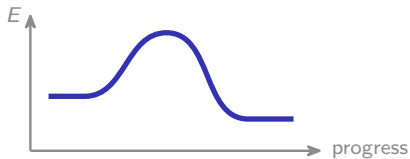
Kinetics

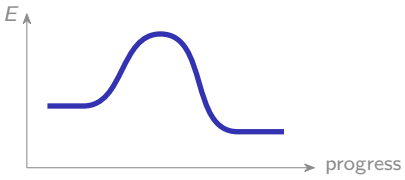
AP Chemistry ▪ Unit 5

AP Chemistry



What we will cover

1. Rate of reaction
2. The rate law
3. Concentration over time
4. Collision theory
5. Energy profiles and Arrhenius
6. Reaction mechanisms
7. Catalysts



1 Rate

Rate of reaction

Kinetics 动力学 asks how fast. The **rate** 反应速率 is a change in concentration over time:

Shared rate

$$\text{rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = +\frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t}$$

Rate is how fast product appears

2 Rate law

The rate law

Found by experiment

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

The **orders** 反应级数 m, n come from data, not the equation.

Method of initial rates 初始速率法: double $[\mathrm{A}]$ – rate $\times 2$ (1st), $\times 4$ (2nd), unchanged (0th).

0 order: k in $\frac{\mathrm{mol}}{\mathrm{L\,s}}$

1st order: k in $\frac{1}{\mathrm{s}}$

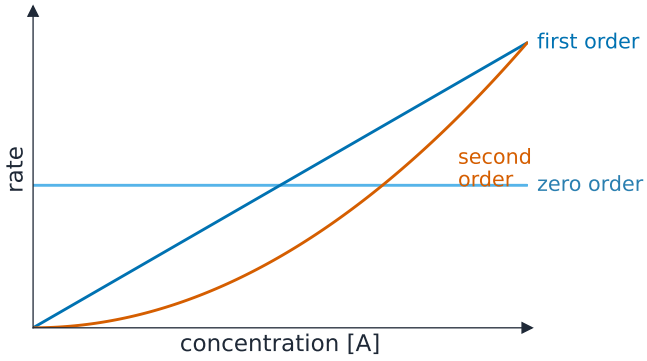
2nd order: k in $\frac{\mathrm{L}}{\mathrm{mol\,s}}$

Rate, and the constant in the rate law

Reaction rate	The **reaction rate** is the change in concentration per unit time – and it is divided by the stoichiometric coefficient so every species gives the same number.
Rate constant	The **rate constant** k in rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$ depends on temperature and on the catalyst – never on concentration.
Its units	k's units follow from the overall order, which is a useful check on an experimentally determined rate law.
Where it comes from	The orders come from experiment – initial rates or an integrated plot – never from the balanced equation.

Arrhenius: $k = Ae^{-E_a/RT}$. Temperature acts on k, which is why a rate law with fixed k describes one temperature only.

Rate against concentration for zero-



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

3 Over time

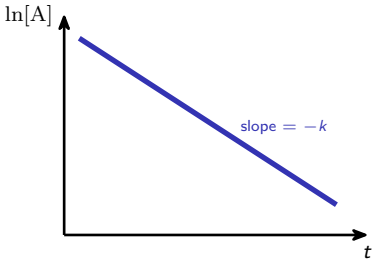
Concentration over time

The **integrated rate law** 积分速率方程 gives concentration at any time – and a straight-line plot that reveals the order:

Which plot is linear?

