



MEGA  
LECTURE

# IB DP CHEMISTRY

**Reactivity 1: What Drives Chemical Reactions?**

## **Reactivity 1.1 Measuring Enthalpy Changes**

Revision Notes · Standard and Higher Level

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## What the syllabus requires

Reactivity 1.1 is the foundation of the whole thermodynamics strand. By the end of it you should be able to define enthalpy change, decide its sign, and measure it in the laboratory using calorimetry. Use this list as a final checklist before the exam.

| Understanding               | You should be able to...                                                                                                                                            |
|-----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Enthalpy change, $\Delta H$ | Describe reactions as exothermic or endothermic and interpret the sign of $\Delta H$ in terms of energy transferred between system and surroundings.                |
| Reaction profiles           | Draw and label enthalpy-level (reaction profile) diagrams for exothermic and endothermic reactions, showing reactants, products, activation energy and $\Delta H$ . |
| Bond energetics             | Explain that $\Delta H$ arises because bond breaking absorbs energy and bond making releases energy.                                                                |
| Standard enthalpy changes   | State the meaning of standard conditions and define standard enthalpies of reaction, formation, combustion and neutralisation.                                      |
| Calorimetry                 | Apply $q = mc\Delta T$ to experimental data to determine an enthalpy change per mole, with the correct sign.                                                        |
| Evaluation                  | Identify assumptions and systematic errors in calorimetry and suggest realistic improvements.                                                                       |

**Exam note:** All of Reactivity 1.1 is common to SL and HL. It is examined at HL in more demanding, multi-step problems and is combined freely with Hess's law and bond enthalpies (Reactivity 1.2 and 1.3). Points that reach further for HL are flagged **(HL)** in these notes.

## 1. Enthalpy and enthalpy change

Every substance stores chemical energy in its bonds and intermolecular forces. **Enthalpy** (symbol  $H$ ) is the total heat content of a substance measured at constant pressure. We cannot measure the absolute enthalpy of a substance, but we can measure the **change** in enthalpy when a reaction occurs. This change is the enthalpy change,  $\Delta H$ , defined as

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

The value refers to the heat energy exchanged with the surroundings at constant pressure, and it is quoted in  $\text{kJ mol}^{-1}$  (kilojoules per mole of reaction as written).

### System and surroundings

To keep the bookkeeping clear we divide the universe into two parts:

- The **system** is the chemicals reacting -- the reactants and products themselves.
- The **surroundings** are everything else that can exchange heat with the system: the solvent, the reaction vessel, the air and, in the laboratory, usually the water in a calorimeter.

Energy is conserved, so any enthalpy lost by the system is gained by the surroundings, and vice versa. This is why a temperature change of the surroundings is our practical signal that a reaction has an enthalpy change.

## Exothermic and endothermic

|                      | Exothermic reaction                                     | Endothermic reaction                                             |
|----------------------|---------------------------------------------------------|------------------------------------------------------------------|
| Energy flow          | System releases heat to the surroundings                | System absorbs heat from the surroundings                        |
| Surroundings         | Temperature rises                                       | Temperature falls                                                |
| Sign of $\Delta H$   | $\Delta H$ is negative (–)                              | $\Delta H$ is positive (+)                                       |
| Enthalpy of products | Lower than reactants                                    | Higher than reactants                                            |
| Everyday example     | Combustion, neutralisation, most displacement reactions | Thermal decomposition, dissolving ammonium salts, photosynthesis |

A useful memory hook: in an **exothermic** change heat **exits** the system, so the products hold less energy and  $\Delta H$  is negative; in an **endothermic** change heat **enters** the system, so the products hold more energy and  $\Delta H$  is positive.

## Enthalpy-level (reaction profile) diagrams

A reaction profile plots enthalpy on the vertical axis against the progress of the reaction on the horizontal axis. The reactants and products sit at fixed enthalpy levels; the difference between them is  $\Delta H$ . The hump between them is the **activation energy**,  $E_a$  -- the minimum energy needed to start breaking bonds (covered fully in Reactivity 2.2).

