

DP IB Chemistry: HL



Your notes

5.1 Energetics

Contents

- * 5.1.1 Energy Changes in Reactions
- * 5.1.2 Standard Enthalpy Change
- * 5.1.3 Calorimetry
- * 5.1.4 Calorimetry Experiments

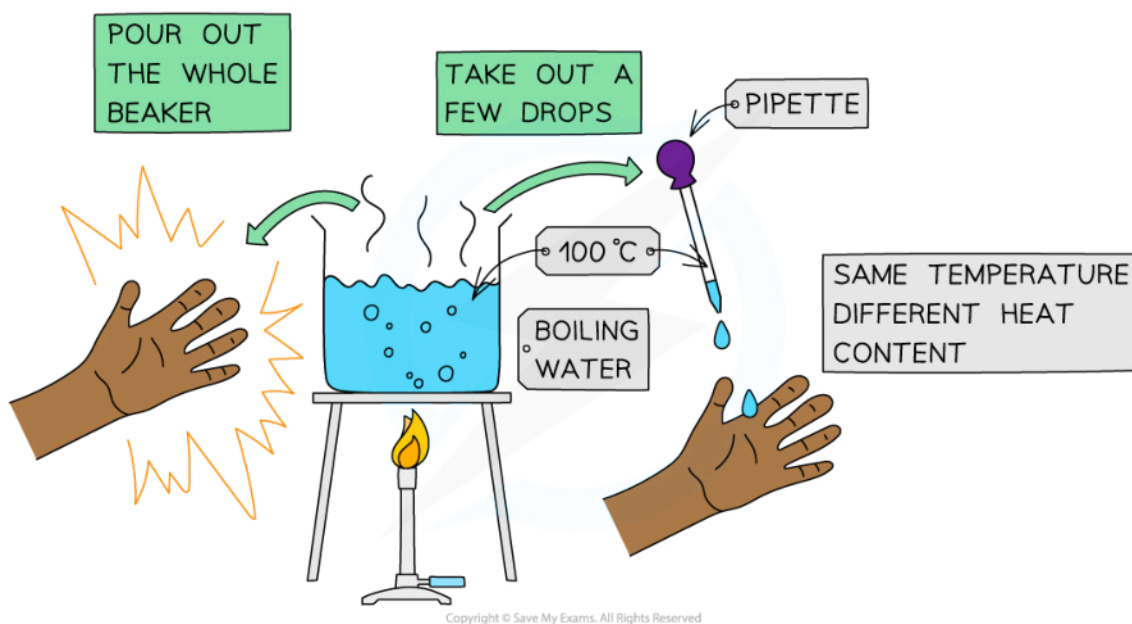


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5.1.1 Energy Changes in Reactions

Temperature & Kinetic Energy

- What is the difference between heat and temperature?
- This can be illustrated using a beaker of boiling water and a pipette:



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

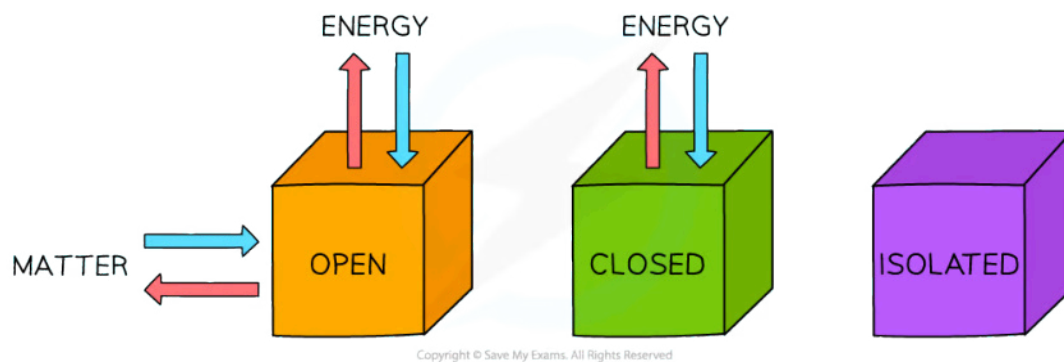
- You would get a very nasty burn if a whole beaker of boiling water spilled onto to your hand, but a drop of boiling water would cause little problem
- The water is at the **same temperature** in the pipette as in the beaker, but the beaker has a much **higher heat content**
- We say that temperature 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



Your notes

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**:



Three types of systems

- Isolated systems are very rare; most chemical reactions are open systems
- Open systems are very important when thinking about chemical equilibrium which is covered in Topic 7
- 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



