



SL IB Chemistry



Your notes

Measuring Enthalpy Change

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- * Exothermic & Endothermic Reactions
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Your notes

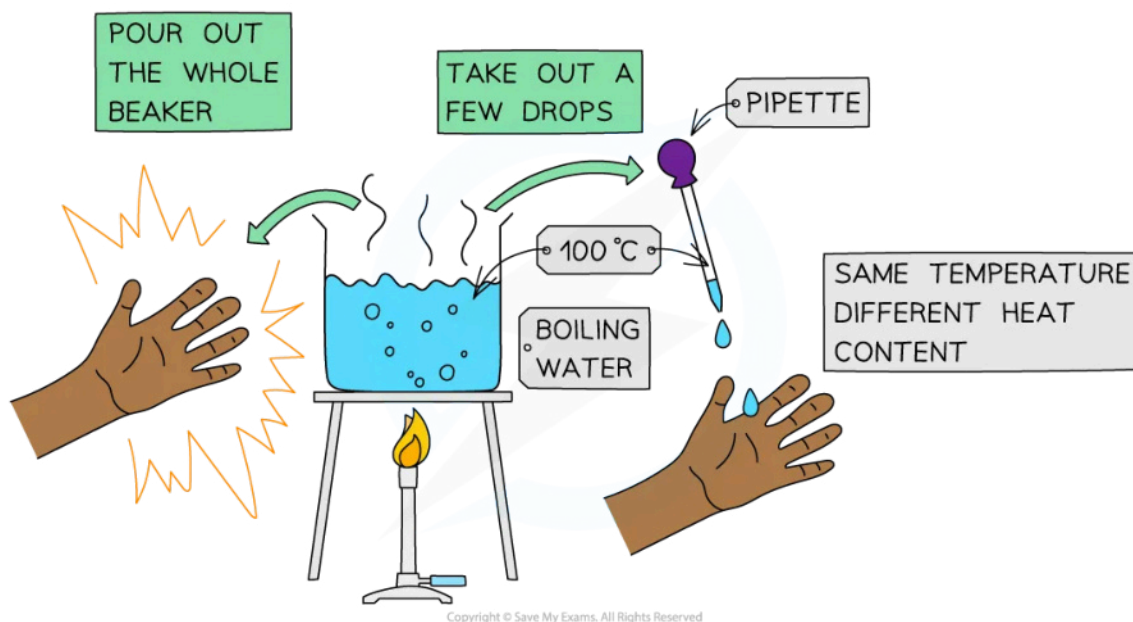
Difference Between Heat & Temperature

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

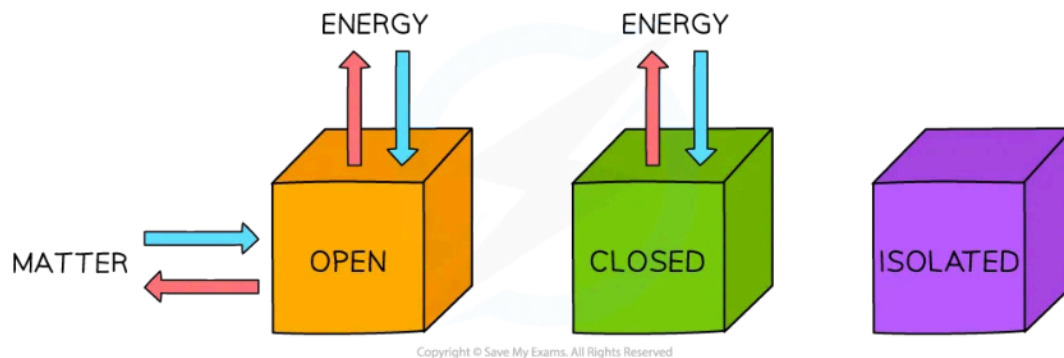
Conservation of energy

- 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

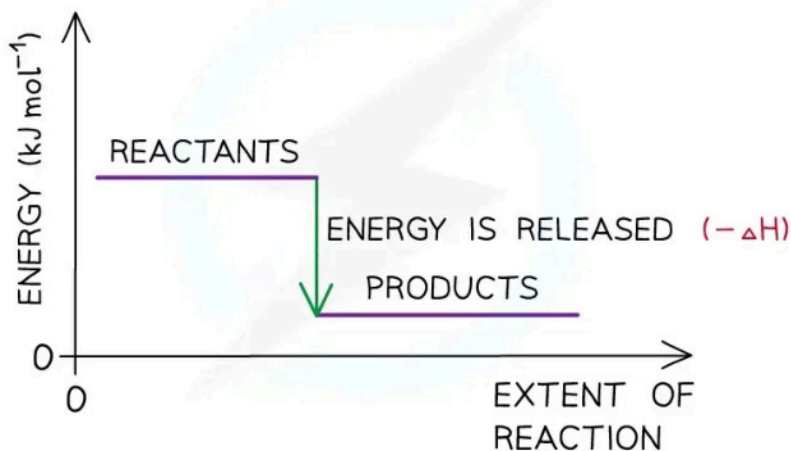
Exothermic & Endothermic Reactions