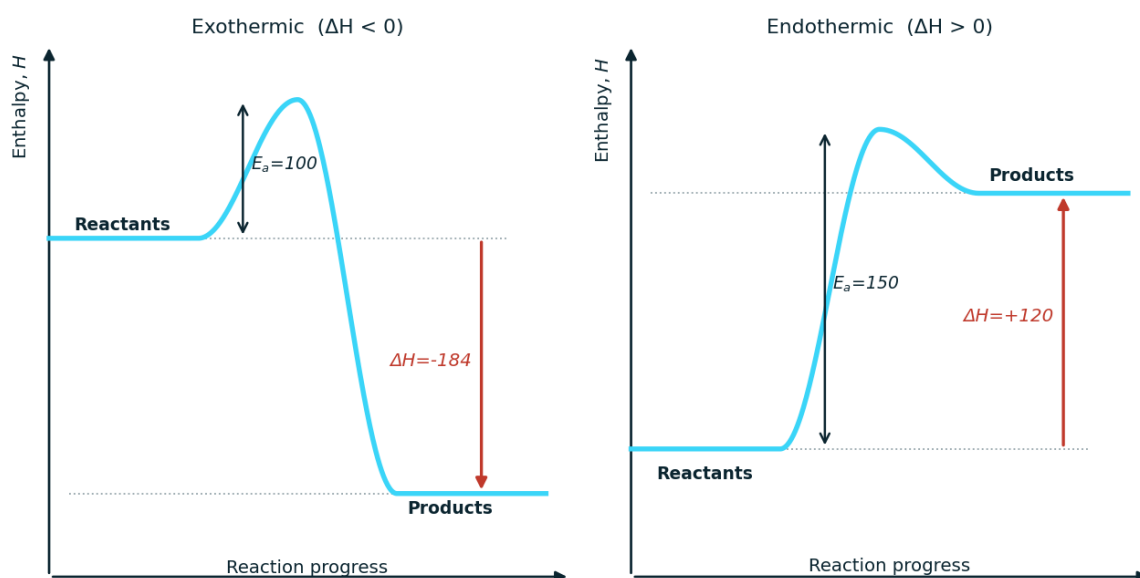


Figure 1. Reaction profiles. Left, an exothermic reaction: the product level lies **below** the reactants, so  $\Delta H = H(\text{products}) - H(\text{reactants}) = -184 \text{ kJ mol}^{-1}$  (negative), with activation energy  $E_a = 100 \text{ kJ mol}^{-1}$ . Right, an endothermic reaction: the product level lies **above** the reactants,  $\Delta H = +120 \text{ kJ mol}^{-1}$  (positive),  $E_a = 150 \text{ kJ mol}^{-1}$ . Both climb the  $E_a$  barrier first.

Read the two diagrams carefully. In the exothermic profile the product level lies *below* the reactant level, so the arrow for  $\Delta H$  points downward and  $\Delta H$  is negative. In the endothermic profile the product level lies *above* the reactant level, the arrow points upward, and  $\Delta H$  is positive. In both cases the reaction must first climb the activation-energy barrier, regardless of the overall sign of  $\Delta H$ .

**Exam technique:** When you draw a profile, always label four things: the reactant level, the product level,  $E_a$  measured from the reactants to the top of the barrier, and  $\Delta H$  as a vertical arrow between the two levels pointing in the correct direction. Marks are lost for unlabelled axes.

## 2. Why reactions have an enthalpy change

The origin of every  $\Delta H$  is the rearrangement of chemical bonds. Two opposing energy processes happen in any reaction:

- **Bond breaking is endothermic.** Energy must be supplied to pull bonded atoms apart, so breaking bonds always *absorbs* energy from the surroundings.
- **Bond making is exothermic.** When new bonds form, energy is *released* to the surroundings.

The overall enthalpy change is the balance of the two:

$$\Delta H \approx (\text{energy absorbed breaking bonds}) - (\text{energy released making bonds})$$