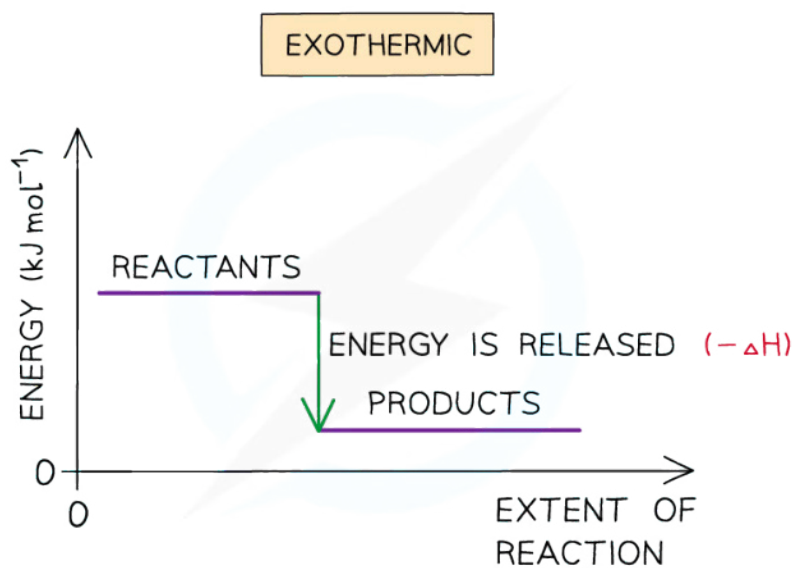
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Exothermic & Endothermic

- 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

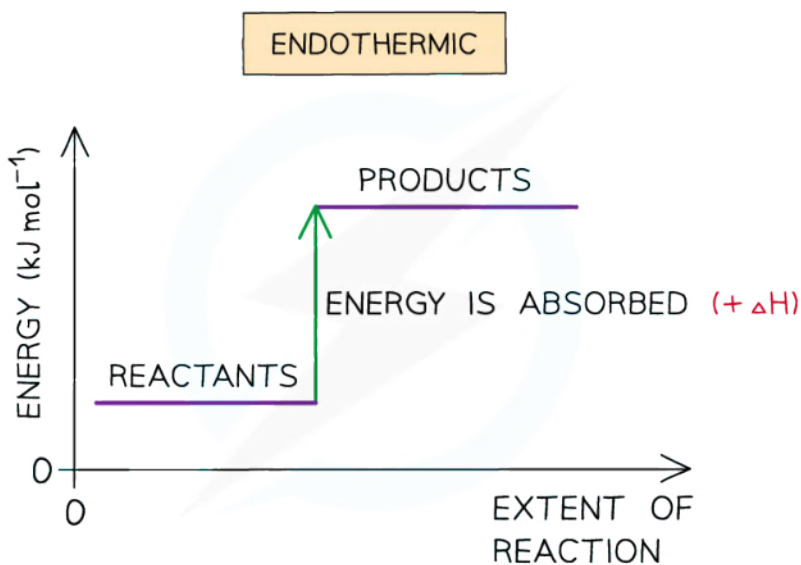
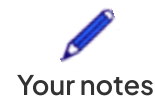


The enthalpy change during an exothermic reaction

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**

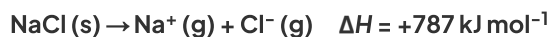
- The **temperature** of the **system** increases
- There is an **enthalpy** increase during the reaction so ΔH is **positive**



The enthalpy change during an endothermic reaction

💡 Examiner Tip

It is important to specify the physical states of each species in an equation when dealing with enthalpy changes as any changes in state can cause very large changes of enthalpy. For example:



Also, 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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5.1.2 Standard Enthalpy Change

Standard Enthalpy Change

Standard conditions

- To compare the changes in enthalpy between reactions, all thermodynamic measurements are made under **standard conditions**
- 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:



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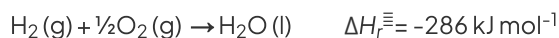
Standard Enthalpy Change of ...	Definition	Symbol	Exothermic/Endothermic
Reaction	The enthalpy change when the reactants in the stoichiometric equation react to give the products under standard conditions	ΔH_r^\ominus	Both
Formation	The enthalpy change when one mole of a compound is formed from its elements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

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- 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 ΔH_r for the reaction below:





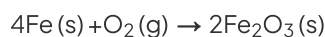
Answer:

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

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

Worked example

Calculate ΔH_f 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:

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

Worked example

Identify each of the following as ΔH_f^\ominus , ΔH_c^\ominus , ΔH_{neut}^\ominus or ΔH_{c}^\ominus

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

Answer:

Answer 1: ΔH_f^\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



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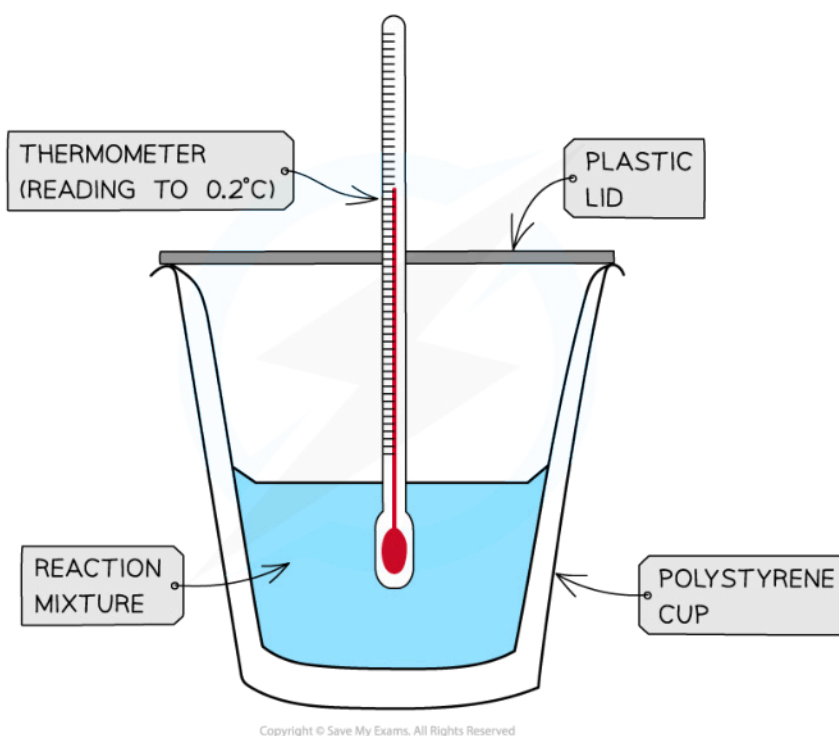
Your notes

5.1.3 Calorimetry

Calorimetry

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**



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



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

$$m (\text{of water}) = 250 \text{ g}$$

$$c (\text{of water}) = 4.18 \text{ J g}^{-1}\text{K}^{-1}$$

$$\Delta T (\text{of water}) = 310 - 298 \text{ K}$$

$$= 12 \text{ K}$$

Step 2: $q = 250 \times 4.18 \times 12$

$$= 12540 \text{ J}$$

Step 3: This is the energy released by 0.01 mol of propan-1-ol

$$\text{Total energy } \Delta H = q \div n = 12540 \text{ J} \div 0.01 \text{ mol} = 1254000 \text{ J mol}^{-1}$$

$$\text{Total energy} = -1254 \text{ kJ mol}^{-1}$$

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



Your notes

5.1.4 Calorimetry Experiments

Calorimetry Experiments

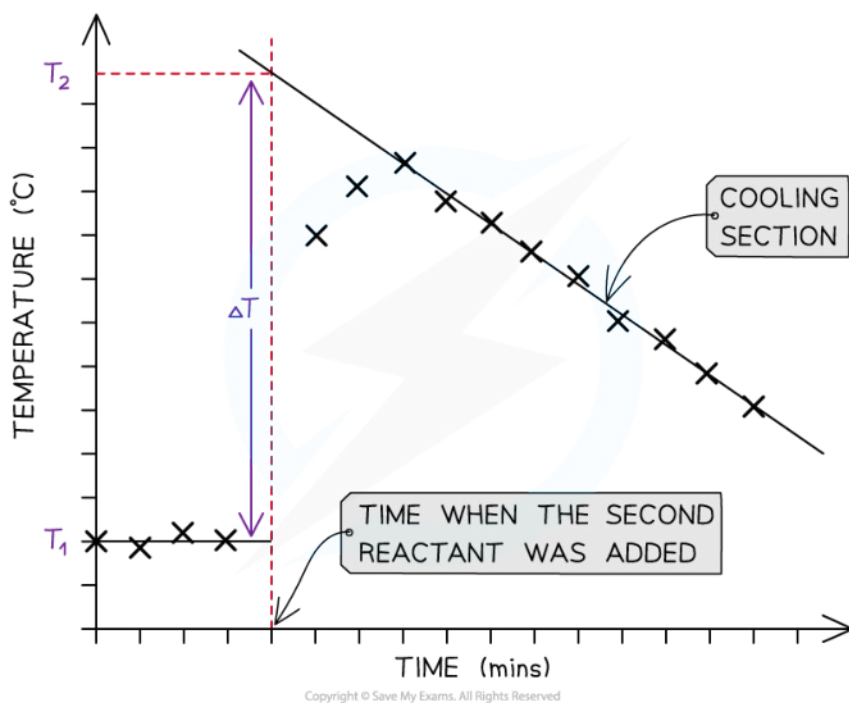
- There are two types of calorimetry experiments you need to know for IB Chemistry:
 - Enthalpy** changes of **reactions in solution**
 - Enthalpy** changes of **combustion**
- In both cases you should be able to give an outline of the experiment and be able to process experimental data using calculations 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
- The apparatus needed to carry out an enthalpy of reaction in solution calorimetry experiment is shown in the previous section **5.1.3 Calorimetry**
- 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. The zinc is added after 4 minutes

