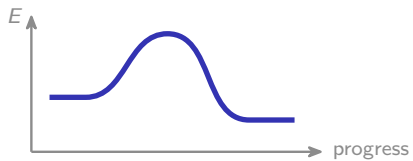


# Kinetics

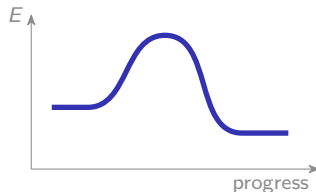
## AP Chemistry ■ Unit 5

### 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

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# 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

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



*Rate is how fast product appears*

2

Rate law

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# The rate law

## Found by experiment

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

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

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

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

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

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

# Rate, and the constant in the rate law

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## 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.

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## Rate constant

The **rate constant**  $k$  in  $\text{rate} = k[A]^m[B]^n$  depends on temperature and on the catalyst – never on concentration.

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## Its units

$k$ 's units follow from the overall order, which is a useful check on an experimentally determined rate law.

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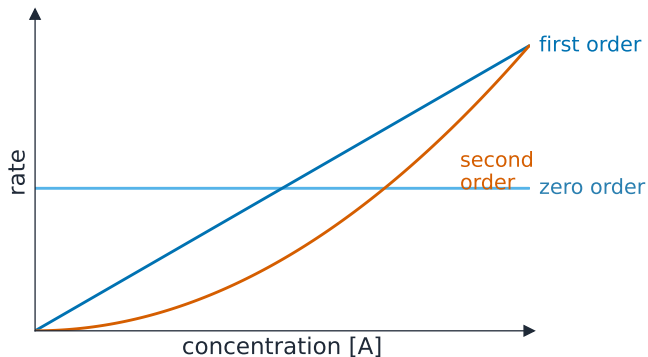
## Where it comes from

The orders come from experiment – initial rates or an integrated plot – never from the balanced equation.

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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: orders 0, 1 and 2



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

3

Over time

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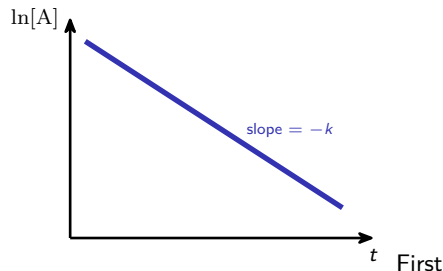
# Concentration over time

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?

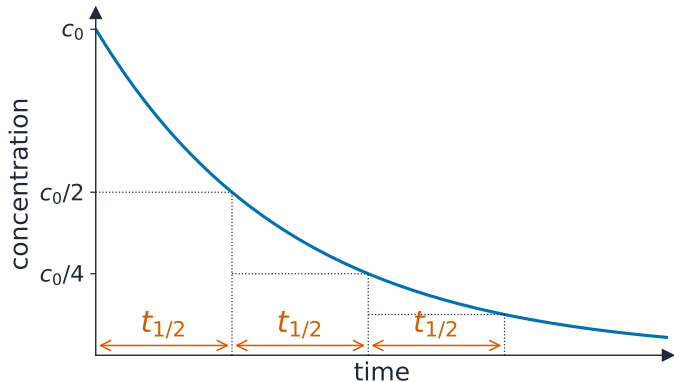
0:  $[A]$  vs  $t$     1st:  $\ln[A]$  vs  $t$     2nd:  $1/[A]$  vs  $t$

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



order:  $\ln[A]$  falls linearly.

## A first-order reaction has a constant half-life



For first order,  $t_{1/2} = \frac{0.693}{k}$ , whatever the concentration: equal half-lives on a graph identify a first-order reaction.

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# Collisions

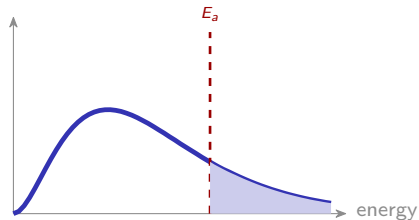
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# Collision theory

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  $E_a$ .

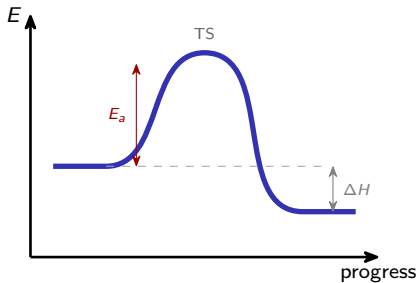


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## Energy profile

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# Energy profiles and Arrhenius



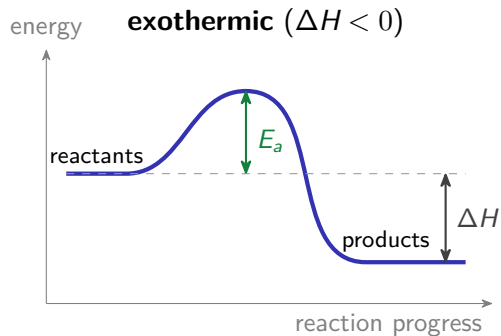
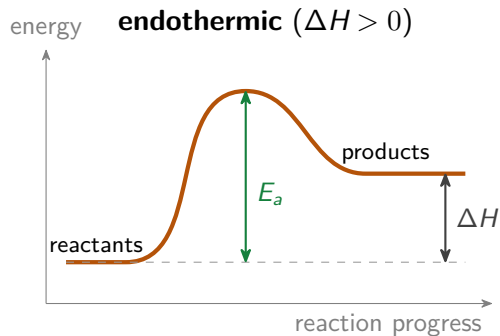
The **transition state** 过渡态 is the peak. Forward  $E_a$  = reactants to peak.