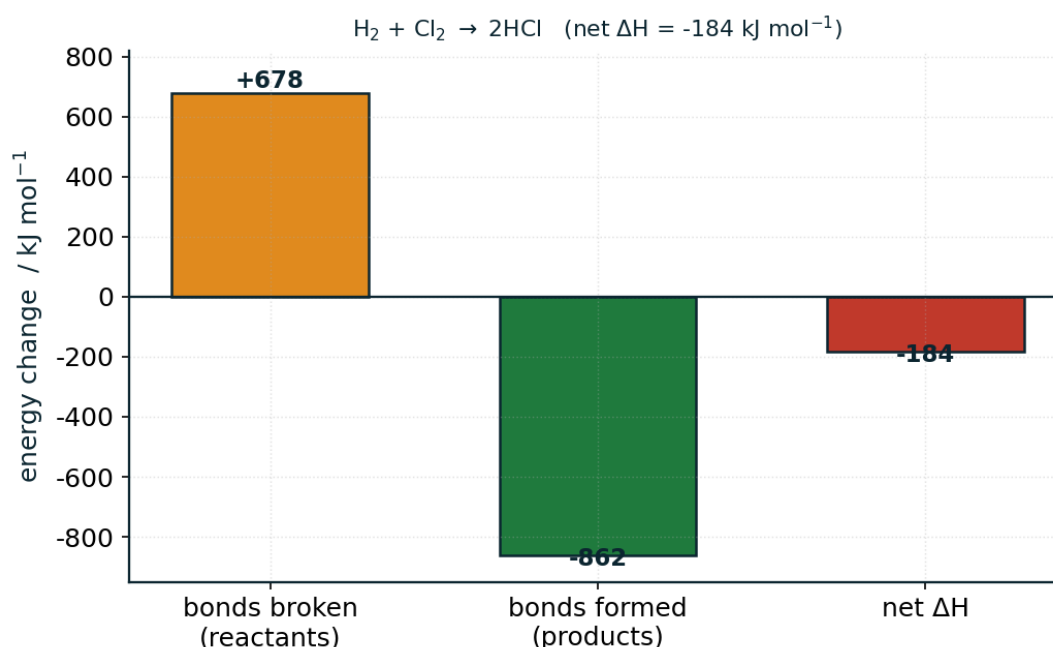


Figure 3. Bond-enthalpy balance for  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ . Breaking the reactant bonds absorbs  $+678 \text{ kJ mol}^{-1}$  ( $\text{H}-\text{H}$  436,  $\text{Cl}-\text{Cl}$  242); forming two  $\text{H}-\text{Cl}$  bonds releases  $-862 \text{ kJ mol}^{-1}$ . The net  $\Delta H = 678 - 862 = -184 \text{ kJ mol}^{-1}$ , so the reaction is exothermic.

If more energy is released forming the product bonds than is absorbed breaking the reactant bonds, the reaction is exothermic ( $\Delta H$  negative). If breaking the reactant bonds costs more than is recovered, the reaction is endothermic ( $\Delta H$  positive). This is exactly the reasoning you will formalise with average bond enthalpies in Reactivity 1.2.

**Common misconception:** It is wrong to say bond breaking releases energy. Breaking a bond always requires energy; it is the *formation* of the new, often stronger, bonds in the products that releases the energy which makes a reaction exothermic.

### 3. Standard enthalpy changes

The enthalpy change of a reaction depends slightly on the conditions (temperature, pressure and the states and concentrations of the substances). To make values comparable, chemists agree on a set of **standard conditions** and write the standard enthalpy change with a degree symbol:  $\Delta H^\circ$ .

| Standard condition         | Agreed value                                    |
|----------------------------|-------------------------------------------------|
| Pressure                   | 100 kPa (1 bar)                                 |
| Temperature                | a stated temperature, usually 298 K (25 °C)     |
| Concentration of solutions | 1 mol dm <sup>-3</sup>                          |
| State of each substance    | the state that is stable under these conditions |

The symbol  $\Delta H^\circ$  (read as delta H standard) therefore means the enthalpy change measured with every substance in its standard state at 100 kPa and the stated temperature. Four particular standard enthalpy changes are named in the syllabus.

| Standard enthalpy change                       | Definition (per mole, standard conditions)                                                                                                                                                  |
|------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Reaction, $\Delta H^\circ_r$                   | The enthalpy change when molar amounts of reactants react as shown in a balanced equation.                                                                                                  |
| Formation, $\Delta H^\circ_f$                  | The enthalpy change when <b>one mole</b> of a compound is formed from its elements in their standard states. $\Delta H^\circ_f$ of any element in its standard state is zero by definition. |
| Combustion, $\Delta H^\circ_c$                 | The enthalpy change when <b>one mole</b> of a substance is completely burned in excess oxygen. Always negative.                                                                             |
| Neutralisation, $\Delta H^\circ_{\text{neut}}$ | The enthalpy change when an acid and a base react to form <b>one mole of water</b> . For strong acid + strong alkali it is close to $-57 \text{ kJ mol}^{-1}$ .                             |

Worked examples of the defining equations:

- **Formation** of liquid water:  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ ,  $\Delta H^\circ_f = -286 \text{ kJ mol}^{-1}$ .
- **Combustion** of methane:  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ ,  $\Delta H^\circ_c = -891 \text{ kJ mol}^{-1}$ .
- **Neutralisation**:  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ ,  $\Delta H^\circ_{\text{neut}} = -57.3 \text{ kJ mol}^{-1}$ .

**HL link: (HL)** Standard enthalpies of formation are the raw material of Hess's law calculations in Reactivity 1.2, where  $\Delta H^\circ_r = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$ . Get the definitions exact now and those cycles become routine.

### 4. Temperature, heat and enthalpy -- keep them separate

These three ideas are constantly confused in exams. They are not the same thing.

| Quantity         | What it is                                                                                                                 | Depends on amount? | Unit    |
|------------------|----------------------------------------------------------------------------------------------------------------------------|--------------------|---------|
| Temperature, $T$ | A measure of the average kinetic energy of the particles. It tells you how hot something is, not how much energy it holds. | No (intensive)     | K or °C |

| Quantity                    | What it is                                                                              | Depends on amount? | Unit                 |
|-----------------------------|-----------------------------------------------------------------------------------------|--------------------|----------------------|
| Heat, $q$                   | Energy transferred between system and surroundings because of a temperature difference. | Yes (extensive)    | J or kJ              |
| Enthalpy change, $\Delta H$ | The heat exchanged by a reaction at constant pressure, expressed per mole of reaction.  | Quoted per mole    | $\text{kJ mol}^{-1}$ |

A small cup of boiling water and a large tank of warm water can be at very different temperatures, yet the tank stores far more heat because it contains many more particles. Temperature is intensive (independent of amount); heat is extensive (depends on amount). A change in temperature ( $\Delta T$ ) of the surroundings is what we actually measure; we then convert it to heat with  $q = mc\Delta T$ , and finally to an enthalpy change per mole.