- 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 ΔH (Δ = 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 ΔH 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

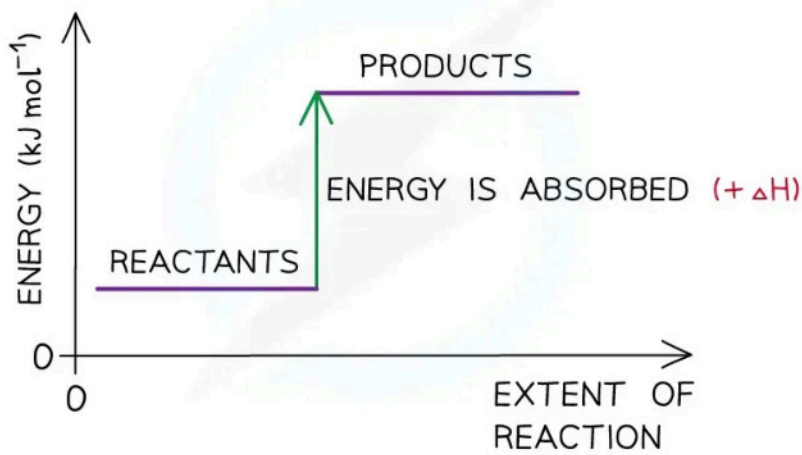


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Endothermic reactions

- 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 ΔH 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).



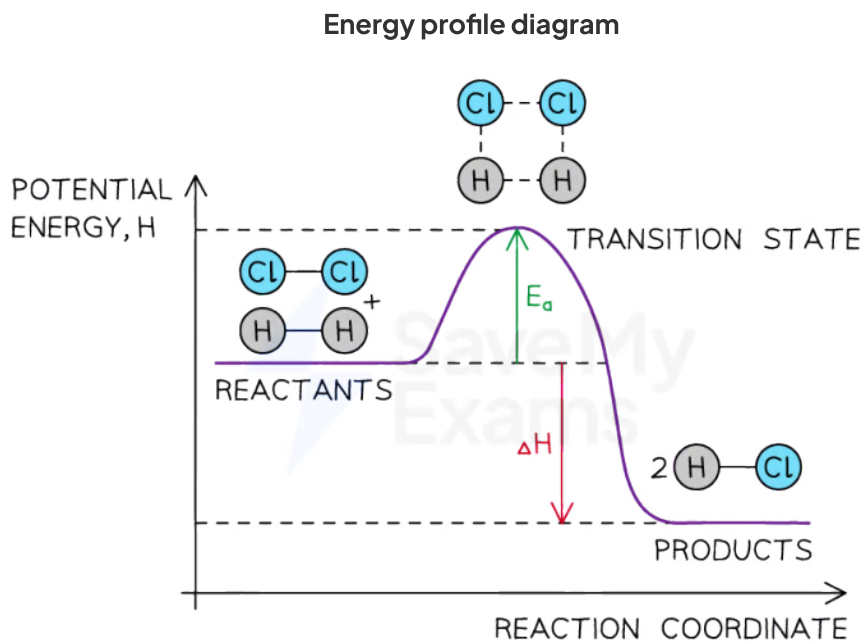
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Energy Profiles

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'