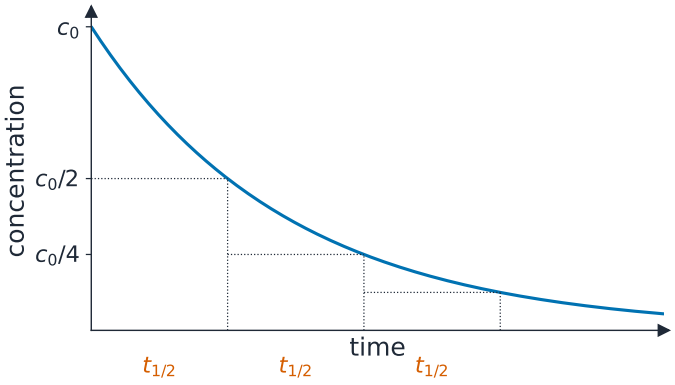
0: $[\mathrm{A}]$ vs t 1st: $\ln[\mathrm{A}]$ vs t 2nd: $1/[\mathrm{A}]$ vs t

First-order **half-life** 半衰期 is constant: $t_{1/2} = \dfrac{0.693}{k}$.



First order: $\ln[\mathrm{A}]$ falls linearly.

A first-order reaction has a constant half-life



A first-order reaction has a constant half-life

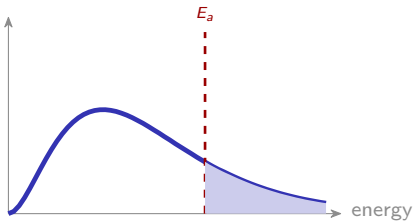
4 Collisions

Collision theory

An **effective collision** 有效碰撞 needs two things:

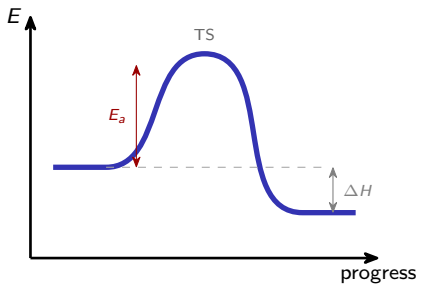
- enough energy – past the **activation energy** 活化能 E_a
- correct **orientation** 取向

> Higher T shifts the Maxwell-Boltzmann tail right – far more particles clear E_a.



5 Energy profile

Energy profiles and Arrhenius



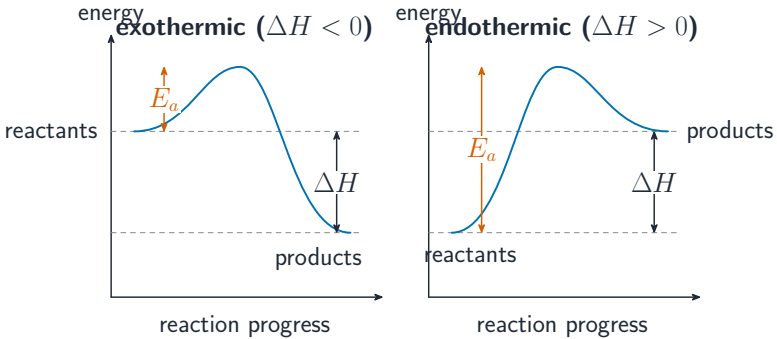
The **transition state** 过渡态 is the peak. Forward E_a = reactants to peak.

Arrhenius equation

$$k = A\, e^{-E_a/(RT)}$$

Larger $E_a \Rightarrow$ smaller k. Products lower = **exothermic** 放热.

Reading an Energy Profile

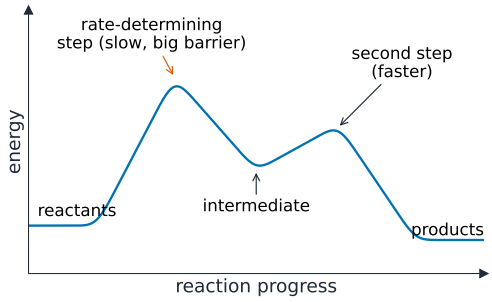


Exothermic reactions end lower than the reactants; endothermic end higher

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.



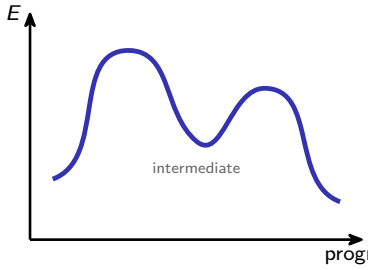
6 Mechanisms

Reaction mechanisms

A **mechanism** 反应机理 is the ordered list of **elementary steps** 基元步骤.