**Note the sign convention:** A temperature **rise** of the surroundings means the system **released** heat, so the reaction is exothermic and  $\Delta H$  is **negative**. A temperature **fall** means the reaction absorbed heat, so  $\Delta H$  is **positive**. The sign of  $\Delta H$  is opposite to the sign of the surroundings' temperature change.

## 5. Calorimetry: measuring $\Delta H$ in the laboratory

Calorimetry measures the heat released or absorbed by a reaction by monitoring the temperature change of a known mass of water (or aqueous solution) that is in thermal contact with the reaction. The central equation is

$$q = mc\Delta T$$

where **q** is the heat energy transferred (J), **m** is the mass of water or solution being heated or cooled (g), **c** is the specific heat capacity of that water ( $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ), and  $\Delta T$  is the temperature change of the water (K, numerically equal to a change in  $^{\circ}\text{C}$ ).

### The four-step method

1. Calculate the heat change of the water:  $q = mc\Delta T$ . 2. Find the amount (in moles) of the limiting reactant that produced that heat. 3. Divide to get the enthalpy change **per mole**:  $\Delta H = -q / n$ . 4. Assign the sign: negative if the surroundings warmed (exothermic), positive if they cooled (endothermic), and convert J to kJ.

The minus sign in step 3 converts between the point of view of the surroundings (which gained heat  $q$  in an exothermic reaction) and the system (whose enthalpy fell by that amount).

### Running the experiment well

The quality of a calorimetry result depends almost entirely on the technique. A reliable combustion experiment (a spirit burner heating water) follows this sequence:

- Weigh the burner and fuel; measure a known mass (or volume) of water into a thin copper calorimeter and record its starting temperature.
- Light the burner directly beneath the calorimeter, shielded from draughts, and stir the water gently.
- Extinguish the flame after a clear temperature rise (about 15 to 20  $^{\circ}\text{C}$ ), record the maximum temperature and immediately reweigh the burner.

- The mass of fuel burned is the loss in mass of the burner; the heat gained is found from the water using  $q = mc\Delta T$ .

For reactions carried out *in solution* -- neutralisation, dissolution and displacement -- the reaction and the water being warmed are one and the same, so the solution is both system and calorimeter. These are done in an insulated polystyrene cup with a lid, and the best results come from a temperature-time graph.

### The temperature-time (extrapolation) method

Because heat leaks away even as the reaction proceeds, the highest temperature you read is already lower than the true maximum. To correct for this, take temperature readings at regular intervals before and after mixing, plot temperature against time, and extrapolate the cooling portion of the graph back to the instant of mixing.

