



# SL IB Chemistry



Your notes

## Measuring Enthalpy Change

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- \* Difference Between Heat & Temperature
- \* Exothermic & Endothermic Reactions
- \* Energy Profiles
- \* Standard Enthalpy Change
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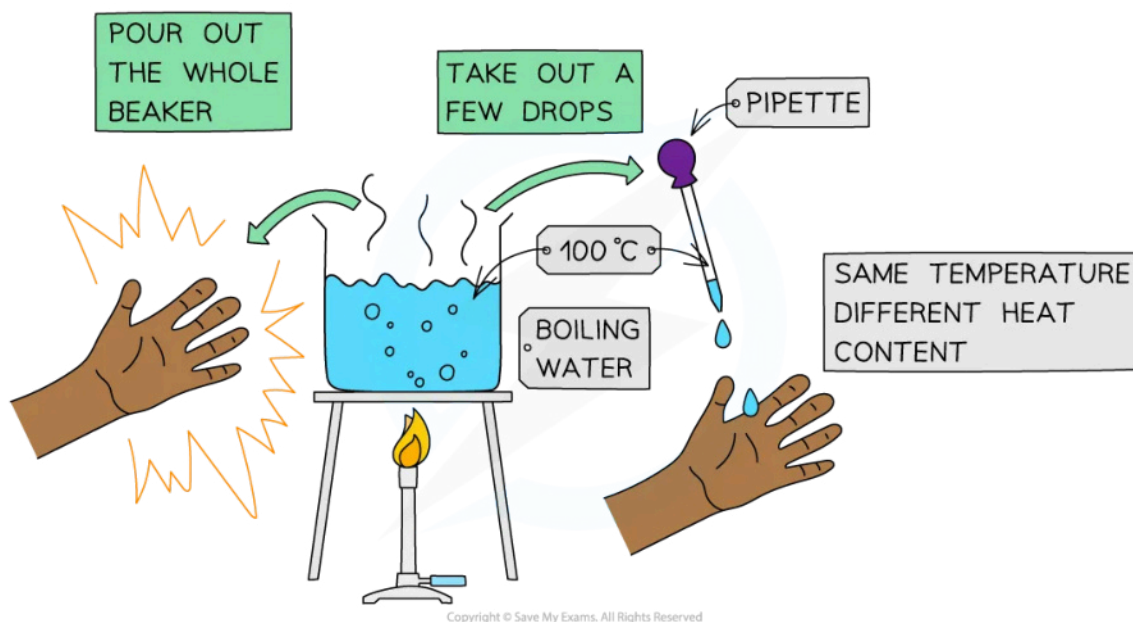
## Difference Between Heat & Temperature

### Difference between heat and temperature

#### What is the difference between heat and temperature?

- This can be illustrated using a beaker of boiling water and a pipette:

#### Diagram to demonstrate the difference between heat and temperature



*The effects of boiling water can be quite different depending on the quantity of water involved!*

- You would get a very nasty burn if a whole beaker of boiling water spilled onto to your hand, but a drop of boiling water would cause little problem
- The water is at the **same temperature** in the pipette as in the beaker, but the beaker has a much **higher heat content**
- We say that temperature is a measure of the **average kinetic energy** of the particles whereas heat is a measure of the **energy content** of a substance
- The particles have **kinetic energy** because they are moving
  - The **faster** they move the **more energy** they have and the higher the temperature of the substance

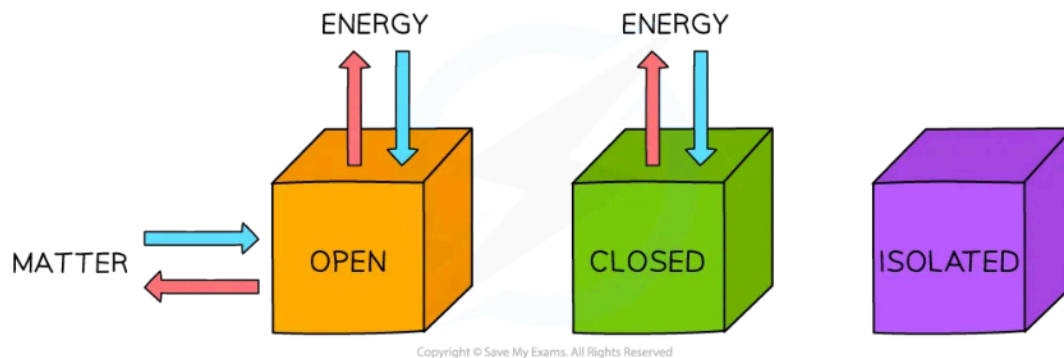
### Conservation of energy

- Energy** is a measure of the ability to do **work**
- There are many different types of **energy** and **heat** is only one of them

- During chemical reactions **energy** flows in and out of the reaction vessels
  - Inside the reaction vessel is known as the **system**
  - Outside the reaction vessel is known as the **surroundings**

