Chemical energetics

Enthalpy changes and their standard definitions, reaction pathway diagrams, bond energies, calorimetry calculations, and Hess's law cycles.

5.1 Enthalpy change, ΔH

Chemical reactions are accompanied by **enthalpy changes**, ΔH, measured at constant pressure.

- **Exothermic:** heat is given out, ΔH is **negative** and the surroundings warm up.
- **Endothermic:** heat is taken in, ΔH is **positive** and the surroundings cool.

Standard conditions in this syllabus are **298 K and 101 kPa**, shown by the symbol $\ominus$, with each substance in its standard state.

Reaction pathway diagrams

Plot enthalpy against the progress of the reaction. The reactants and products sit at different levels, the difference being ΔH. The height from the reactants to the top of the peak is the **activation energy**, E_a. For an exothermic reaction the products are lower than the reactants.

Standard enthalpy changes

Name	Symbol	Definition (standard conditions)
Reaction	$\Delta H_r^{\ominus}$	The enthalpy change when the amounts shown in the equation react
Formation	$\Delta H_f^{\ominus}$	One mole of a compound formed from its elements in their standard states
Combustion	$\Delta H_c^{\ominus}$	One mole of a substance completely burnt in excess oxygen
Neutralisation	$\Delta H_{neut}^{\ominus}$	One mole of water formed by the reaction of an acid with an alkali

$\Delta H_f^{\ominus}$ of an element in its standard state is zero. The neutralisation of a strong acid by a strong alkali is about −57 kJ mol^{-1}.

Bond energies

Energy transfers happen because **bonds are broken (endothermic, ΔH positive)** and **bonds are made (exothermic)**.

$$\Delta H_r = \sum(\text{bond energies broken}) - \sum(\text{bond energies made})$$

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Some bond energies are **exact** (for diatomic molecules such as $H-H$) and some are **averages** over different compounds (such as $C-H$), so answers that use averages are approximate.

> **TRY IT**
>
> Use bond energies (C–H 410, Cl–Cl 244, C–Cl 340, H–Cl 431 kJ mol^{-1}) to find ΔH for $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$.

Broken: $410 + 244 = 654$. Made: $340 + 431 = 771$. $\Delta H = 654 - 771 = -117$ kJ mol^{-1}.

Calorimetry

The energy transferred to the water or solution is

$$q = mc\Delta T \qquad \Delta H = -\frac{mc\Delta T}{n}$$

where q is in J, m is the mass of water or solution (g), $c = 4.18$ J g^{-1} K^{-1} and n is the amount in moles of the limiting reagent. Give ΔH in kJ mol^{-1} (divide q by 1000). The sign is **negative** if the temperature rises.

> **TRY IT**
>
> 25.0 cm^3 of 1.00 mol dm^{-3} HCl is mixed with 25.0 cm^3 of 1.00 mol dm^{-3} NaOH. The temperature rises by 6.5 °C. Find ΔH_{neut}.

$q = 50.0 \times 4.18 \times 6.5 = 1358$ J and $n = 0.0250$ mol. $\Delta H = -1.358/0.0250 = -54$ kJ mol^{-1} (2 s.f.). Heat lost to the surroundings makes this less exothermic than the true value.

