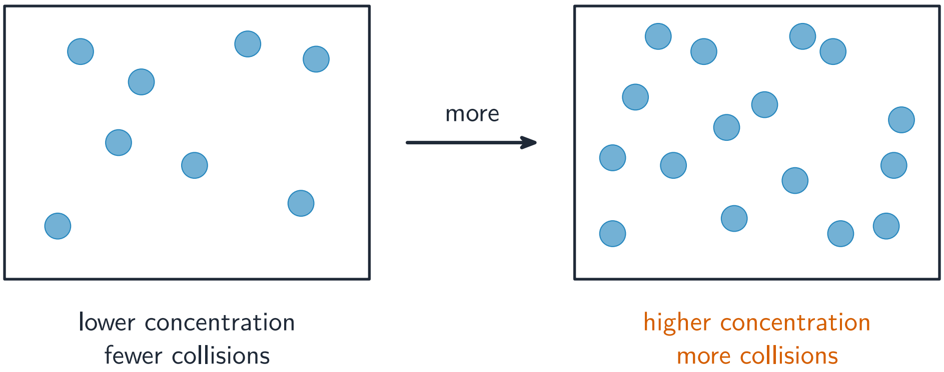
Kinetics

AP Chemistry

How Fast a Reaction Goes

Kinetics 动力学 studies **reaction rate** 反应速率–how fast reactants become products. Rate is the change in concentration per unit time, and it typically **decreases** as reactants are used up. Rate rises with higher concentration, higher temperature, greater surface area, and a catalyst.



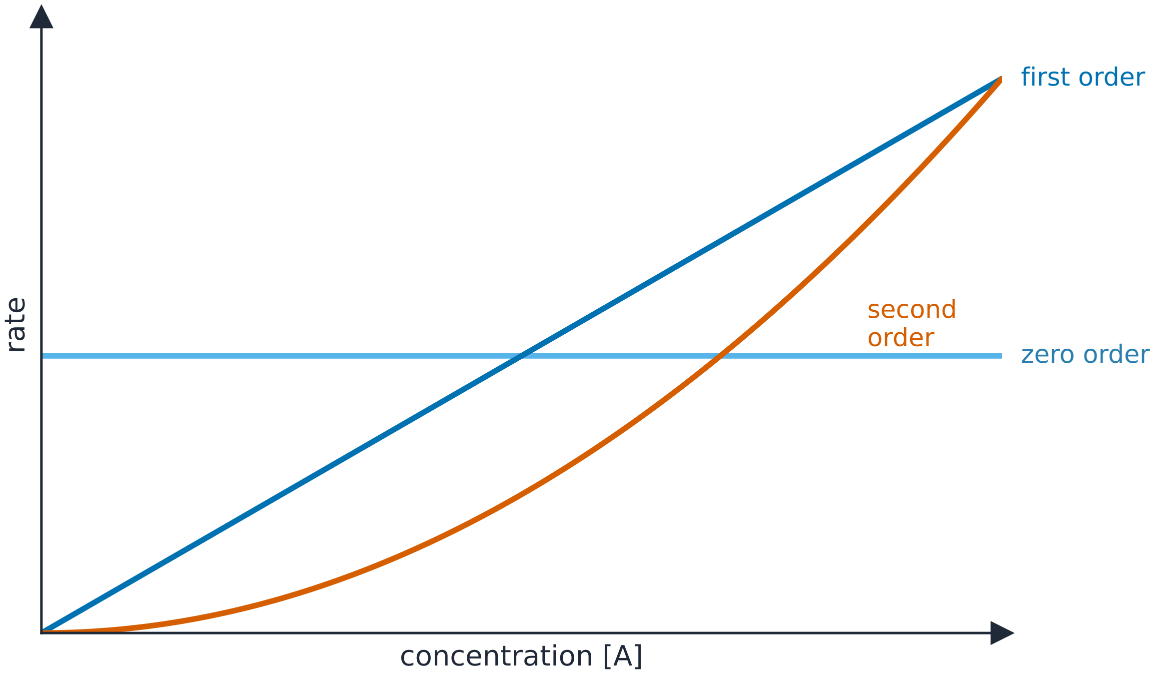
More particles in the same volume collide more often, so the rate rises

Writing the Rate Law

The **rate law** 速率方程 relates rate to reactant concentrations:

$$\text{rate} = k[\text{A}]^m[\text{B}]^n,$$

where k is the **rate constant** 速率常数 and m, n are the **orders** 级数. Orders are found **experimentally** (not from the balanced coefficients) by seeing how the rate changes when you change one concentration at a time.