Systems come in three types: **open, closed** and **isolated**

### Diagram to show energy and matter transfer in three types of system



**Open systems are the most common for chemical reactions**

- Most chemical reactions take place in open systems in which energy and matter can be exchanged with the surroundings
- In a closed system, energy can be exchanged with the surroundings but matter cannot
- Although energy can be exchanged between open and closed systems and the surroundings, the total energy of the process cannot change
- This is known as the **Law of Conservation of Energy** and is a cornerstone to understanding how chemical changes affect the energy flow in and out of systems
- An isolated system cannot exchange matter or energy with the surrounding and are rare



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## Exothermic & Endothermic Reactions

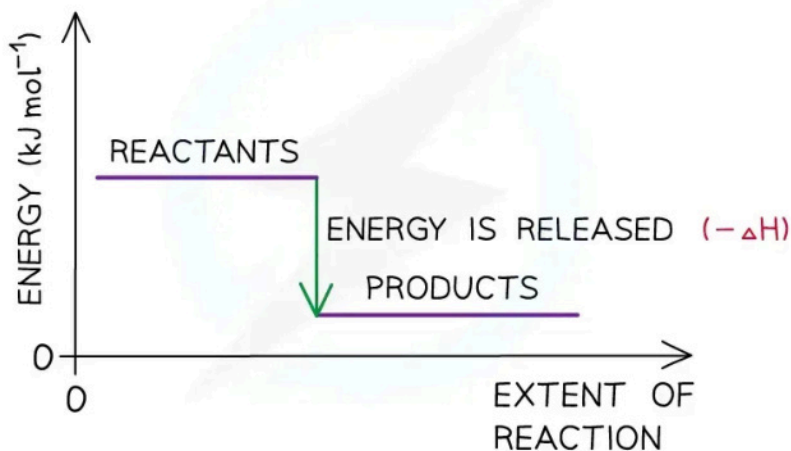
### Exothermic & Endothermic Reactions

- The total chemical energy inside a substance is called the **enthalpy** (or heat content)
- When chemical reactions take place, changes in chemical energy take place and therefore the **enthalpy** changes
- An **enthalpy** change is represented by the symbol  $\Delta H$  ( $\Delta$  = change;  $H$  = enthalpy)
- An **enthalpy change** can be positive or negative

### Exothermic reactions

- A reaction is **exothermic** when the products have less **enthalpy** than the reactants
- Heat energy is given off **by** the system **to** the surroundings
  - The **temperature** of the **surroundings increases**
  - The **temperature** of the **system decreases**
- There is an **enthalpy** decrease during the reaction so  $\Delta H$  is **negative**
- **Exothermic** reactions are **thermodynamically** possible (because the enthalpy of the reactants is higher than that of the products)
- However, if the rate is too slow, the reaction may not occur.
  - In this case the reaction is **kinetically** controlled

#### Energy level diagram for an exothermic reaction



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*The enthalpy change during an exothermic reaction is negative*

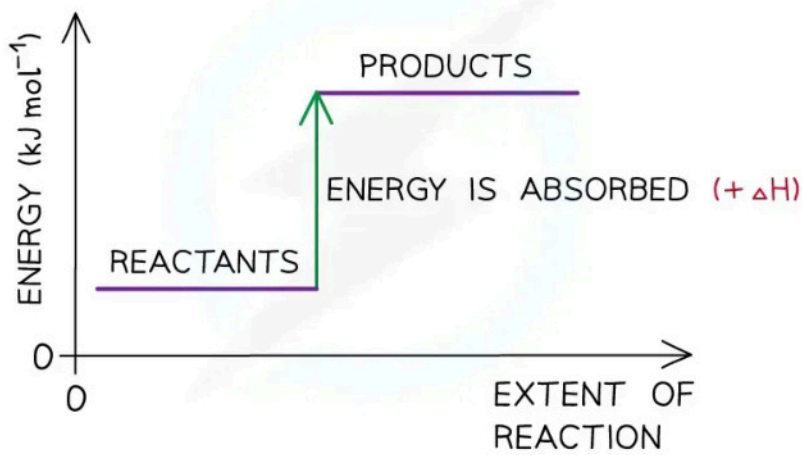


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## Endothermic reactions

- A reaction is **endothermic** when the products have more **enthalpy** than the reactants
- Heat energy is absorbed **by** the system **from** the **surroundings**
  - The **temperature** of the **surroundings** **decreases**
  - The **temperature** of the **system** **increases**
- There is an **enthalpy** increase during the reaction so  $\Delta H$  is **positive**

### Energy level diagram for an endothermic reaction



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*The enthalpy change during an endothermic reaction is positive*

#### Examiner Tip

Remember that the **system** is the **substances** that are reacting (ie. the reaction itself) and the **surroundings** is everything else (eg. the flask the reaction is taking place in).