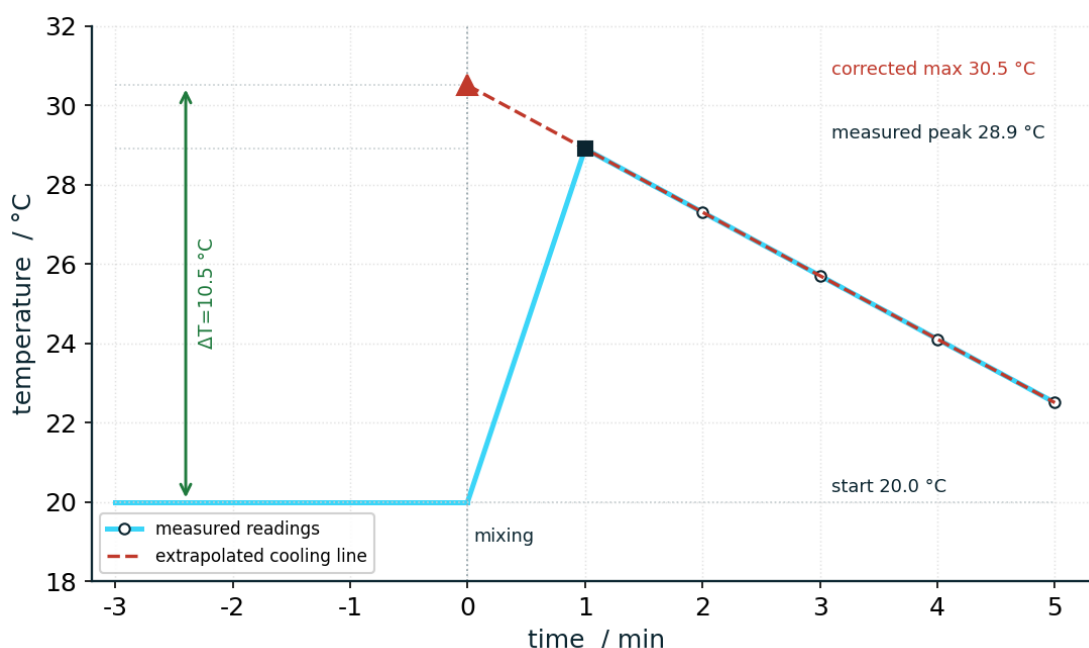


Figure 2. Temperature–time graph for a displacement reaction in an insulated cup. Extrapolating the cooling line back to the moment of mixing lifts the measured peak (28.9 °C) to a corrected maximum of 30.5 °C. With  $m = 50.0$  g,  $c = 4.18$  J g<sup>-1</sup> K<sup>-1</sup> and  $\Delta T = 10.5$  °C,  $q = 2.19$  kJ and  $\Delta H = -q/n = -219$  kJ mol<sup>-1</sup> ( $n = 0.0100$  mol).

### What we can measure this way

| Enthalpy change       | Typical set-up                                     | Mass used in $q = mc\Delta T$            |
|-----------------------|----------------------------------------------------|------------------------------------------|
| Combustion            | Spirit burner heating water in a metal calorimeter | Mass of water heated                     |
| Neutralisation        | Acid + alkali mixed in an insulated cup            | Combined mass of the two solutions       |
| Solution (dissolving) | Solid dissolved in water in an insulated cup       | Mass of water (or of the final solution) |
| Displacement          | Metal added to a salt solution in an insulated cup | Mass of the solution                     |

### Assumptions and systematic errors

Simple calorimetry always gives a value smaller in magnitude than the data-book figure, mainly because of the assumptions built into  $q = mc\Delta T$ :

- **Heat loss to the surroundings.** Not all the heat reaches (or stays in) the water; some warms the air, the thermometer and the container. This is the biggest error, and it makes both exothermic and endothermic values too small in magnitude.
- **Incomplete combustion.** In a spirit burner the fuel may burn to carbon and carbon monoxide (seen as soot), releasing less energy than complete combustion would.
- **Evaporation of fuel** from an open wick between weighings overstates the mass burned.
- **The apparatus absorbs heat.** We assume all heat goes to the water and ignore the heat capacity of the calorimeter itself.
- **Non-standard conditions.** The experiment is rarely done at exactly 298 K and 100 kPa, and we assume the solution has the density and specific heat capacity of pure water.

## Improvements

- Insulate the calorimeter (lid, lagging, polystyrene cup) and shield the flame with a draught shield to cut heat loss.
- Position the flame close to a thin metal (copper) calorimeter and stir the water for even heating.
- Use a bomb calorimeter for combustion (excess oxygen ensures complete combustion; the whole apparatus is calibrated).
- For neutralisation, dissolution and displacement, plot temperature against time and extrapolate back to the moment of mixing to correct for heat loss during the reaction.

**HL extension: (HL)** A more rigorous experiment calibrates the *calorimeter constant* (the heat capacity of the vessel plus contents) so that the heat absorbed by the apparatus, not just the water, is included in  $q$ . This removes one of the assumptions above.

## 6. Worked calorimetry problems

Work through each example with the four-step method. Watch the sign, keep track of J versus kJ, and always finish with a value **per mole**.

### Worked example 1 -- basic $q = mc\Delta T$

A beaker containing 150 g of water is heated from 18.0 °C to 43.0 °C. How much heat energy did the water absorb?

$$\Delta T = 43.0 - 18.0 = 25.0 \text{ }^{\circ}\text{C}.$$

$$q = mc\Delta T = 150 \times 4.18 \times 25.0 = 15675 \text{ J} \approx \mathbf{15.7 \text{ kJ}}.$$

This is the raw heat step that begins every calorimetry calculation -- nothing yet is per mole.

**Worked example 2 -- enthalpy of combustion (spirit burner)**

A spirit burner of ethanol,  $\text{C}_2\text{H}_5\text{OH}$  ( $M = 46.08 \text{ g mol}^{-1}$ ), is used to heat  $200.0 \text{ g}$  of water. The temperature rises by  $22.0^\circ\text{C}$  and the burner loses  $1.15 \text{ g}$  of fuel. Determine  $\Delta H_c$  of ethanol.

**Step 1**  $q = mc\Delta T = 200.0 \times 4.18 \times 22.0 = 18392 \text{ J} = 18.392 \text{ kJ}$  (heat gained by the water).

**Step 2**  $n(\text{ethanol}) = 1.15 / 46.08 = 0.02496 \text{ mol}$ .

**Step 3**  $\Delta H_c = -q / n = -18.392 / 0.02496 = -737 \text{ kJ mol}^{-1}$ .

**Step 4** The water warmed, so the reaction is exothermic and the sign is negative. The data-book value is  $-1367 \text{ kJ mol}^{-1}$ ; our value is far smaller in magnitude, mainly because of heat loss and incomplete combustion -- a classic evaluation point.