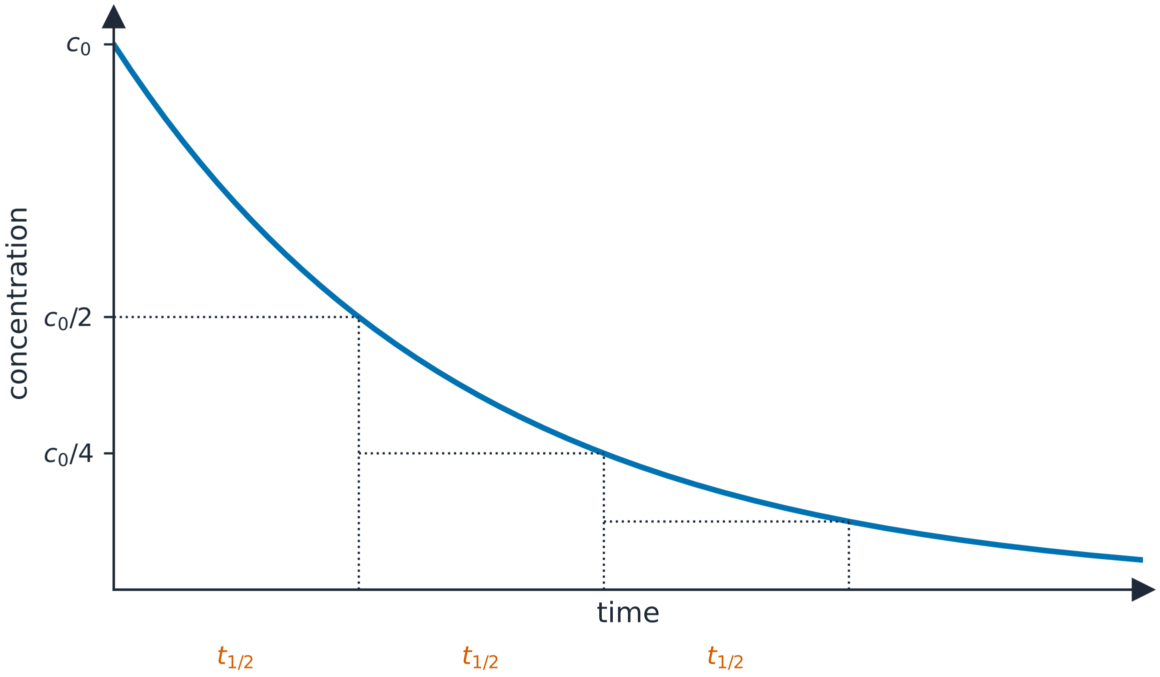


Rate against concentration for zero-, first-, and second-order reactions

Worked example. In experiments, doubling [A] makes the rate **four times** larger, while doubling [B] leaves the rate unchanged. So the reaction is **second order** in A ($2^2 = 4$) and **zero order** in B, giving rate $= k[\mathrm{A}]^2$. The overall order is $2 + 0 = 2$. Never read the orders off the balanced coefficients –only experiment gives them.

Concentration Over Time

The **integrated rate laws** describe how concentration falls with time and give straight-line tests:



A first-order reaction has a constant half-life

- **Zero order:** [A] vs t is linear.
- **First order:** $\ln[\mathrm{A}]$ vs t is linear; constant **half-life** 半衰期.
- **Second order:** $\frac{1}{[\mathrm{A}]}$ vs t is linear.

Whichever plot is straight tells you the order and gives k from its slope.

Worked example. A first-order reaction has rate constant $k = 0.030\ \mathrm{s}^{-1}$. Its half-life is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.030} = 23\ \mathrm{s},$$

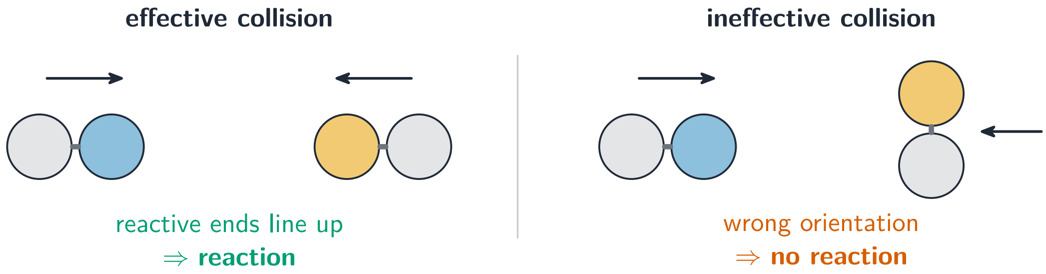
and, being first order, that half-life stays the same no matter how much reactant remains –so after 46 s (2 half-lives) one quarter is left.

The Steps a Reaction Really Takes

A **reaction mechanism** 反应机理 is the sequence of **elementary steps** 基元反应 that actually occur. Their **molecularity** (how many particles collide in a step) sets that step's rate law directly. Species made in one step and used up in a later one are **intermediates** 中间体.