- an **intermediate** 中间体 is made, then used up
- steps must add to the overall equation
- for an elementary step, the rate law comes from its stoichiometry

> The slow **rate-determining step** 决速步 sets the overall rate.



One peak per step; a valley is the intermediate.

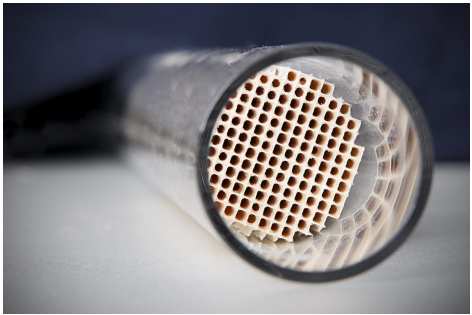
7 Catalysts

Catalysts

A **catalyst** 催化剂 opens a new route with a lower E_a – without being used up.

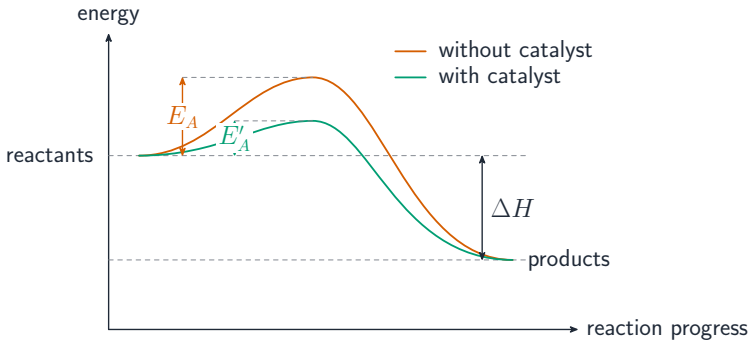
- **homogeneous** 均相催化剂 – same phase
- **heterogeneous** 非均相催化剂 – a solid surface
- **enzyme** 酶 – a biological catalyst

It lowers both barriers equally – so it does *not* change ΔH or the equilibrium, only the speed.



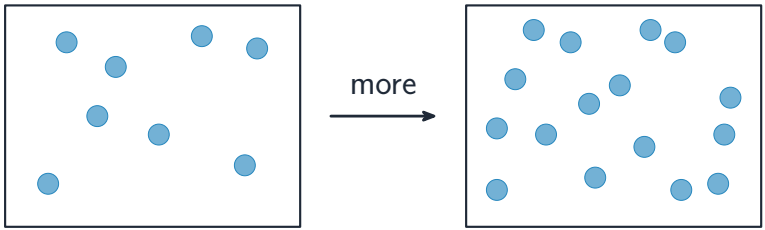
Catalysts open a lower-energy path

How Catalysts Speed Things Up



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

How Fast a Reaction Goes



lower concentration
fewer collisions

higher concentration
more collisions

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

Why Collisions Do or Do Not React

effective collision

reactive ends line up

$\Rightarrow$ **reaction**

ineffective collision

wrong orientation

$\Rightarrow$ **no reaction**

A collision only reacts with the right orientation and enough energy

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.

8 Recap

Unit 5 – key takeaways

1 Rate law

rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$; orders from experiment

2 Over time

integrated laws; first-order $t_{1/2} = 0.693/k$

3 Barrier

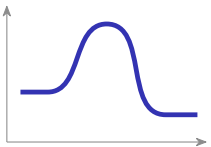
E_a and orientation; $k = Ae^{-E_a/RT}$

4 Catalyst

lowers E_a; the slow step is rate-determining

Check yourself

1. Where do the orders in a rate law come from?
2. Double $[\mathrm{A}]$ and the rate quadruples – what order in A?
3. What two things does an effective collision need?
4. Does a catalyst change ΔH?



Answers **1.** experiment **2.** second order **3.** enough energy + right orientation **4.** no