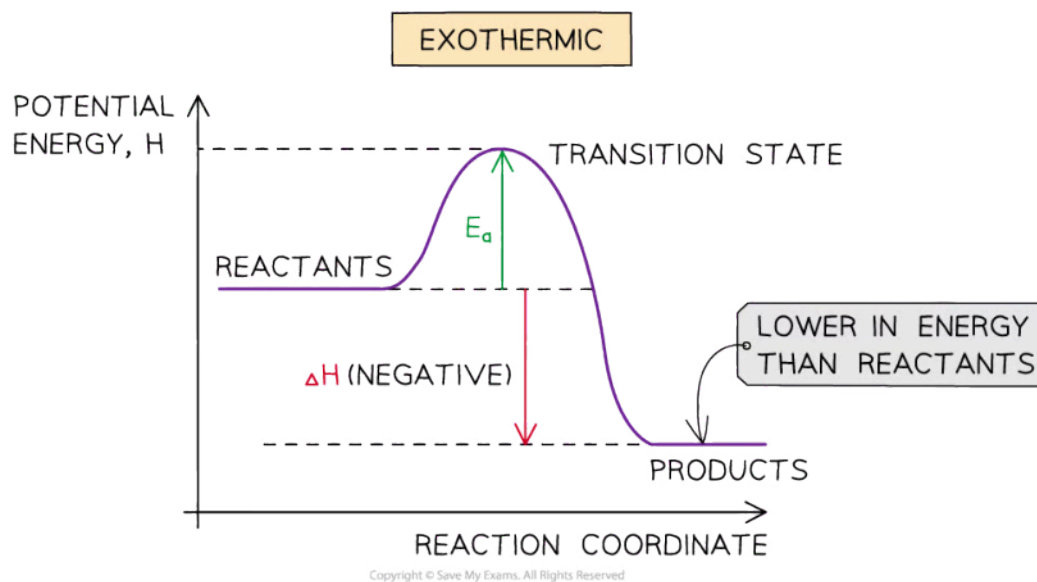
The energy profile for the reaction of hydrogen with chlorine to form hydrogen chloride gas

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

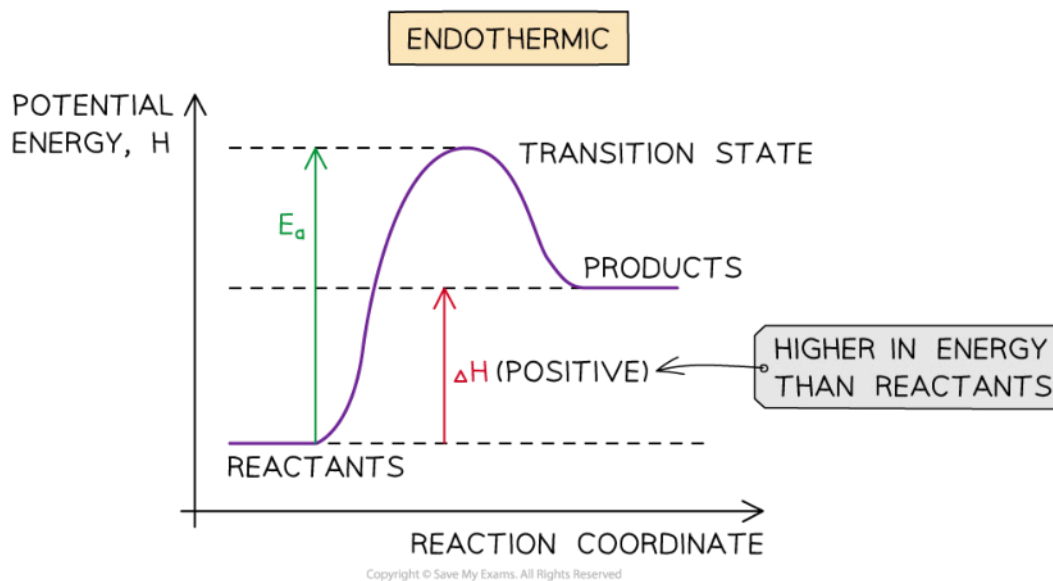
Diagram to show an energy profile for an endothermic reaction



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The potential energy of the products is lower than the reactants

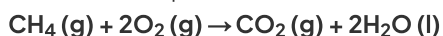
Worked example

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

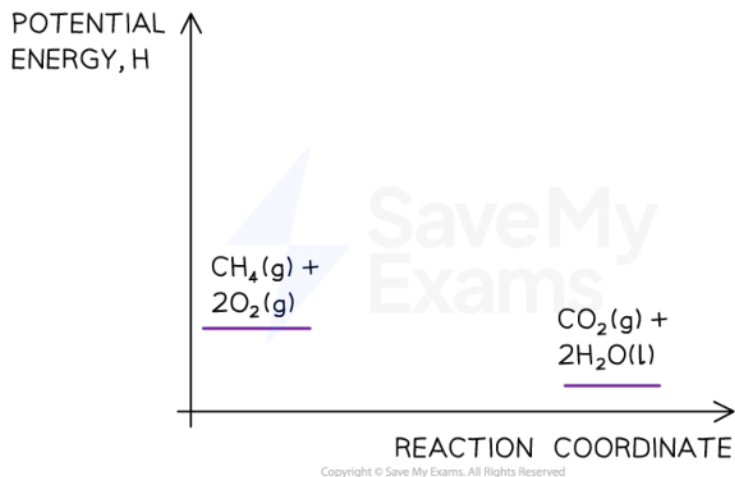
Draw a labelled energy level diagram for this reaction.