Why Collisions Do or Do Not React

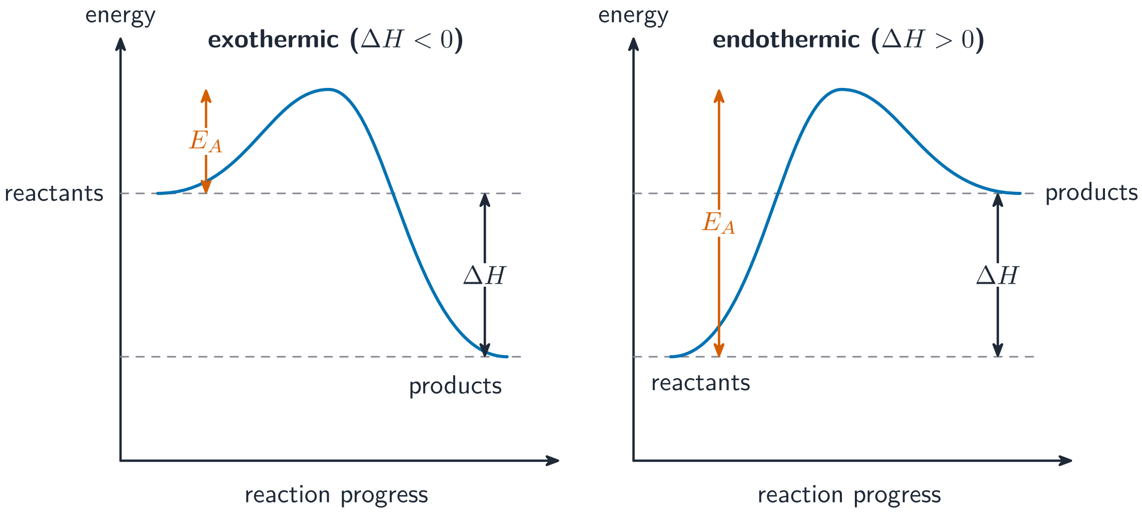
Collision theory 碰撞理论: molecules must collide with enough energy (the **activation energy** 活化能, E_a) and the correct **orientation** to react. Higher temperature means more molecules exceed E_a, so the reaction speeds up sharply.



A collision only reacts with the right orientation and enough energy

Reading an Energy Profile

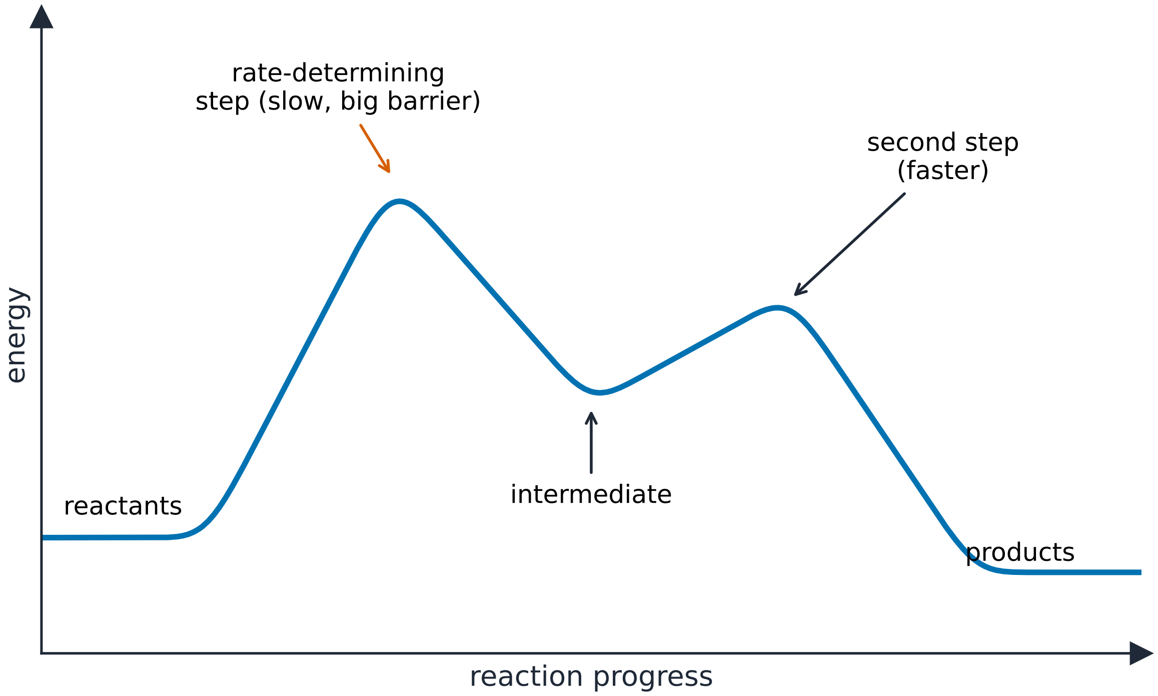
An **energy profile** 能量图 plots energy along the reaction path. The peak is the **transition state** 过渡态; the climb from reactants to the peak is E_a; the difference between reactant and product energies is the enthalpy change ΔH (down for exothermic).



