Chemical energetics

A-Level Chemistry

Enthalpy change, ΔH

Burning fuel is exothermic, releasing energy to the surroundings.

An instant cold pack uses an endothermic reaction that takes in heat.

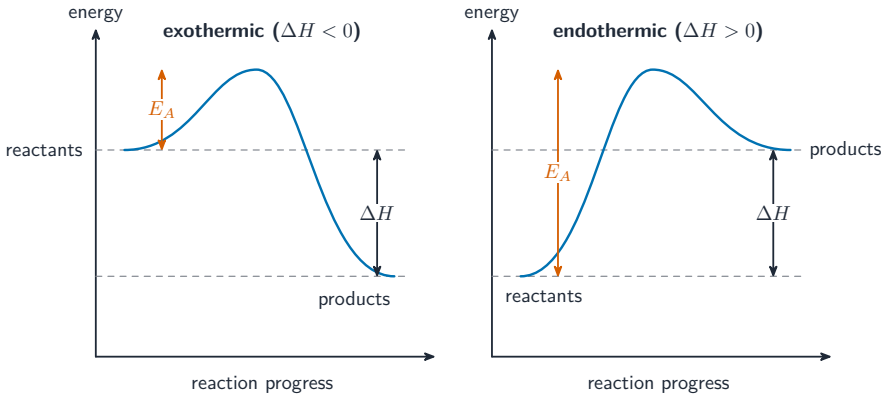
Every chemical reaction takes in or gives out energy. This energy change, measured at constant pressure, is the **enthalpy change** 焓变, with symbol ΔH.

- in an **exothermic** 放热 reaction the system gives out heat, so the products have less energy than the reactants and ΔH is **negative**.
- in an **endothermic** 吸热 reaction the system takes in heat, so the products have more energy than the reactants and ΔH is **positive**.

Reaction pathway diagrams

A **reaction pathway diagram** 反应路径图 shows the energy of the reactants and products, and the energy "hill" between them. The height of the hill is the **activation energy** 活化能 — the least energy the particles need before they can react.

- exothermic: products sit **lower** than reactants ($\Delta H < 0$).
- endothermic: products sit **higher** than reactants ($\Delta H > 0$).

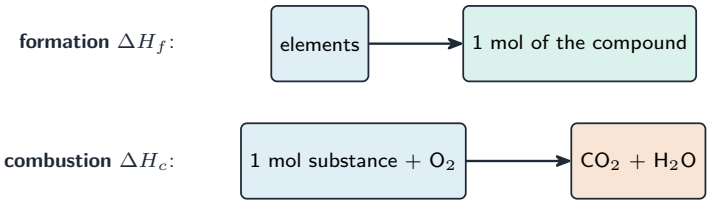


Exothermic reactions end lower than they start ($\Delta H < 0$); endothermic reactions end higher ($\Delta H > 0$)

Standard conditions and types of enthalpy change

Energy values are compared under **standard conditions** 标准条件: 298 K and 101 kPa, shown by the symbol $^{\ominus}$. Each substance is in its normal physical state at those conditions.

Symbol	Name	Definition (per mole, under standard conditions)
$\Delta H_r^{\ominus}$	**enthalpy change of reaction** 反应焓变	for the amounts shown in the equation
$\Delta H_f^{\ominus}$	**enthalpy change of formation** 生成焓变	one mole of a compound forms from its elements
$\Delta H_c^{\ominus}$	**enthalpy change of combustion** 燃烧焓变	one mole of a substance burns completely in oxygen
$\Delta H_{\text{neut}}^{\ominus}$	**enthalpy change of neutralisation** 中和焓变	one mole of water forms from an acid and an alkali



Don't confuse them: formation builds 1 mol of a compound from its elements; combustion burns 1 mol of a substance in oxygen

Energy from breaking and making bonds

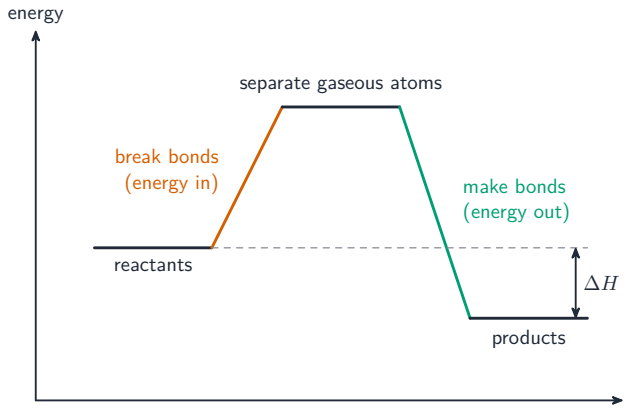
During a reaction, old bonds break and new bonds form. **Breaking** a bond needs energy (endothermic); **making** a bond releases energy (exothermic). The enthalpy change of the reaction is the difference between the two:

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

The **bond energy** 键能 is the energy needed to break one mole of a particular bond in the gas state, so it is always positive. Some bond energies are exact (for one specific molecule); others are averages taken over many different molecules, so calculations using them are only approximate.