**Worked example 3 -- enthalpy of neutralisation**

$50.0 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3}$   $\text{HCl}$  at  $21.0^\circ\text{C}$  is mixed with  $50.0 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3}$   $\text{NaOH}$  at  $21.0^\circ\text{C}$  in a polystyrene cup. The temperature rises to  $27.8^\circ\text{C}$ . Find  $\Delta H_{\text{neut}}$ .

**Step 1** Total volume =  $100.0 \text{ cm}^3$ , so mass of solution  $\approx 100.0 \text{ g}$  (density  $1.00 \text{ g cm}^{-3}$ ).  $\Delta T = 27.8 - 21.0 = 6.8^\circ\text{C}$ .

$q = 100.0 \times 4.18 \times 6.8 = 2842 \text{ J} = 2.842 \text{ kJ}$ .

**Step 2**  $n(\text{H}_2\text{O formed}) = n(\text{HCl}) = 0.0500 \text{ dm}^3 \times 1.00 = 0.0500 \text{ mol}$ .

**Step 3**  $\Delta H_{\text{neut}} = -2.842 / 0.0500 = -56.8 \text{ kJ mol}^{-1}$  -- close to the accepted  $-57.3 \text{ kJ mol}^{-1}$ .

Note: use the mass of the *whole solution* ( $100 \text{ g}$ ), never the mass of solute.

**Worked example 4 -- enthalpy of solution (endothermic)**

$4.00 \text{ g}$  of ammonium nitrate,  $\text{NH}_4\text{NO}_3$  ( $M = 80.05 \text{ g mol}^{-1}$ ), is dissolved in  $50.0 \text{ g}$  of water. The temperature falls from  $21.0^\circ\text{C}$  to  $14.8^\circ\text{C}$ . Find  $\Delta H_{\text{sol}}$ .

**Step 1**  $\Delta T = 21.0 - 14.8 = 6.2^\circ\text{C}$  (a fall).  $q = 50.0 \times 4.18 \times 6.2 = 1296 \text{ J} = 1.296 \text{ kJ}$  absorbed from the water.

**Step 2**  $n(\text{NH}_4\text{NO}_3) = 4.00 / 80.05 = 0.04997 \text{ mol}$ .

**Step 3** The water cooled, so the system absorbed heat:  $\Delta H_{\text{sol}}$  is **positive**.  $\Delta H_{\text{sol}} = +1.296 / 0.04997 = +25.9 \text{ kJ mol}^{-1}$ .

Getting the sign right is worth a mark on its own: a temperature fall always gives a positive  $\Delta H$ .

**Worked example 5 -- enthalpy of displacement**

Excess zinc powder is added to 50.0 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> copper(II) sulfate solution. The temperature rises from 20.0 °C to 30.2 °C. Find  $\Delta H$  for  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$ .

**Step 1** mass of solution  $\approx$  50.0 g;  $\Delta T = 30.2 - 20.0 = 10.2$  °C.  $q = 50.0 \times 4.18 \times 10.2 = 2132 \text{ J} = 2.132 \text{ kJ}$ .

**Step 2** Zn is in excess, so  $\text{Cu}^{2+}$  is limiting:  $n(\text{Cu}^{2+}) = 0.0500 \times 0.200 = 0.0100 \text{ mol}$ .

**Step 3** Exothermic (temperature rose):  $\Delta H = - 2.132 / 0.0100 = -213 \text{ kJ mol}^{-1}$  (accepted value  $\approx -217 \text{ kJ mol}^{-1}$ ).

Identifying the limiting reactant is essential -- the excess metal does not appear in the mole calculation.

**Worked example 6 -- combustion, watch J vs kJ**

Burning 0.720 g of methanol,  $\text{CH}_3\text{OH}$  ( $M = 32.04 \text{ g mol}^{-1}$ ), raises the temperature of 100.0 g of water by 14.5 °C. Find  $\Delta H_c$ .

$q = 100.0 \times 4.18 \times 14.5 = 6061 \text{ J}$ . Convert now: 6061 J = 6.061 kJ.

$n(\text{methanol}) = 0.720 / 32.04 = 0.02247 \text{ mol}$ .

$\Delta H_c = - 6.061 / 0.02247 = -270 \text{ kJ mol}^{-1}$ .

If you forget to convert J to kJ you get an answer 1000 times too large ( $-270000$ ). Always carry the unit through the division.

**Worked example 7 -- using an extrapolated temperature**

In a displacement experiment the measured peak temperature is 28.9 °C, but extrapolating the cooling curve back to the moment of mixing gives a corrected maximum of 30.5 °C. The starting temperature was 20.0 °C and 50.0 g of solution contained 0.0100 mol of the limiting reactant. Compare the two  $\Delta H$  values.