Exothermic reactions end lower than the reactants; endothermic end higher

The Sequence of Steps

In a multi-step mechanism, the steps must **add up** to the overall balanced equation (intermediates cancel). Each step has its own energy hill; the tallest hill is the slowest step.



The slow step with the higher barrier is rate-determining

Finding the Rate Law From a Mechanism

The **rate-determining step** 决速步骤 is the slowest step; its molecularity gives the overall rate law. A valid mechanism must (1) add to the overall reaction and (2) predict the experimentally observed rate law.

Worked example. Suppose the slow (rate-determining) step is the bimolecular collision $NO_2 + NO_2 \rightarrow NO_3 + NO$. Its molecularity gives the rate law directly: rate $= k[NO_2]^2$. If experiment shows exactly this, the proposed mechanism is consistent; if experiment gave rate $= k[NO_2]$, the mechanism would be wrong.

When the First Step Is Fast

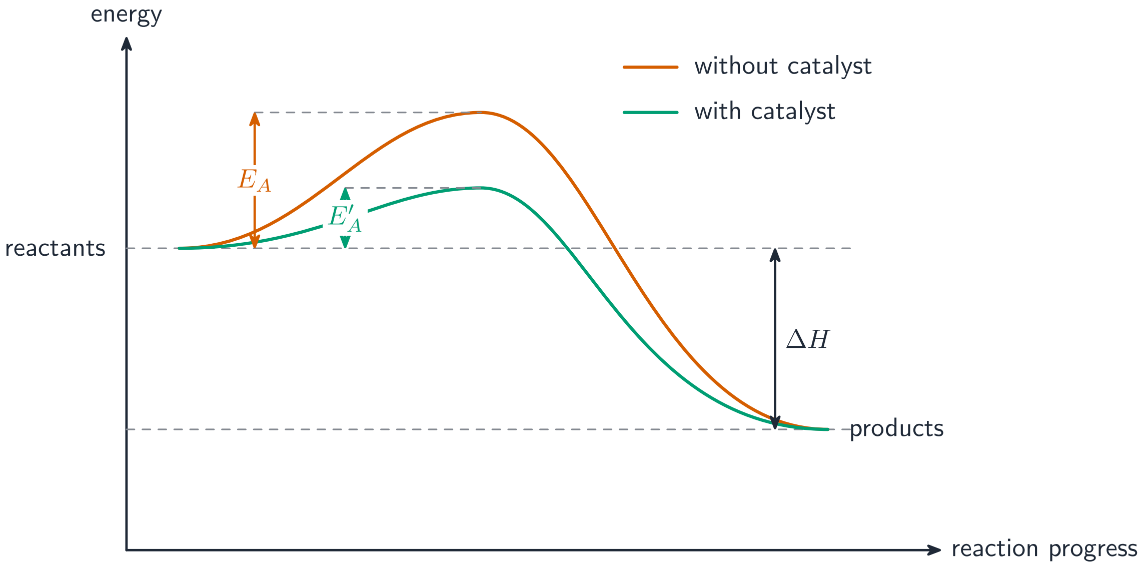
If a fast step precedes the slow one, an intermediate appears in the slow step's rate law. Use the **fast pre-equilibrium** to rewrite that intermediate in terms of reactants, so the final rate law contains only measurable species.

Energy Profiles for Many Steps

A multi-step reaction's profile shows several peaks (one per step) with valleys (intermediates) between them. The **highest** peak is the rate-determining transition state –it controls the overall rate.

How Catalysts Speed Things Up

A **catalyst** 催化剂 speeds a reaction by providing a new pathway with a **lower activation energy**, without being consumed. It does not change ΔH or the equilibrium position –only how fast equilibrium is reached. On an energy profile, a catalyst lowers the peak(s).



A catalyst gives a route with lower activation energy; the enthalpy change is unchanged

Exam tips

- Rate rises with **concentration, temperature, surface area, and a catalyst** — explain each with **collision theory** (more, or more energetic, successful collisions).
- Temperature works mainly by getting **more particles above the activation energy**, not just more collisions.
- **Reaction orders come from experiment**, not the balanced coefficients —see how the rate changes when one concentration is varied.
- On an **energy profile** the hill height is the activation energy and the reactant–product gap is ΔH.
- A **catalyst** lowers the activation energy (a new pathway) but leaves ΔH and the equilibrium position unchanged.