Worked example. Use bond energies to find ΔH for $H_2 + Cl_2 \rightarrow 2HCl$. Bond energies (kJ mol^{-1}): H–H = 436, Cl–Cl = 242, H–Cl = 431.

$$\Delta H = \sum(\text{broken}) - \sum(\text{made}) = (436 + 242) - (2 \times 431) = 678 - 862 = -184 \text{ kJ mol}^{-1}.$$



Breaking bonds takes energy in; making bonds gives energy out. ΔH is the difference between the two

Measuring enthalpy change in the lab

When a reaction heats up (or cools down) a known mass of water or solution, the heat transferred is:

$$q = mc\Delta T$$

where m is the mass, c is the **specific heat capacity** 比热容 (how much energy raises 1 g by 1 K), and ΔT is the temperature change. The enthalpy change per mole is then:

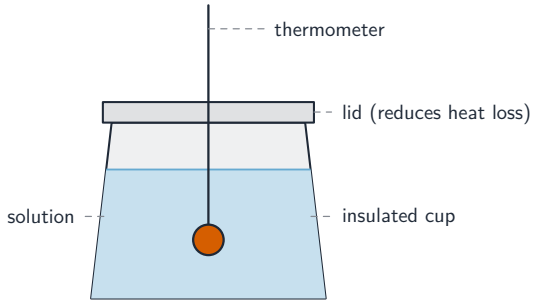
$$\Delta H = -\frac{mc\Delta T}{n}$$

The minus sign makes ΔH negative when the temperature rises (an exothermic reaction).

Worked example. Burning 0.50 g of methanol ($M_r = 32$) raises the temperature of 100 g of water by 18 °C. Find the enthalpy change of combustion per mole. ($c = 4.18$ J g^{-1} K^{-1}.)

The heat released is $q = mc\Delta T = 100 \times 4.18 \times 18 = 7520$ J. The amount burnt is $n = 0.50/32 = 0.0156$ mol, so

$$\Delta H_c = -\frac{q}{n} = -\frac{7520}{0.0156} \approx -480 \text{ kJ mol}^{-1}.$$

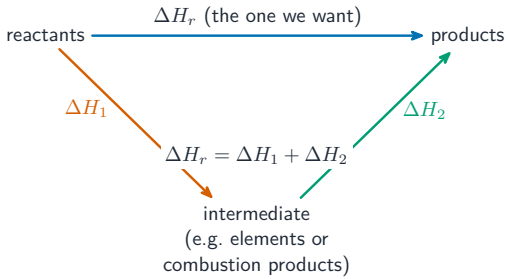


An insulated cup and a thermometer measure the temperature change of a known mass of solution

Hess's law

Hess's law 盖斯定律 says that the total enthalpy change for a reaction is the same, no matter which route you take from reactants to products. This is because energy is conserved.

This lets you draw an **energy cycle** 能量循环: link the reactants and products by a direct step and by an indirect route, then add the steps so that both routes give the same total.



The direct route equals the indirect route, so $\Delta H_r = \Delta H_1 + \Delta H_2$

Hess's law is useful in two ways:

- it lets you find an enthalpy change that you **cannot** measure directly (for example, the formation of a compound that forms slowly or with side reactions).
- it lets you calculate ΔH_r from bond energy data, or from formation or combustion data given in the question.

Exam tips

- Define each enthalpy change with its **exact standard conditions** (e.g. combustion = one mole burned completely in excess oxygen).
- Use $\Delta H = \sum$(bonds broken) $- \sum$(bonds made); breaking is endothermic (+), making is exothermic (−) — getting the sign the wrong way round is the classic error.
- In $q = mc\Delta T$ use the mass of the **water/solution**, then divide by moles and add the minus sign for an exothermic reaction.
- Draw **Hess cycles** with arrows the same way round, follow the alternative route, and always give ΔH a sign and units (kJ mol^{-1}).