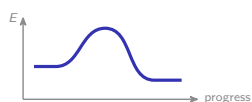


Kinetics

AP Chemistry • Unit 5

AP Chemistry



Kinetics

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

Kinetics

↳ 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

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



Rate is how fast product appears

2

Rate law

Kinetics

↳ Rate law

The rate law

Found by experiment

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

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

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

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

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

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

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

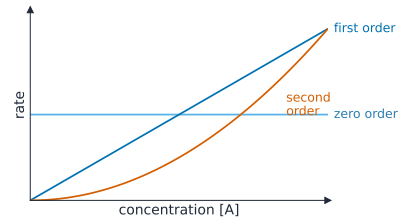
Its units k 's units follow from the overall order, which is a useful check on an experimentally determined rate law.

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.

Kinetics
└ Rate law

Rate against concentration for zero-



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

3 Over time

Kinetics
└ Over time

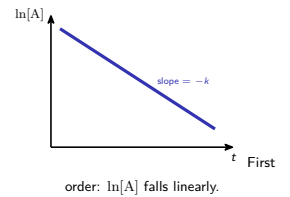
Concentration over time

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?

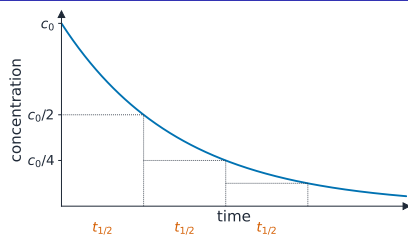
0: $[A]$ vs t 1st: $\ln[A]$ vs t 2nd: $1/[A]$ vs t

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



Kinetics
└ Over time

A first-order reaction has a constant half-life



A first-order reaction has a constant half-life

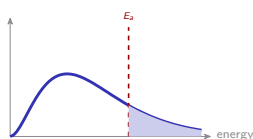
4 Collisions

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

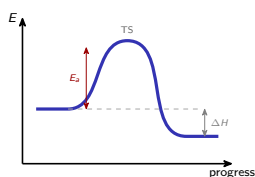
Higher T shifts the Maxwell-Boltzmann tail right – far more particles clear E_a .



5

Energy profile

Energy profiles and Arrhenius



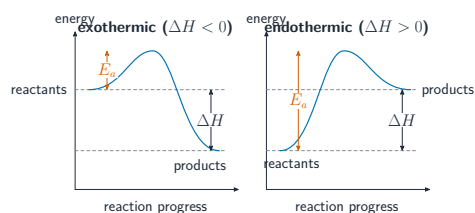
The **transition state** 过渡态 is the peak. Forward E_a = reactants to peak.

Arrhenius equation

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

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

Reading an Energy Profile

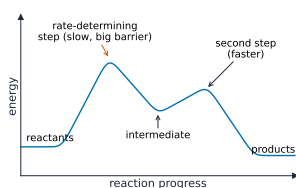


Exothermic reactions end lower than the reactants; endothermic end higher

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

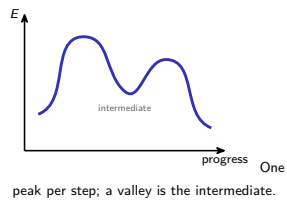
Mechanisms

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.



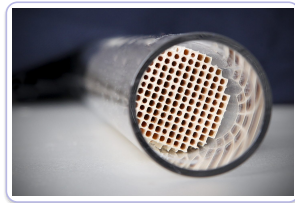
7 Catalysts

Catalysts

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

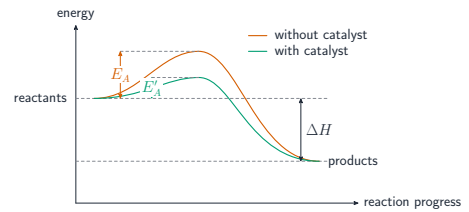
- **homogeneous** 均相催化剂 – same phase
- **heterogeneous** 非均相催化剂 – a solid surface
- **enzyme** 酶 – a biological catalyst

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



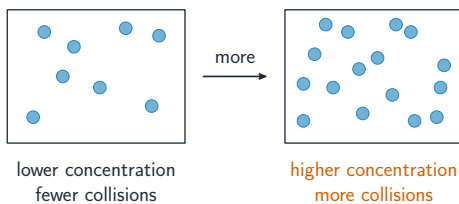
Catalysts open a lower-energy path

How Catalysts Speed Things Up



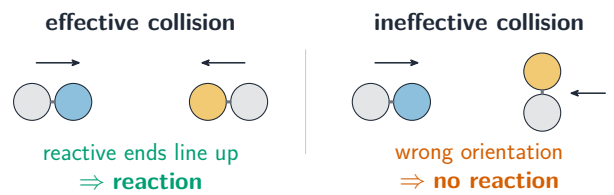
A catalyst gives a route with lower activation energy; the enthalpy change is unchanged

How Fast a Reaction Goes



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

Why Collisions Do or Do Not React



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.

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Recap

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

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 $[A]$ 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