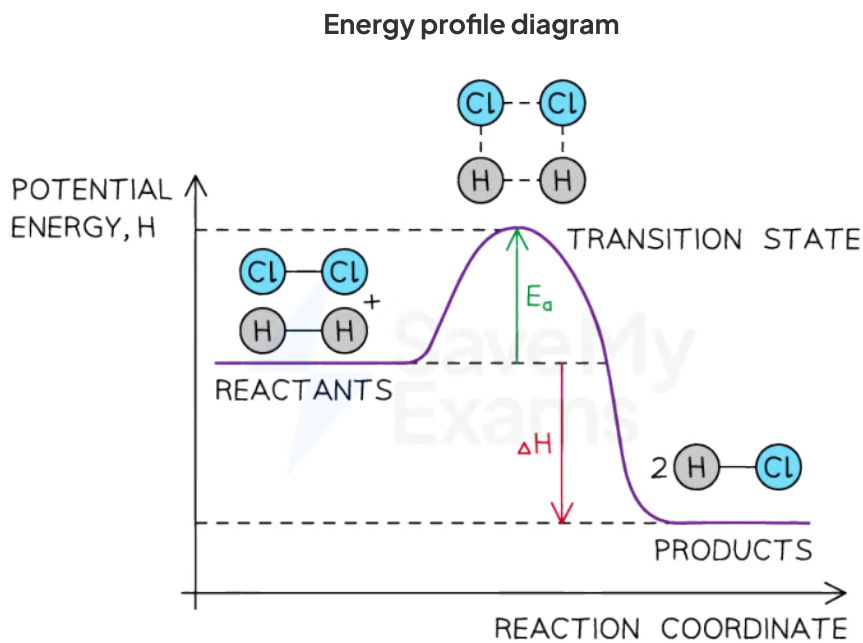
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## Energy Profiles

### Energy Profiles

- An energy profile shows the energies of the reactants, the **transition state(s)** and the products of the reaction with time
  - The **transition state** is a stage during the reaction at which chemical bonds are partially broken and formed
  - The **transition state** is very unstable – it cannot be isolated and is higher in energy than the reactants and products
- The **activation energy ( $E_a$ )** is the energy needed to reach the **transition state**
- We can define the **activation energy** as

*'the minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction'*



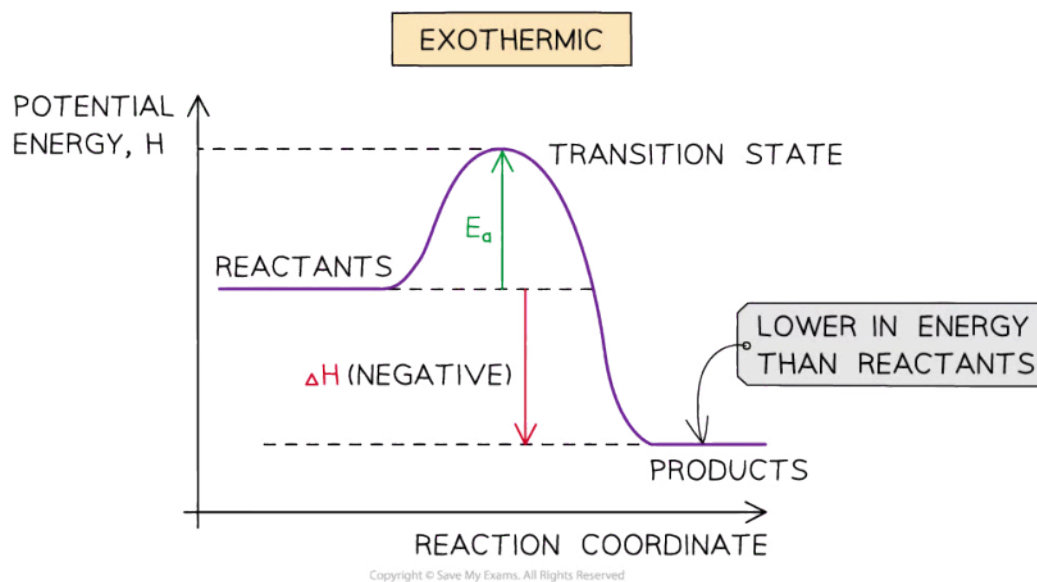
*The energy profile for the reaction of hydrogen with chlorine to form hydrogen chloride gas*

### Exothermic reaction

- In an **exothermic** reaction, the reactants are higher in energy than the products
- The reactants are therefore closer in energy to the **transition state**

- This means that **exothermic** reactions have a lower **activation energy** compared to **endothermic** reactions

### Diagram to show an energy profile for an exothermic reaction



*The potential energy of the products is lower than the reactants*

### Endothermic reaction

- In an **endothermic** reaction, the reactants are lower in energy than the products
- The reactants are therefore further away in energy to the **transition state**
- This means that **endothermic** reactions have a higher **activation energy** compared to **exothermic** reactions

