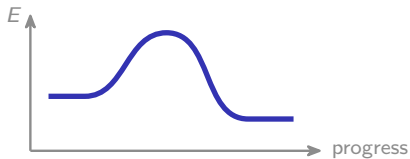
Kinetics

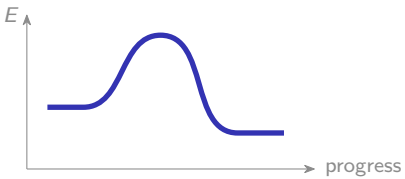
AP Chemistry ▪ Unit 5

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



Rate of reaction

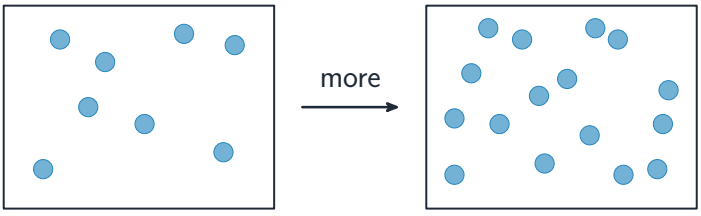
Kinetics 动力学 asks how fast. The **rate** 反应速率 is a change in concentration over time:

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

Rate of reaction



lower concentration
fewer collisions

higher concentration
more collisions

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.

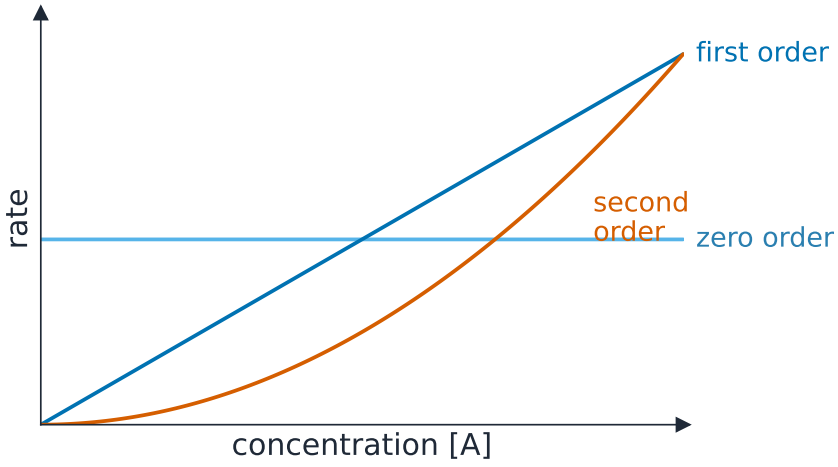
Method of initial rates 初始速率法: double $[\mathrm{A}]$ – rate $\times 2$ (1st), $\times 4$ (2nd), unchanged (0th).

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

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

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

The rate law



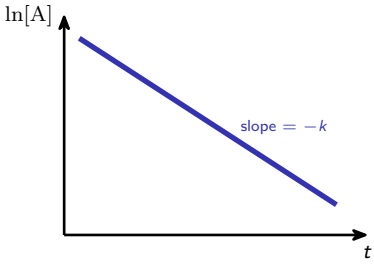
Concentration over time

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?

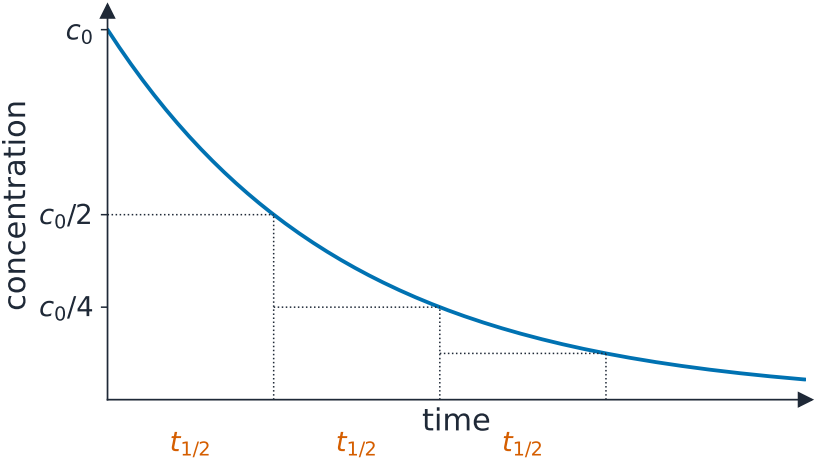
0: $[\mathrm{A}]$ vs t 1st: $\ln[\mathrm{A}]$ vs t 2nd: $1/[\mathrm{A}]$ vs t

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



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

Concentration over time

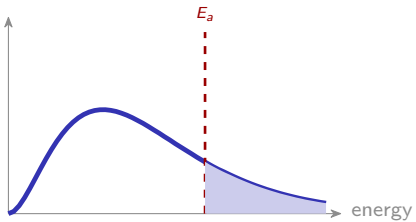


Collision theory

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.