Answer:

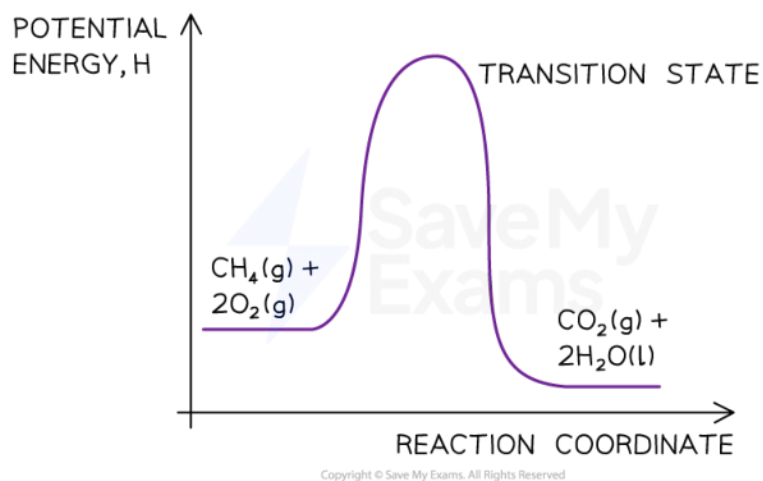
- Step 1: The chemical equation for the complete combustion of methane is:



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



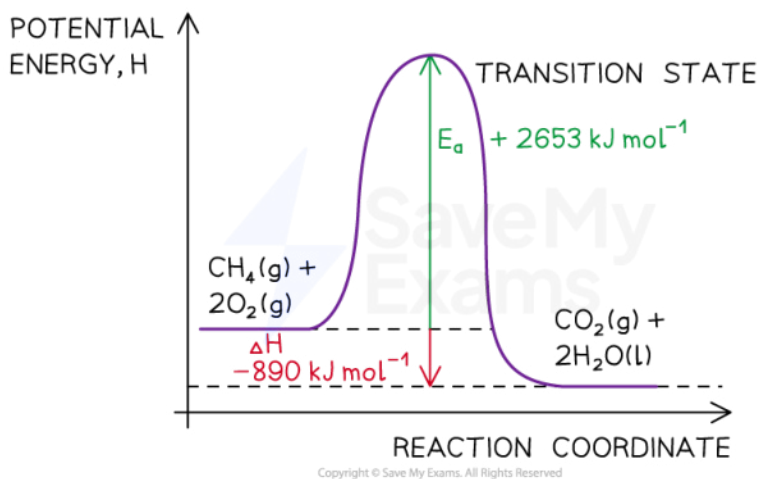
- Step 3: Draw the curve in the energy level diagram clearly showing the transition state