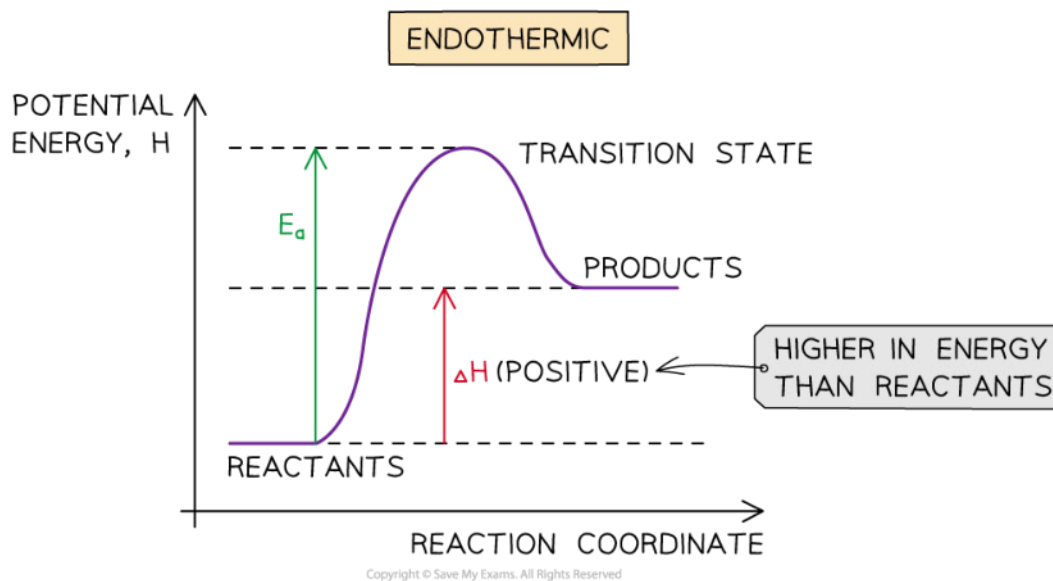
### Diagram to show an energy profile for an endothermic reaction



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*The potential energy of the products is lower than the reactants*



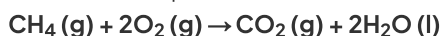
### Worked example

The enthalpy of combustion for methane is  $-890 \text{ kJ mol}^{-1}$  and the activation energy is  $+2653 \text{ kJ mol}^{-1}$ .

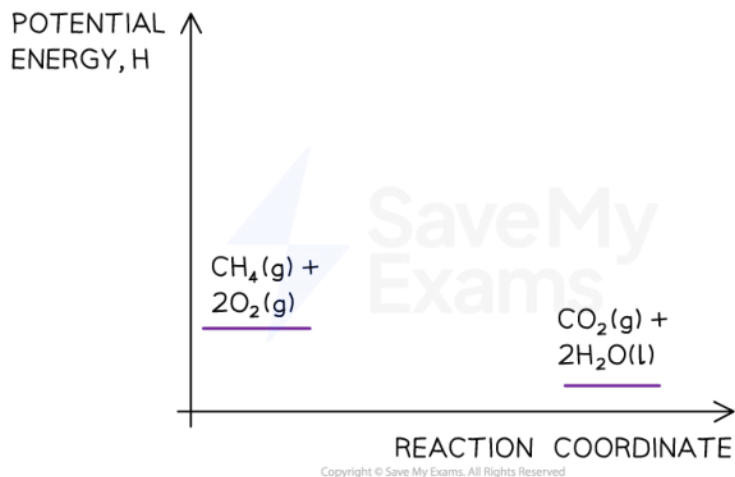
Draw a labelled energy level diagram for this reaction.

Answer:

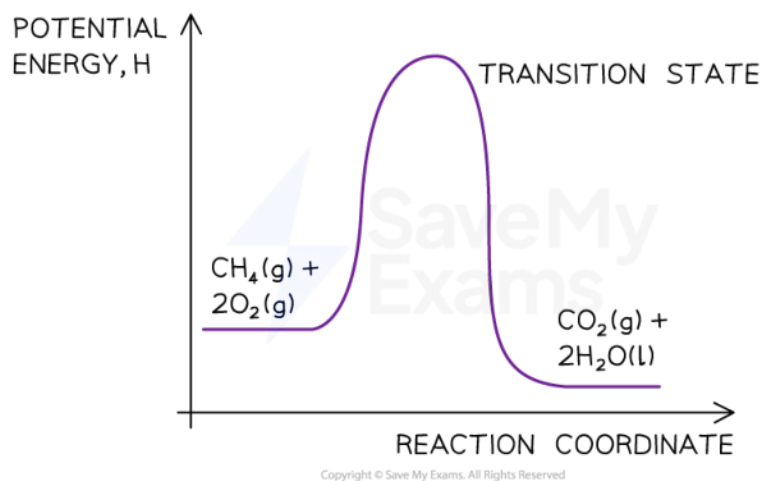
- Step 1: The chemical equation for the complete combustion of methane is:



