Energetics

Enthalpy changes and their standard definitions, enthalpy level diagrams, calorimetry, Hess's law cycles, and bond enthalpies.

Enthalpy change

The **enthalpy change**, ΔH, is the heat energy change measured at **constant pressure**. By convention:

- **exothermic** reactions release heat to the surroundings: ΔH is **negative**, and the temperature of the surroundings rises.
- **endothermic** reactions take in heat: ΔH is **positive**, and the temperature of the surroundings falls.

Standard conditions are a pressure of 100 kPa and a stated temperature, usually 298 K, with each substance in its standard state. The symbol $\Delta H^{\ominus}$ is used.

Enthalpy level diagrams

An enthalpy level diagram has enthalpy on the vertical axis. For an exothermic reaction the products are lower than the reactants and ΔH is shown as a downward arrow; for an endothermic reaction the products are higher and the arrow is upward.

Standard enthalpy changes

Name	Symbol	Definition (all under standard conditions)
Reaction	$\Delta_r H$	The enthalpy change when the amounts of reactants in the equation react to give the products
Formation	$\Delta_f H$	The enthalpy change when **one mole of a compound** forms from its **elements in their standard states**
Combustion	$\Delta_c H$	The enthalpy change when **one mole of a substance burns completely in oxygen**
Neutralisation	$\Delta_{neut} H$	The enthalpy change when an acid and an alkali react to form **one mole of water**
Atomisation	$\Delta_{at} H$	The enthalpy change when **one mole of gaseous atoms** forms from the element in its standard state

The enthalpy change of formation of an element in its standard state is zero. Remember to

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write the elements as they are at 298 K: $O_2(g)$, $Br_2(l)$, C (graphite).

Measuring enthalpy changes

The energy transferred to a known mass of water or solution is

$$q = mc\Delta T$$

where q is in J, m is the mass of solution in g, c is the specific heat capacity (4.18 J g^{-1} °C^{-1} for water) and ΔT is the temperature change in °C.

$$\Delta H = -\frac{q}{n} \text{ (in kJ mol}^{-1}\text{, with } q \text{ in kJ)}$$

TRY IT

50.0 cm^3 of 1.00 mol dm^{-3} HCl is mixed with 50.0 cm^3 of 1.00 mol dm^{-3} NaOH. The temperature rises by 6.8 °C. Find $\Delta_{neut}H$. (Assume the density of the solution is 1.00 g cm^{-3}.)

$q = 100 \times 4.18 \times 6.8 = 2842$ J. Moles of water $= 0.0500$. $\Delta H = -2.842/0.0500 = -56.8$ kJ mol^{-1}.

Experiment types

- **Solutions in an insulated container** (polystyrene cup with a lid): mix reagents and record the temperature over time.
- **Combustion** (spirit burner and a copper calorimeter): burn a fuel to heat a known mass of water.

Evaluating the experiment

Sources of error are heat lost to the surroundings (the main one), incomplete combustion, heat absorbed by the container, evaporation of fuel, and the use of a thermometer with limited resolution. Improve by insulating and using a lid, stirring, and using a draught shield. For solutions, plot temperature against time, then **extrapolate** the cooling line back to the time of mixing to estimate the maximum temperature rise that would have occurred with no heat loss (a **cooling curve correction**).

Hess's law

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

Using enthalpy of formation

$$\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$$

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Using enthalpy of combustion

$\Delta_r H = \sum \Delta_c H(\text{reactants}) - \sum \Delta_c H(\text{products})$

> **TRY IT**
>
> Use these data to find $\Delta_r H$ for $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$: $\Delta_f H$ values $C_2H_4 = +52$, $H_2O(g) = -242$, $C_2H_5OH(g) = -235$ kJ mol^{-1}.

$\Delta_r H = (-235) - (+52 + -242) = -235 + 190 = -45$ kJ mol^{-1}.

Draw the cycle with arrows: elements at the bottom, reactants and products above. Follow the direction of the arrow when adding and reverse the sign if you go against it.

> **NOTE**
>
> **Core Practical 2** finds an enthalpy change that cannot be measured directly using Hess's law. For example, the decomposition of calcium carbonate: measure the temperature rise on adding acid to $CaCO_3$ and to CaO separately, then combine the two enthalpy changes.

Bond enthalpy

The **bond enthalpy** is the enthalpy change when **one mole of a covalent bond is broken in the gas phase**. It is always endothermic. The **mean bond enthalpy** is the average value over a range of compounds with the same bond (for example C–H in different molecules).

$\Delta_r H = \sum(\text{bonds broken}) - \sum(\text{bonds made})$

> **TRY IT**
>
> Calculate ΔH for $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (all gases) using mean bond enthalpies in kJ mol^{-1}: C–H 413, O=O 497, C=O 805, O–H 464.

Bonds broken: $4(413) + 2(497) = 2646$. Bonds made: $2(805) + 4(464) = 3466$. $\Delta H = 2646 - 3466 = -820$ kJ mol^{-1}.

Mean bond enthalpies can be found from a known $\Delta_r H$ and the other bond enthalpies.

Limitations

Mean values differ from the actual bond enthalpy in a specific molecule, and the method only applies to **gaseous** species. Answers from bond enthalpies are less accurate than those from formation data.

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Bond enthalpy also gives an indication of which bond breaks first and how fast a reaction proceeds. A weaker bond breaks more easily, which is why the C–I bond in iodoalkanes reacts faster than the C–Cl bond in chloroalkanes.

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