Using the raw peak:  $\Delta T = 28.9 - 20.0 = 8.9$  °C;  $q = 50.0 \times 4.18 \times 8.9 = 1860 \text{ J}$ ;  $\Delta H = - 1.860 / 0.0100 = -186 \text{ kJ mol}^{-1}$ .

Using the corrected maximum:  $\Delta T = 30.5 - 20.0 = 10.5$  °C;  $q = 50.0 \times 4.18 \times 10.5 = 2195 \text{ J}$ ;  $\Delta H = - 2.195 / 0.0100 = -219 \text{ kJ mol}^{-1}$ .

The extrapolated value is more exothermic and closer to the true figure, because it compensates for the heat lost while the reaction was still going on.

**Worked example 8 -- (HL) allowing for the calorimeter**

**(HL)** When 0.0500 mol of a reaction releases heat into 100.0 g of solution, the temperature rises by 7.00 °C. The calorimeter itself has a heat capacity of 45 J K<sup>-1</sup>. Find  $\Delta H$ , first ignoring and then including the calorimeter.

Water only:  $q = 100.0 \times 4.18 \times 7.00 = 2926 \text{ J}$ .

Calorimeter also absorbs heat:  $q(\text{cal}) = 45 \times 7.00 = 315 \text{ J}$ .

Total heat released = 2926 + 315 = 3241 J = 3.241 kJ.  $\Delta H = - 3.241 / 0.0500 = -64.8 \text{ kJ mol}^{-1}$ , versus  $-58.5 \text{ kJ mol}^{-1}$  if the calorimeter is ignored.

Including the calorimeter constant removes one assumption and gives a larger (more accurate) magnitude.

## 7. Common pitfalls

- **Sign of  $\Delta H$ .** Temperature up → exothermic →  $\Delta H$  negative. Temperature down → endothermic →  $\Delta H$  positive. The sign of  $\Delta H$  is opposite to the sign of  $\Delta T$ .
- **Mass of solution, not solute.** In  $q = mc\Delta T$ ,  $m$  is the mass of water or solution being heated, never the mass of the fuel or solid that reacted.
- **$\Delta T$  is a difference.** Use final – initial. In K or °C the numerical value of  $\Delta T$  is identical, so no conversion is needed for the difference.
- **Per mole conversion.** Divide the heat by the moles of the *limiting* reactant, or the substance the definition refers to (one mole of fuel, one mole of water for neutralisation).
- **J versus kJ.**  $q$  from  $mc\Delta T$  comes out in joules; enthalpy changes are quoted in kJ mol<sup>-1</sup>. Divide  $q$  by 1000 once, before or after dividing by moles.
- **Significant figures.** Quote  $\Delta H$  to 3 significant figures, matching the precision of the data.

## 8. Quick reference

| Item                    | Statement                                                                                    |
|-------------------------|----------------------------------------------------------------------------------------------|
| Enthalpy change         | $\Delta H = H(\text{products}) - H(\text{reactants})$ ; unit kJ mol <sup>-1</sup>            |
| Exothermic              | Releases heat; surroundings warm; $\Delta H$ negative; products below reactants              |
| Endothermic             | Absorbs heat; surroundings cool; $\Delta H$ positive; products above reactants               |
| Bond energetics         | Breaking bonds absorbs energy; making bonds releases energy                                  |
| Standard conditions     | 100 kPa, stated T (usually 298 K), 1 mol dm <sup>-3</sup> solutions; symbol $\Delta H^\circ$ |
| Calorimetry             | $q = mc\Delta T$ , with $c(\text{water}) = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$             |
| Per mole                | $\Delta H = - q / n$ ( $q$ in kJ, $n$ in mol)                                                |
| Neutralisation (strong) | $\Delta H_{\text{neut}} \approx -57 \text{ kJ mol}^{-1}$ per mole of water formed            |

Some standard values worth recognising (298 K); use them to sense-check your own experimental answers.

| Substance / reaction                               | Change                         | Value / $\text{kJ mol}^{-1}$ |
|----------------------------------------------------|--------------------------------|------------------------------|
| Methane, $\text{CH}_4(\text{g})$                   | $\Delta H^\circ_{\text{c}}$    | −891                         |
| Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$ | $\Delta H^\circ_{\text{c}}$    | −1367                        |
| Methanol, $\text{CH}_3\text{OH}(\text{l})$         | $\Delta H^\circ_{\text{c}}$    | −726                         |
| Water, $\text{H}_2\text{O}(\text{l})$              | $\Delta H^\circ_{\text{f}}$    | −286                         |
| Carbon dioxide, $\text{CO}_2(\text{g})$            | $\Delta H^\circ_{\text{f}}$    | −394                         |
| Strong acid + strong alkali                        | $\Delta H^\circ_{\text{neut}}$ | −57.3                        |
| Dissolving $\text{NH}_4\text{NO}_3(\text{s})$      | $\Delta H^\circ_{\text{sol}}$  | +25.7                        |

## 9. Test yourself

Attempt all eight without notes, then check against the full worked answers. Take  $c(\text{water}) = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$  and assume solution densities of  $1.00 \text{ g cm}^{-3}$  throughout.