- Step 2: Combustion reactions are always exothermic ( $\Delta H$  is negative) so the reactants should be drawn higher in energy than the products



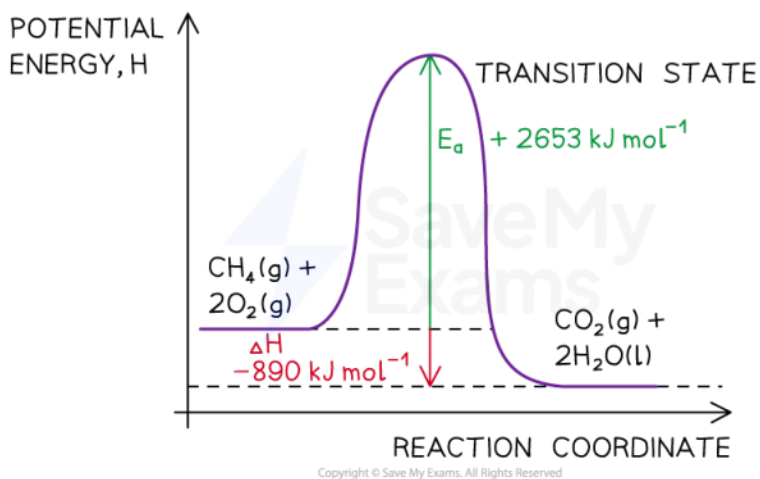
- Step 3: Draw the curve in the energy level diagram clearly showing the transition state



- Step 4: Draw arrows to show the  $E_a$  and  $\Delta H$  including their values

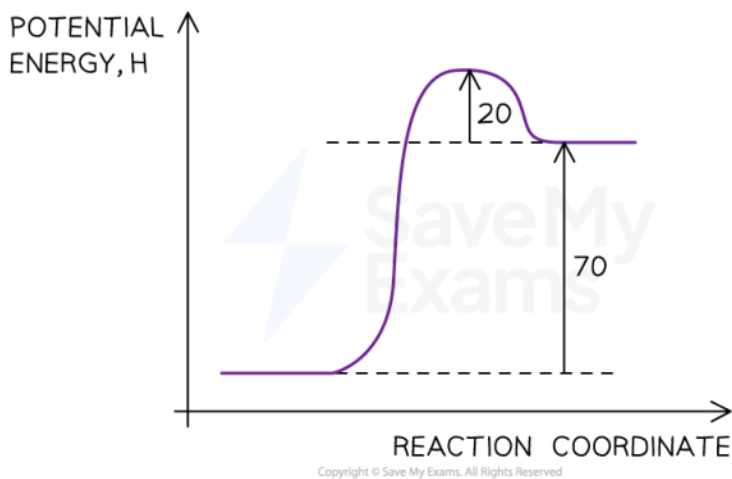


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 **Worked example**

Use the energy level diagram below to identify the activation energy,  $E_a$ , for the reaction.



*The reaction pathway diagram for a reversible reaction*

**Answer:**

- The  $E_a$  is the energy difference from the energy level of the reactants to the top of the 'hump'
- $E_a$  (forward reaction) =  $(+70 \text{ kJ mol}^{-1}) + (+20 \text{ kJ mol}^{-1}) = +90 \text{ kJ mol}^{-1}$

### Examiner Tip

The activation energy is the energy difference from **reactants** to **transition state**. The enthalpy change of the reaction is the energy difference from **reactants** to **products**. Remember to label the axis of the energy level diagrams!



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## Standard Enthalpy Change

### Standard Enthalpy Change

- The standard enthalpy change for a chemical reaction,  $\Delta H^{\ominus}$ , refers to the heat transferred at **constant pressure** under **standard conditions** and **states**
- These **standard conditions** are:
  - A **pressure** of 100 kPa
  - A **concentration** of  $1 \text{ mol dm}^{-3}$  for all solutions
  - Each substance involved in the reaction is in its **standard state** (solid, gas or liquid)
- Temperature is not part of the definition of **standard state**, but a temperature of **298 K** ( $25^{\circ}\text{C}$ ) is usually given as the specified temperature
- To show that a reaction has been carried out under standard conditions, the symbol  $\ominus$  is used
  - Eg.  $\Delta H^{\ominus}$  = the standard enthalpy change

### Standard Enthalpies

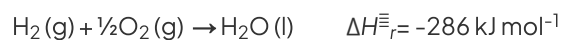
- There are a few **Standard Enthalpy** changes which are used commonly in energy calculations and they are summarised below:

Standard Enthalpy Change of ...	Definition	Symbol	Exothermic/ Endothermic
Reaction	The enthalpy change when the reactants in the <b>stoichiometric equation</b> react to give the products under standard conditions	$\Delta H^{\ominus}_r$	Both
Formation	The enthalpy change when <b>one mole</b> of a compound is formed from its <b>elements</b> under standard conditions	$\Delta H^{\ominus}_f$	Both
Combustion	The enthalpy change when <b>one mole</b> of a substance is <b>burnt</b> in excess oxygen under standard conditions	$\Delta H^{\ominus}_c$	Exothermic
Neutralisation	The enthalpy change when <b>one mole of water</b> is formed by reacting an acid and alkali under standard conditions	$\Delta H^{\ominus}_{neut}$	Exothermic

- Practice your understanding of enthalpy changes on the following worked examples:

### Worked example

One mole of water is formed from hydrogen and oxygen releasing 286 kJ



Calculate  $\Delta H_r$  for the reaction below:



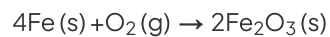
**Answer:**

- Since two moles of water molecules are formed in the question above, the energy released is simply:

$$\begin{aligned} \Delta H_r &= 2 \text{ mol} \times (-286 \text{ kJ mol}^{-1}) \\ &= -572 \text{ kJ} \end{aligned}$$

### Worked example

Calculate  $\Delta H_r$  for the reaction below



given that  $\Delta H_f^\ominus [\text{Fe}_2\text{O}_3(\text{s})] = -824 \text{ kJ mol}^{-1}$

**Answer:**

- Since two moles of  $\text{Fe}_2\text{O}_3(\text{s})$  are formed the total change in enthalpy for the reaction above is:

$$\begin{aligned} \Delta H_r &= 2 \text{ mol} \times (-824 \text{ kJ mol}^{-1}) \\ &= -1648 \text{ kJ} \end{aligned}$$



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### Worked example

Identify each of the following as  $\Delta H_r^\ominus$ ,  $\Delta H_f^\ominus$ ,  $\Delta H_c^\ominus$  or  $\Delta H_{neut}^\ominus$

1.  $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$
2.  $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
3.  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

**Answers:**

- **Answer 1:**  $\Delta H_r^\ominus$
- **Answer 2:**  $\Delta H_f^\ominus$  as one mole of  $\text{CO}_2$  is formed from its elements in standard state and  $\Delta H_c^\ominus$  as one mole of carbon is burnt in oxygen
- **Answer 3:**  $\Delta H_{neut}^\ominus$  as one mole of water is formed from the reaction of an acid and alkali

### Examiner Tip

You need to learn well the Standard Enthalpy change definitions as they are frequently tested in exam papers



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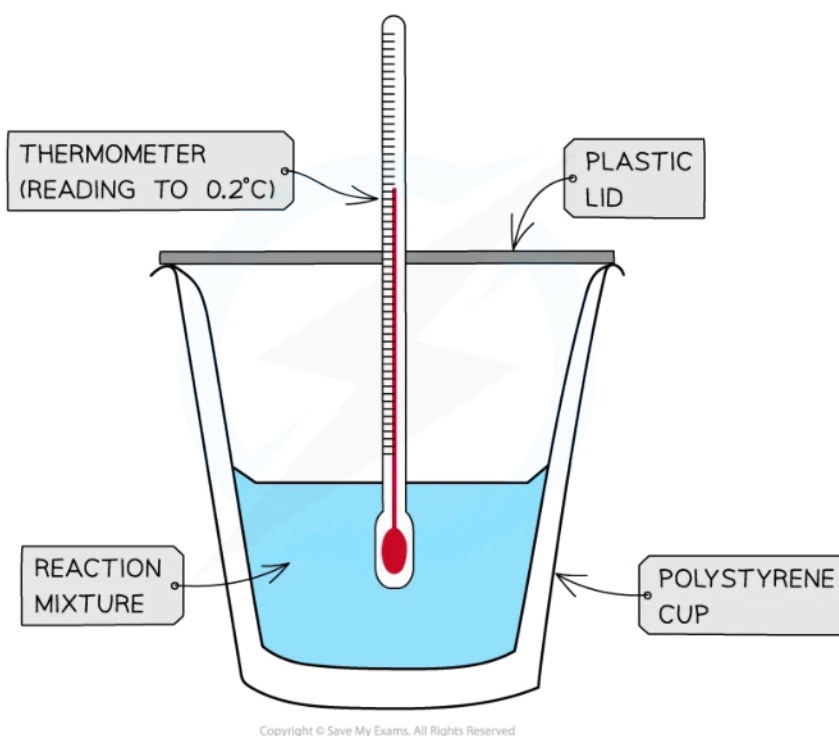
## Calorimetry Experiments

### Calorimetry Experiments

#### Measuring enthalpy changes

- **Calorimetry** is a technique used to measure changes in enthalpy of chemical reactions
- A **calorimeter** can be made up of a **polystyrene drinking cup**, a **vacuum flask** or **metal can**

Diagram to show how to set up a simple calorimeter



*A polystyrene cup can act as a calorimeter to find enthalpy changes in a chemical reaction*

