Chemical energetics

A-Level Chemistry

Enthalpy change, ΔH

Burning fuel is exothermic, releasing energy to the surroundings.

Image: Jason Woodhead, CC BY 2.0 (commons.wikimedia.org)

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

Image: photo: Qurren (talk) Taken with Canon PowerShot G9 X, CC BY-SA 4.0 (commons.wikimedia.org)

Every chemical reaction takes in or gives out energy. This energy change, measured at

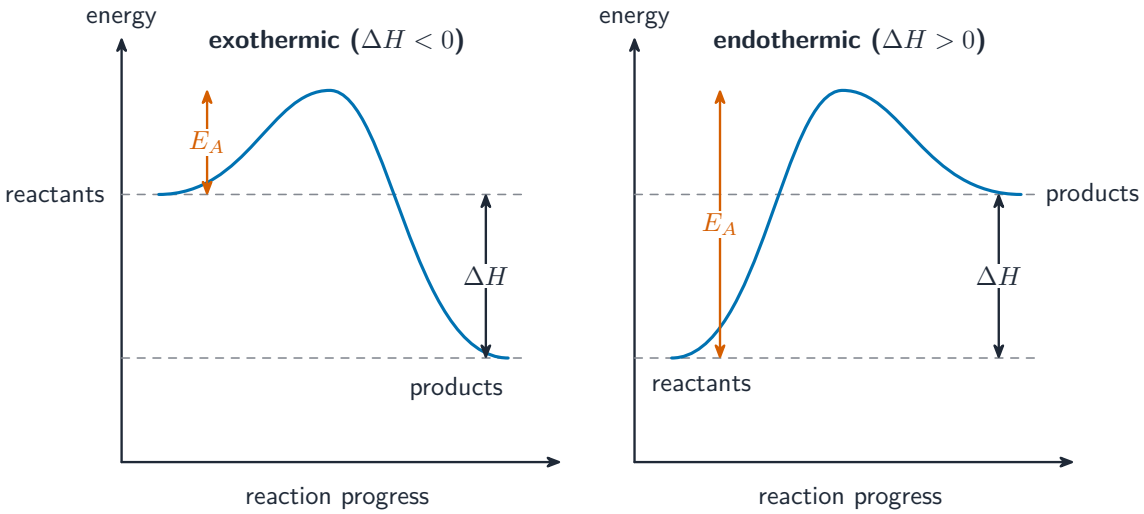
constant pressure, is the **enthalpy change** 焓变, with symbol ΔH.

- 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 ($\Delta H > 0$).

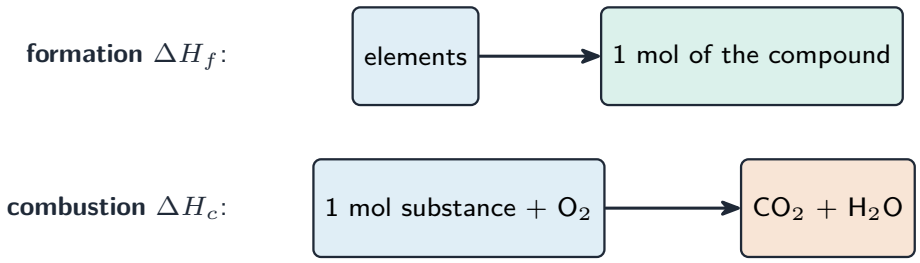


Exothermic reactions end lower than they start ($\Delta H < 0$); endothermic reactions end higher ($\Delta H > 0$)

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

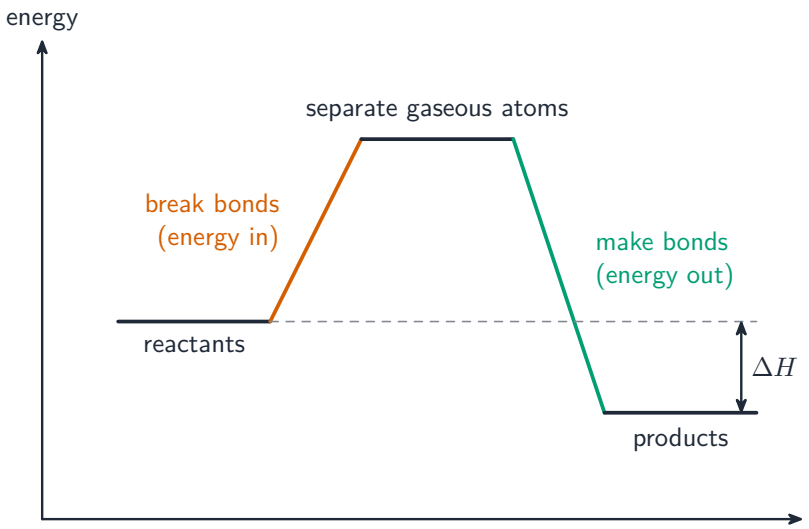
During a reaction, old bonds break and new bonds form. **Breaking** a bond needs energy (endothermic); **making** a bond releases energy (exothermic). The enthalpy change of the reaction is the difference between the two:

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

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:

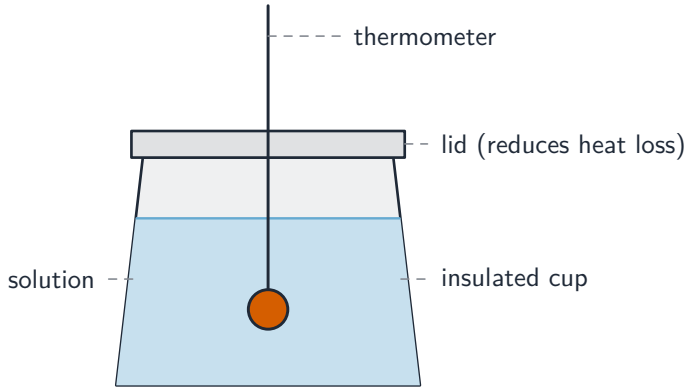
$$\Delta H = -\frac{mc\Delta T}{n}$$

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

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

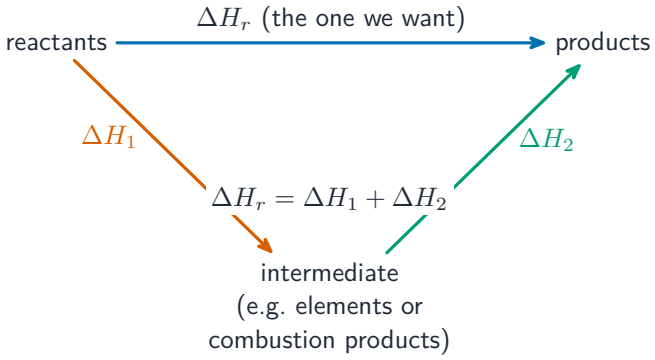


An insulated cup and a thermometer measure the temperature change of a known mass of solution

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}).