wood, coke, peat, charcoal etc.
  - Liquid fuels; petrol, ethanol, paraffin, diesel, oil, etc.
  - Gaseous fuels; coal gas, water gas, producer gas, natural gas, biogas etc.
- ❖ Under perfect conditions and in excess supply of air (oxygen), the fuels undergo **complete combustion** to form **carbon dioxide** and **water**. Heat and light are also given out.
- ❖ In limited supply of oxygen (air), incomplete combustion occurs and the common products are; carbon monoxide, water and soot (unburnt carbon).
- ❖ **Definition:**

The **energy content of a fuel** is the heat evolved when one kilogram of a solid or liquid fuel or one cubic metre of a gaseous fuel is completely burnt in oxygen.
- ❖ A perfect fuel should:
  - be cheap
  - be easily handled and transported
  - not pollute the environment
  - be easily stored
  - be readily available
  - burn easily, producing large amount heat (i.e. should have a high **heating value**)
- ❖ **Definition:**

**Heating value** of a fuel is the amount of energy per gram of a fuel (or number of kilojoules of energy given out for every gram of fuel burnt).

Heating value of a fuel =  $\frac{\text{heat of combustion}}{\text{molar mass}}$
- ❖ Biogas mainly contains methane and is obtained from waste products like bean pods, cow dung, and marshy vegetable materials.

### Trial Question

The table below shows some heats of combustion of organic fuels. Complete the table below:

Fuel	Heat of combustion (kJ mol <sup>-1</sup> )	Molar mass	Heating value
CH <sub>4</sub>	-890		
C <sub>2</sub> H <sub>6</sub>	-1560		
C <sub>4</sub> H <sub>10</sub>	-2877		
CH <sub>3</sub> CH <sub>2</sub> OH	-1367		
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	-2020		
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	-2680		