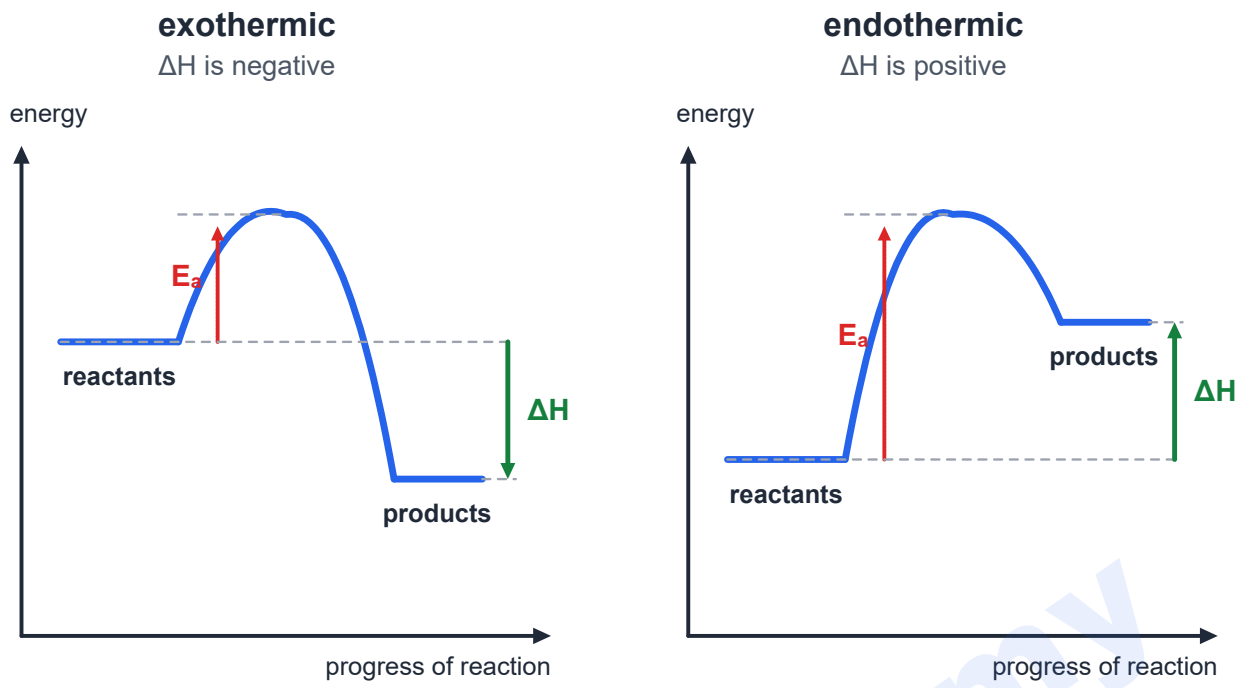
System, surroundings and sign conventions

The reacting chemicals are the system; the solution, container and air receiving or supplying heat are surroundings. If a solution warms during a reaction, it has gained heat and the reacting system has lost it: $q_{reaction} = -q_{surroundings}$. This is why a positive measured temperature rise gives a negative reaction enthalpy. Endothermic reactions cool their surroundings because energy is transferred into the system.

An enthalpy value belongs to the equation **as written**. Reversing the equation reverses the sign; doubling every coefficient doubles the enthalpy. Standard formation of one mole of water is $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, not the doubled equation. The physical state matters: forming water vapour and forming liquid water have different enthalpy changes.

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Reading an energy profile



E_a is the energy needed to start the reaction; ΔH is the difference between the energy of the products and the reactants

On a profile, the vertical axis is enthalpy and the horizontal axis is reaction progress, not elapsed time. Activation energy is measured from the reactant level to the transition-state peak. The reverse activation energy is measured from the product level to the same peak. For a forward reaction with $E_a = 80$ kJ mol^{-1} and $\Delta H = -30$ kJ mol^{-1}, the reverse barrier is $80 - (-30) = 110$ kJ mol^{-1}. A catalyst lowers barriers without changing either endpoint or ΔH.

> **TRY IT**
>
> The forward activation energy is 65 kJ mol^{-1} and the reaction enthalpy is +20 kJ mol^{-1}. Find the reverse activation energy.

Answer: Products lie 20 kJ mol^{-1} above reactants, so the reverse barrier is $65 - 20 = 45$ kJ mol^{-1}. The reverse reaction is exothermic by 20 kJ mol^{-1}.

Calorimetry: amounts, assumptions and uncertainty

For solution calorimetry, approximate the reacting mixture's density as 1.00 g cm^{-3} and its specific heat capacity as water's only when appropriate. Use the **combined solution mass**, rather than the volume of just one reagent. The divisor must match the enthalpy definition: for neutralisation use moles of water formed; for a stated reaction use the corresponding amount of reaction. A polyprotic acid may form more than one mole of water per mole of acid.