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^3 of $0.200 \text{ mol dm}^{-3}$ copper(II)sulfate solution in a calorimeter. The reaction equation was as follows



The maximum temperature rise was $7.5 \text{ }^\circ\text{C}$. 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 $\text{CuSO}_4(\text{aq})$

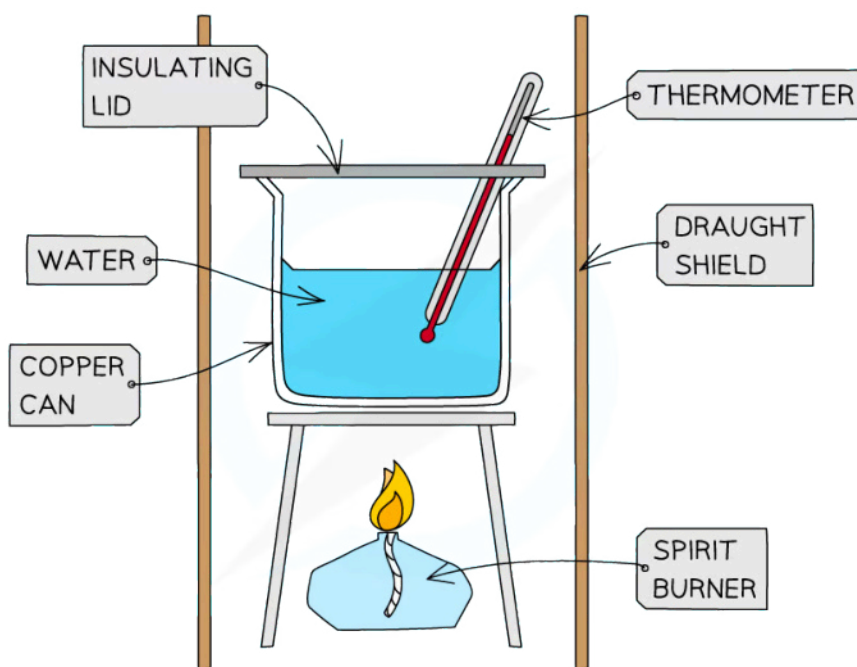
$$\text{moles} = \text{volume in dm}^3 \times \text{concentration} = 0.1 \times 0.2 = 0.02 \text{ mol}$$

Step 3: Calculate ΔH

$$\Delta H = q \div n = -3135 \text{ J} \div 0.02 \text{ mol} = -156750 \text{ J} = -156.75 \text{ kJ} = \mathbf{-160 \text{ kJ}} \text{ (2 sig figs)}$$

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



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A simple combustion calorimeter

- 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

$$\text{moles} = \text{mass} \div \text{molar mass} = 1.023 \text{ g} \div 60.11 \text{ g mol}^{-1} = 0.01702 \text{ mol}$$

Step 3: Calculate ΔH

$$\Delta H = q \div n = -25\,080 \text{ J} \div 0.01702 \text{ mol} = -1\,473\,560 \text{ J} = -1\,474 \text{ kJ} = \mathbf{-1.5 \times 10^3 \text{ kJ}}$$

Examiner Tip

There are many potential sources of error in calorimetry experiments, both quantitative and qualitative. Determining % errors and comparing ΔH results to data book values is an important part of this topic and is covered in more detail in **Topic 11 Measurement and Data Processing**