Collision theory

effective collision

reactive ends line up

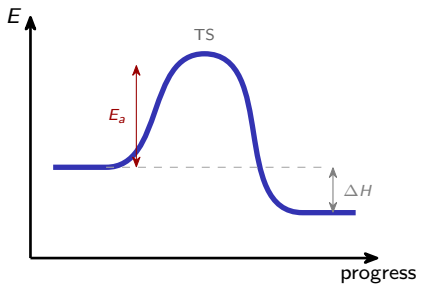
$\Rightarrow$ **reaction**

ineffective collision

wrong orientation

$\Rightarrow$ **no reaction**

Energy profiles and Arrhenius



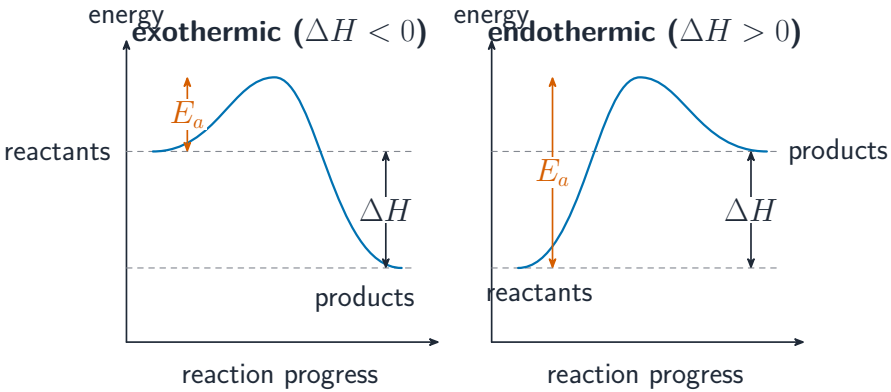
The **transition state** 过渡态 is the peak. Forward E_a = reactants to peak.

Arrhenius equation

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

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

Energy profiles and Arrhenius

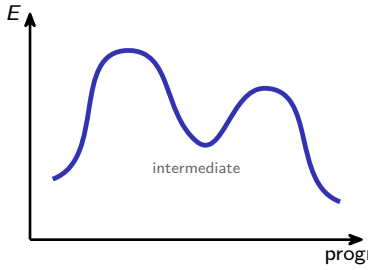


Reaction mechanisms

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

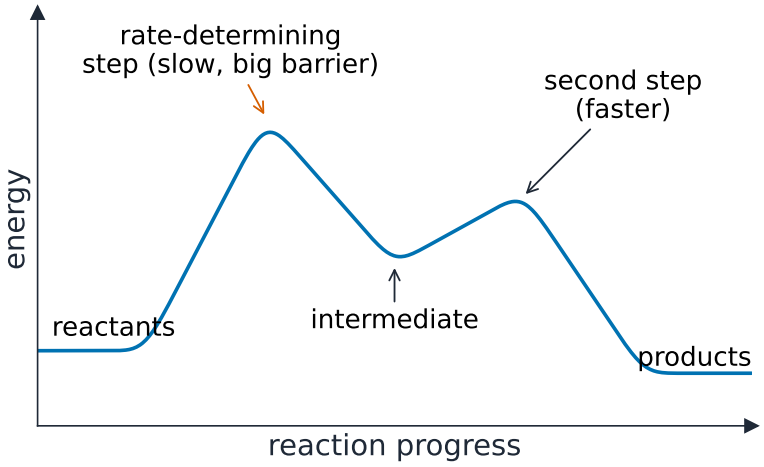
- an **intermediate** 中间体 is made, then used up
- steps must add to the overall equation
- for an elementary step, the rate law comes from its stoichiometry

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



One peak per step; a valley is the intermediate.

Reaction mechanisms

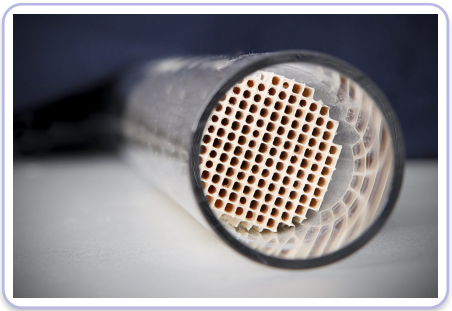


Catalysts

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

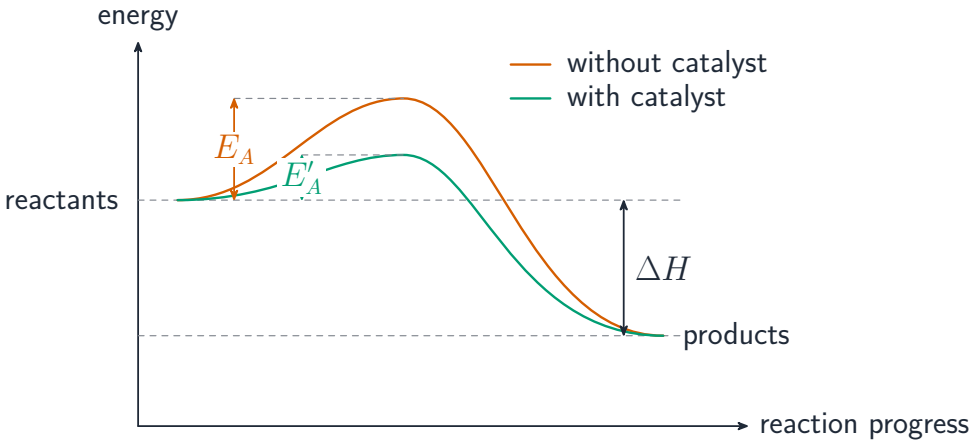
- **homogeneous** 均相催化剂 – same phase
- **heterogeneous** 非均相催化剂 – a solid surface
- **enzyme** 酶 – a biological catalyst

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



Catalysts open a lower-energy path

Catalysts


energy
without catalyst
with catalyst
E_A
E'_A
reactants
ΔH
products
reaction progress

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

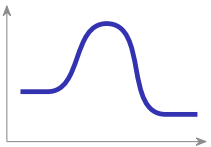
E_a and orientation; $k = Ae^{-E_a/RT}$

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