- 120 g of water is heated from  $19.0^\circ\text{C}$  to  $61.0^\circ\text{C}$ . Calculate the heat absorbed, in kJ.
- Burning 0.660 g of propan-1-ol,  $\text{C}_3\text{H}_7\text{OH}$  ( $M = 60.10$ ), raises the temperature of 200.0 g of water by  $18.5^\circ\text{C}$ . Find  $\Delta H_{\text{c}}$ .
- $25.0 \text{ cm}^3$  of  $2.00 \text{ mol dm}^{-3}$  HCl is neutralised by  $25.0 \text{ cm}^3$  of  $2.00 \text{ mol dm}^{-3}$  NaOH; the temperature rises by  $13.4^\circ\text{C}$ . Find  $\Delta H_{\text{neut}}$  per mole of water.
- 5.00 g of potassium nitrate,  $\text{KNO}_3$  ( $M = 101.1$ ), dissolves in 100.0 g of water and the temperature falls by  $3.0^\circ\text{C}$ . Find  $\Delta H_{\text{sol}}$ , with its sign.
- Excess magnesium is added to  $50.0 \text{ cm}^3$  of  $0.500 \text{ mol dm}^{-3}$  copper(II) sulfate; the temperature rises by  $25.0^\circ\text{C}$ . Find  $\Delta H$  per mole of  $\text{Cu}^{2+}$ .
- A student's experimental  $\Delta H_{\text{c}}$  for a candle wax is only 40% of the data-book value. State three reasons and one improvement.
- Explain, in terms of system and surroundings, why an endothermic reaction feels cold and has a positive  $\Delta H$ .
- (HL link)** Write the equation, including state symbols, that represents the standard enthalpy of formation of ethanol,  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ , and state why  $\Delta H^\circ_{\text{f}}$  of  $\text{O}_2(\text{g})$  is zero.

## Answers

- $\Delta T = 61.0 - 19.0 = 42.0^\circ\text{C}$ .  $q = 120 \times 4.18 \times 42.0 = 21067 \text{ J} \approx \mathbf{21.1 \text{ kJ}}$ .
- $q = 200.0 \times 4.18 \times 18.5 = 15466 \text{ J} = 15.47 \text{ kJ}$ .  $n = 0.660 / 60.10 = 0.01098 \text{ mol}$ .  $\Delta H_{\text{c}} = -15.47 / 0.01098 = \mathbf{-1409 \text{ kJ mol}^{-1}}$  (data-book  $-2021$ ; heat loss and incomplete combustion account for the shortfall).
- mass = 50.0 g;  $q = 50.0 \times 4.18 \times 13.4 = 2801 \text{ J} = 2.801 \text{ kJ}$ .  $n(\text{H}_2\text{O}) = 0.0250 \times 2.00 = 0.0500 \text{ mol}$ .  $\Delta H_{\text{neut}} = -2.801 / 0.0500 = \mathbf{-56.0 \text{ kJ mol}^{-1}}$ .

4.  $q = 100.0 \times 4.18 \times 3.0 = 1254 \text{ J} = 1.254 \text{ kJ}$  (absorbed; temperature fell).  $n = 5.00 / 101.1 = 0.04946 \text{ mol}$ .  $\Delta H_{\text{sol}} = +1.254 / 0.04946 = \mathbf{+25.4 \text{ kJ mol}^{-1}}$  (positive: endothermic).

5. mass = 50.0 g;  $q = 50.0 \times 4.18 \times 25.0 = 5225 \text{ J} = 5.225 \text{ kJ}$ .  $n(\text{Cu}^{2+}) = 0.0500 \times 0.500 = 0.0250 \text{ mol}$  (Mg in excess).  $\Delta H = -5.225 / 0.0250 = \mathbf{-209 \text{ kJ mol}^{-1}}$ .

6. Reasons: heat lost to the surroundings and to the apparatus; incomplete combustion (soot lowers the energy released); evaporation of wax or absorption of heat by the calorimeter; non-standard conditions. Improvement: shield the flame with a draught shield and insulate/lag the calorimeter, or use a bomb calorimeter.

7. The reacting chemicals (the system) absorb heat energy from the surroundings (the water and container), so the surroundings lose energy and cool -- the mixture feels cold. Because the products end up with more enthalpy than the reactants,  $\Delta H = H(\text{products}) - H(\text{reactants})$  is positive.

8.  $2\text{C}(\text{s, graphite}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$ . One mole of ethanol is formed from its elements in their standard states.  $\Delta H^\circ_f$  of  $\text{O}_2(\text{g})$  is zero because  $\text{O}_2(\text{g})$  is an element already in its standard state, so no formation reaction (and no enthalpy change) is needed to make it.