## Arrhenius equation

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

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

# Reading an Energy Profile



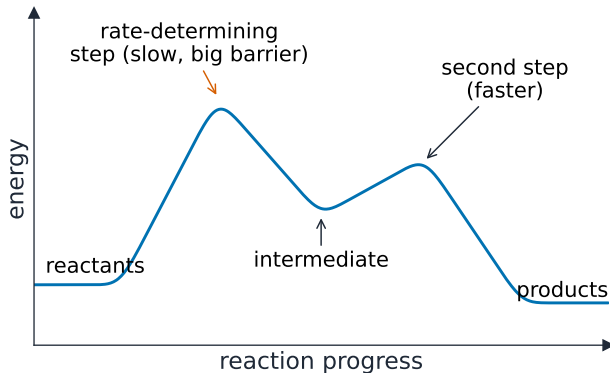
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

negative: heat released; positive: heat absorbed

# 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.



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## Mechanisms

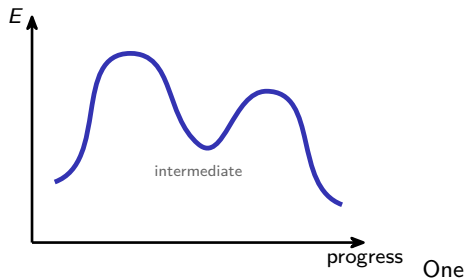
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# Reaction mechanisms

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.



peak per step; a valley is the intermediate.

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# Catalysts

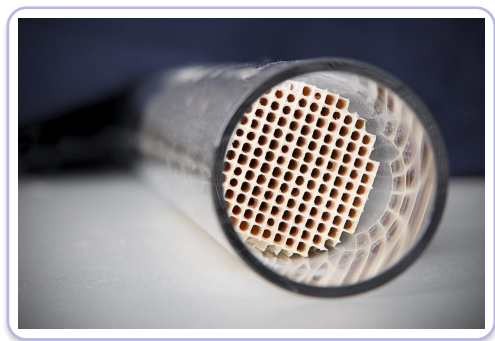
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# Catalysts

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

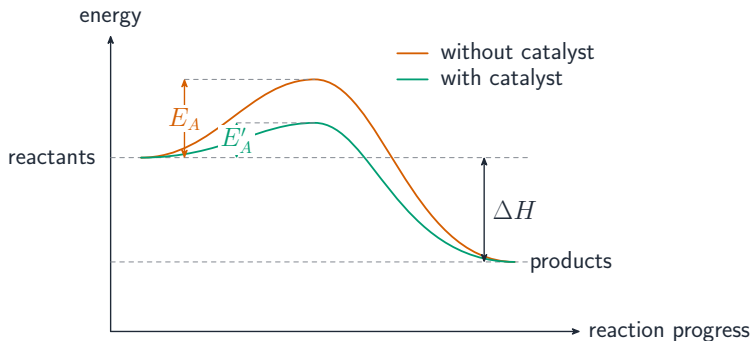
- **homogeneous** 均相催化剂 – same phase
- **heterogeneous** 非均相催化剂 – a solid surface
- **enzyme** 酶 – a biological catalyst

It lowers **both** barriers equally – so it does *not* change  $\Delta H$  or the equilibrium, only the speed.



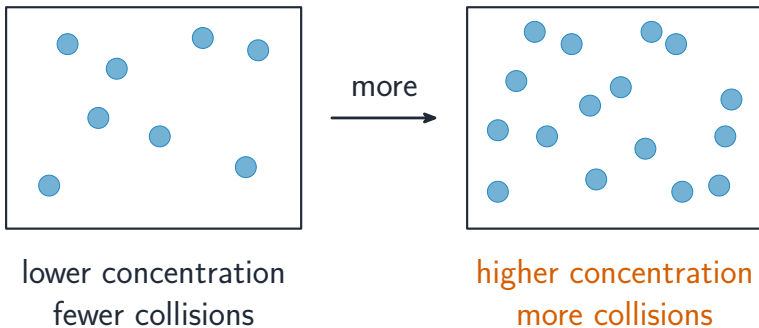
*Catalysts open a lower-energy path*

# How Catalysts Speed Things Up



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

## How Fast a Reaction Goes



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  $\Delta H$ .
- A **catalyst** lowers the activation energy (a new pathway) but leaves  $\Delta H$  and the equilibrium position unchanged.

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Recap

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## Unit 5 – key takeaways

1

### Rate law

rate =  $k[A]^m[B]^n$ ; orders from experiment

2

### Over time

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

3

### Barrier

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

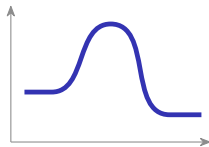
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### Catalyst

lowers  $E_a$ ; the slow step is rate-determining

## Check yourself

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



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