- Step 4: Draw arrows to show the E_a and ΔH including their values

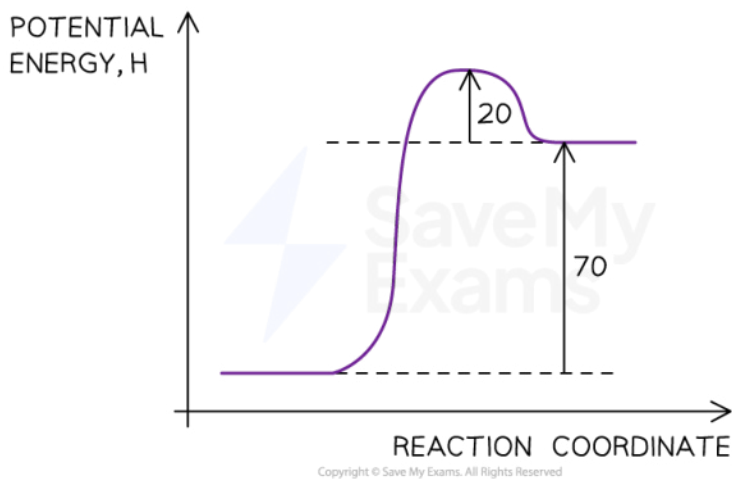


Your notes



 **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, ΔH^\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 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°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. ΔH^\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 stoichiometric equation react to give the products under standard conditions	ΔH^\ominus_r	Both
Formation	The enthalpy change when one mole of a compound is formed from its elements under standard conditions	ΔH^\ominus_f	Both
Combustion	The enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions	ΔH^\ominus_c	Exothermic
Neutralisation	The enthalpy change when one mole of water is formed by reacting an acid and alkali under standard conditions	ΔH^\ominus_{neut}	Exothermic

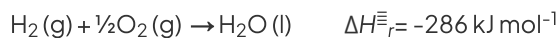
- Practice your understanding of enthalpy changes on the following worked examples:



Your notes

Worked example

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



Calculate ΔH_r for the reaction below:



Answer:

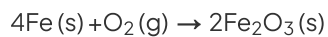
- Since two moles of water molecules are formed in the question above, the energy released is simply:

$$\Delta H_r = 2 \text{ mol} \times (-286 \text{ kJ mol}^{-1})$$

$$= -572 \text{ kJ}$$

Worked example

Calculate ΔH_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:

$$\Delta H_r = 2 \text{ mol} \times (-824 \text{ kJ mol}^{-1})$$

$$= -1648 \text{ kJ}$$



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Worked example

Identify each of the following as ΔH_r^\ominus , ΔH_f^\ominus , ΔH_c^\ominus or ΔH_{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:** ΔH_r^\ominus
- **Answer 2:** ΔH_f^\ominus as one mole of CO_2 is formed from its elements in standard state and ΔH_c^\ominus as one mole of carbon is burnt in oxygen
- **Answer 3:** ΔH_{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



Your notes

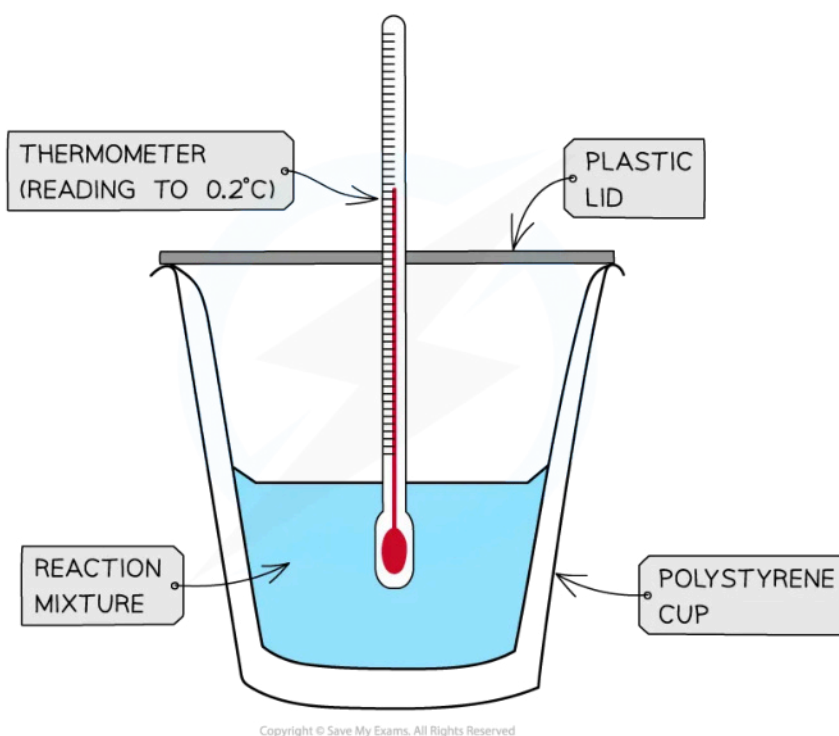
Calorimetry Experiments

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**

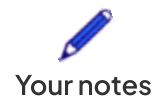
Diagram to show how to set up a simple calorimeter



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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:



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

q = THE HEAT TRANSFERRED, J
m = THE MASS OF WATER, g
c = THE SPECIFIC HEAT CAPACITY, $\text{J g}^{-1}\text{K}^{-1}$
 ΔT = 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) = $4.18 \text{ J g}^{-1}\text{K}^{-1}$
 ΔT (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⁻¹**

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:



Your notes

- 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

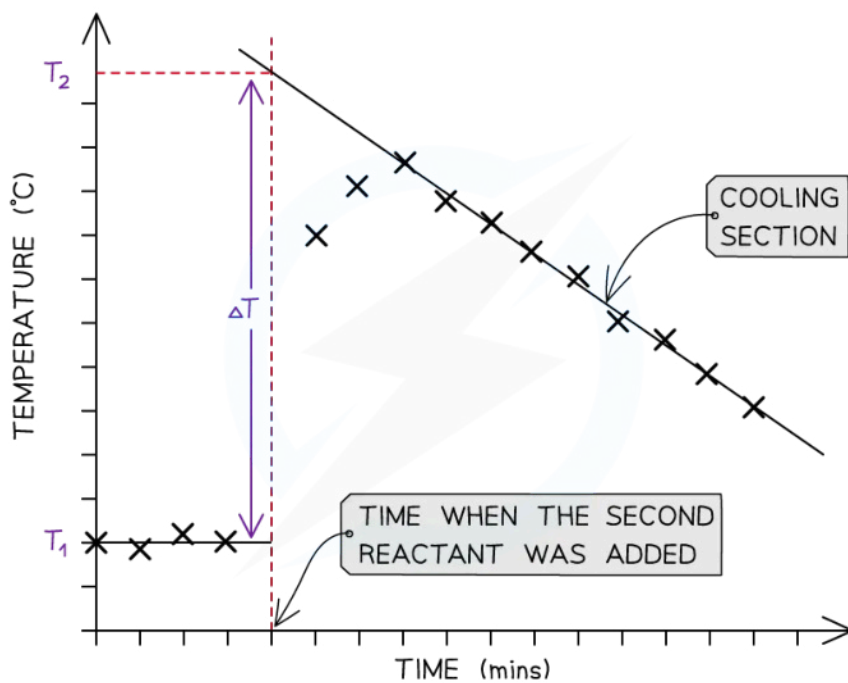
Enthalpy changes for reactions in solution

- 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 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





Your notes

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 cm³ of 0.200 mol dm⁻³ 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.

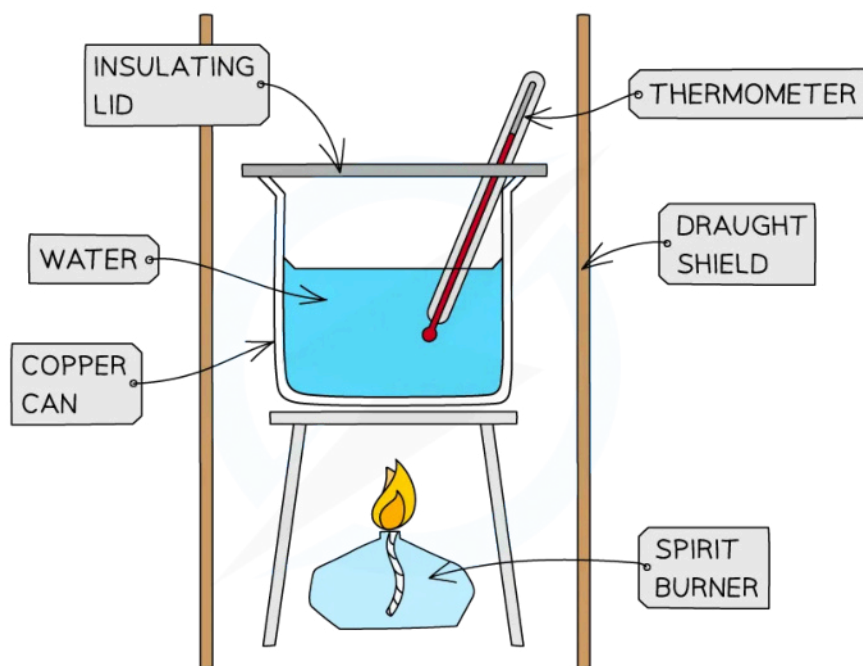
Answer:

- **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 CuSO₄(aq)
 moles = volume in dm³ x concentration = 0.1 x 0.2 = 0.02 mol
- **Step 3:** Calculate ΔH
 $\Delta H = q \div n = -3135 \text{ J} \div 0.02 \text{ mol} = -156750 \text{ J} = -156.75 \text{ kJ}$
 $= -160 \text{ kJ (2 sig figs)}$

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**



Your notes

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 ΔH

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

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