- The energy needed to raise the temperature of 1 g of a substance by 1 K is called the **specific heat capacity** ( $c$ ) of the liquid
- The **specific heat capacity** of water is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$
- The energy transferred as heat can be calculated by:



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$$q = m \times c \times \Delta T$$

q = THE HEAT TRANSFERRED, J  
m = THE MASS OF WATER, g  
c = THE SPECIFIC HEAT CAPACITY,  $\text{J g}^{-1}\text{K}^{-1}$   
 $\Delta T$  = THE TEMPERATURE CHANGE, K

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*Equation for calculating energy transferred in a calorimeter*

### Worked example

The energy from 0.01 mol of propan-1-ol was used to heat up 250 g of water. The temperature of the water rose from 298K to 310K (the specific heat capacity of water is  $4.18 \text{ J g}^{-1}\text{K}^{-1}$ ). Calculate the enthalpy of combustion.

**Answer:**

- **Step 1:**  $q = m \times c \times \Delta T$   
 $m$  (of water) = 250 g  
 $c$  (of water) =  $4.18 \text{ J g}^{-1}\text{K}^{-1}$   
 $\Delta T$  (of water) =  $310 - 298 \text{ K}$   
 $= 12 \text{ K}$
- **Step 2:**  $q = 250 \times 4.18 \times 12$   
 $= 12\,540 \text{ J}$
- **Step 3:** This is the energy released by 0.01 mol of propan-1-ol  
Total energy  $\Delta H = q \div n = 12\,540 \text{ J} \div 0.01 \text{ mol} = 1\,254\,000 \text{ J mol}^{-1}$   
Total energy = - **1254 kJ mol<sup>-1</sup>**

### Examiner Tip

There's no need to convert the temperature units in calorimetry as the change in temperature in  $^{\circ}\text{C}$  is equal to the change in temperature in K

## Calorimetry experiments

- There are two types of calorimetry experiments you need to know for IB Chemistry:





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- Enthalpy changes of **reactions in solution**
- Enthalpy changes of **combustion**

- In both cases you should be able to give an outline of the experiment and be able to process experimental data using calculations or graphical methods

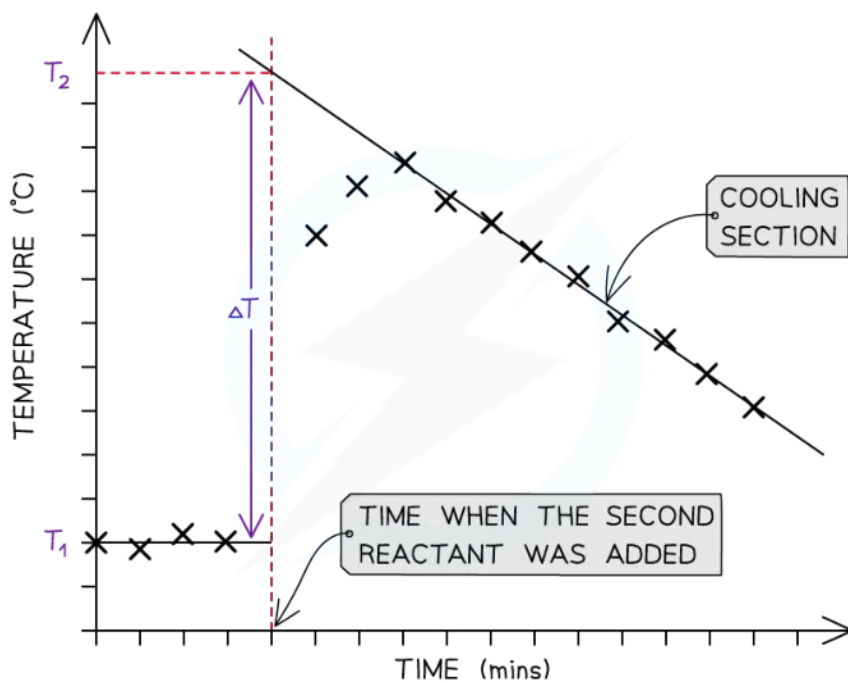
### Enthalpy changes for reactions in solution

- The principle of these calorimetry experiments is to carry out the reaction with an excess of one reagent and measure the temperature change over the course of a few minutes
- For the purposes of the calculations, some assumptions are made about the experiment:
  - That the specific heat capacity of the solution is the same as pure water, i.e.  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$
  - That the density of the solution is the same as pure water, i.e.  $1 \text{ g cm}^{-3}$
  - The specific heat capacity of the container is ignored
  - The reaction is complete
  - There are negligible heat losses

### Temperature correction graphs

- For reactions which are not instantaneous there may be a delay before the maximum temperature is reached
- During that delay the substances themselves may be losing heat to the surroundings, so that the true maximum temperature is never actually reached
- To overcome this problem we can use graphical analysis to determine the maximum enthalpy change

### A temperature correction graph for a metal displacement reaction between zinc and copper sulfate solution





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**The cooling section of the graph is extrapolated back to the time when the reaction started to allow for heat loss**

- The steps to make a temperature correction graph are:
  1. Take a temperature reading before adding the reactants for a few minutes to get a steady value
  2. Add the second reactant and continue recording the temperature and time
  3. Plot the graph and **extrapolate** the cooling part of the graph until you intersect the time at which the second reactant was added
- An assumption made here is that the rate of cooling is constant
- The analysis can also be used for endothermic reactions, but this time there will be a 'warming' section as the substances return to room temperature

### Worked example

Excess iron powder was added to 100.0 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> copper(II) sulfate solution in a calorimeter. The reaction equation was as follows



The maximum temperature rise was 7.5 °C. Determine the enthalpy of reaction, in kJ.