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Worked example: mix 50.0 cm^3 of 0.500 mol dm^{-3} HCl with 25.0 cm^3 of 1.00 mol dm^{-3} NaOH. Each supplies 0.0250 mol reactive ions, so 0.0250 mol water forms. For a 4.00 K rise, $q = 75.0(4.18)(4.00) = 1254$ J. Thus $\Delta H_{neut} = -1.254/0.0250 = -50.2$ kJ mol^{-1}. Dividing by 0.0750 mol because that is the total volume would have no chemical justification.

Heat loss, heat absorbed by the cup and incomplete reaction can reduce the observed temperature rise. A lid and insulation reduce energy exchange; a temperature–time extrapolation can estimate the temperature at the mixing time. Stirring helps obtain a representative temperature. Repeating improves assessment of random variation but does not automatically remove systematic heat loss. In combustion calorimetry, incomplete combustion and evaporation of fuel also affect the inferred energy per mole.

> **TRY IT**
>
> A reaction releases 2.09 kJ into 100 g water. Estimate the temperature rise using $c = 4.18$ J g^{-1} K^{-1}.

Answer: $\Delta T = q/(mc) = 2090/(100 \times 4.18) = 5.00$ K. Convert kilojoules to joules before using this heat-capacity value.

Using bond energies without double-counting

Draw the reactant and product structures, identify which bonds change, and count their coefficients. Bonds unchanged on both sides cancel. All bond breaking consumes energy, even in a strongly exothermic reaction; the exothermic overall result arises because making the new bonds releases more energy than breaking the old bonds requires.

Worked example: for $H_2 + Br_2 \rightarrow 2HBr$, illustrative gaseous bond energies are H–H 436, Br–Br 193 and H–Br 366 kJ mol^{-1}. Broken bonds require $436 + 193 = 629$; made bonds release $2(366) = 732$. Therefore $\Delta H \approx -103$ kJ mol^{-1}. The calculation refers to gaseous bond data; a liquid bromine starting state would require appropriate additional state-change information.

5.2 Hess's law

Hess's law: the total enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions are the same. It follows from the conservation of energy.

Use it to find enthalpy changes that **cannot be measured directly**.

- From formation data: $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$.
- From combustion data: $\Delta H_r = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$.
- Or draw an **energy cycle** and follow the arrows, reversing the sign of any step taken against its arrow. Bond energy data can be used in a cycle too.

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> **TRY IT**
>
> Find ΔH_f of C_2H_6 from ΔH_c values: C(graphite) −394, H_2 −286, C_2H_6 −1560 kJ mol^{-1}.

For $2C + 3H_2 \rightarrow C_2H_6$: $\Delta H_f = 2(-394) + 3(-286) - (-1560) = -86$ kJ mol^{-1}.

Following a cycle rather than guessing signs

Choose a common starting point or common endpoint and write two routes between the same states. A formation cycle starts with elements and goes to reactants or products. A combustion cycle sends both sides to the same fully oxidised products. When traversing an arrow backwards, change its sign; when multiplying a reaction, multiply its enthalpy by the same factor.

Worked example — formation data: for $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, use illustrative $\Delta H_f(CO) = -111$ and $\Delta H_f(CO_2) = -394$ kJ mol^{-1}. Oxygen in its standard state has zero formation enthalpy. Hence $\Delta H_r = -394 - (-111) = -283$ kJ mol^{-1}. An element's formation enthalpy is zero by definition; that does not mean it contains no energy or has no entropy.

> **TRY IT**
>
> For $A \rightarrow B$, formation enthalpies are −120 and −200 kJ mol^{-1} respectively. Find ΔH for $2B \rightarrow 2A$.

Answer: $A \rightarrow B$ has $-200 - (-120) = -80$ kJ mol^{-1}. Reversing and doubling gives **+160 kJ mol^{-1}**. Both operations must be applied.

Chapter check: identify the amount to which the enthalpy refers, show states, keep joules and kilojoules consistent, and use the same endpoints in a cycle. Further energy cycles, entropy and feasibility appear in **A Level energetics**.

References and further reading

Scope follows section 5 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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