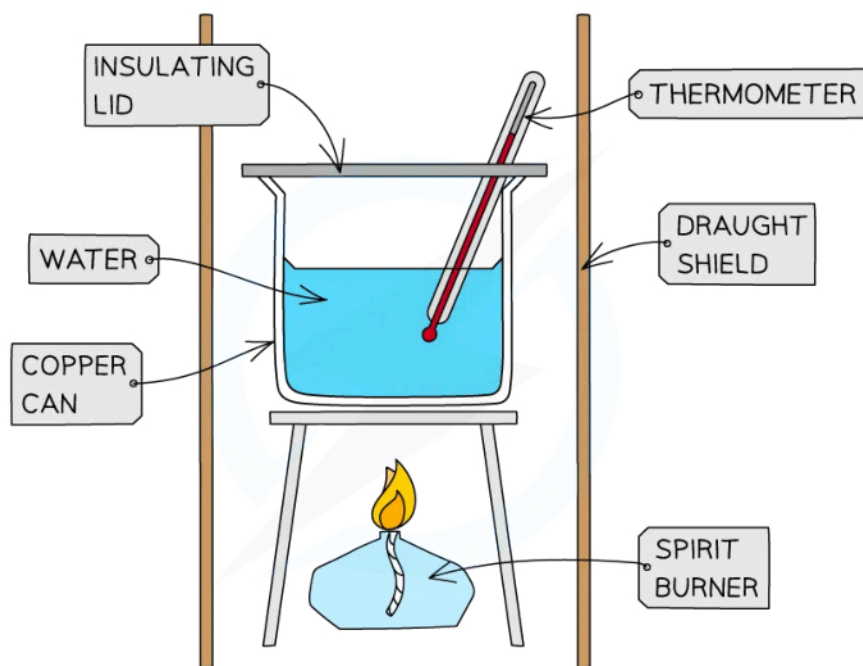
**Answer:**

- **Step 1:** Calculate  $q$   
 $q = m \times c \times \Delta T$   
 $q = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 7.5 \text{ K} = -3135 \text{ J}$
- **Step 2:** Calculate the amount of CuSO<sub>4</sub>(aq)  
 moles = volume in dm<sup>3</sup> x concentration = 0.1 x 0.2 = 0.02 mol
- **Step 3:** Calculate  $\Delta H$   
 $\Delta H = q \div n = -3135 \text{ J} \div 0.02 \text{ mol} = -156750 \text{ J} = -156.75 \text{ kJ}$   
 = **-160 kJ** (2 sig figs)

## Enthalpy of combustion experiments

- The principle here is to use the heat released by a combustion reaction to increase the heat content of water
- A typical simple calorimeter is used to measure the temperature changes to the water

**Diagram to show the set up of a typical calorimeter**



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- Not all the heat produced by the combustion reaction is transferred to the water
  - Some heat is lost to the surroundings
  - Some heat is absorbed by the calorimeter
- To minimise the heat losses the copper calorimeter should not be placed too far above the flame and a lid placed over the calorimeter
- Shielding can be used to reduce draughts
- In this experiment the main sources of error are
  - **Heat losses**
  - **Incomplete combustion**



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### Worked example

1.023 g of propan-1-ol ( $M = 60.11 \text{ g mol}^{-1}$ ) was burned in a spirit burner and used to heat 200 g of water in a copper calorimeter. The temperature of the water rose by  $30 \text{ }^{\circ}\text{C}$ . Calculate the enthalpy of combustion of propan-1-ol using this data.

#### Answer:

- **Step 1:** Calculate  $q$

$$q = m \times c \times \Delta T$$

$$q = 200 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 30 \text{ K} = -25\,080 \text{ J}$$

- **Step 2:** Calculate the amount of propan-1-ol burned  
moles = mass  $\div$  molar mass =  $1.023 \text{ g} \div 60.11 \text{ g mol}^{-1} = 0.01702 \text{ mol}$

- **Step 3:** Calculate  $\Delta H$

$$\Delta H = q \div n = -25\,080 \text{ J} \div 0.01702 \text{ mol} = -1\,473\,560 \text{ J} = -1\,474 \text{ kJ}$$

$$= -1.5 \times 10^3 \text{ kJ}$$