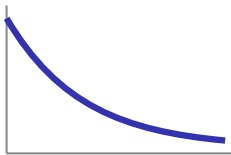


Reaction Kinetics

A-Level Chemistry ■ Topic 26

A-Level Chemistry



What we will cover

- 1 Rate equations & orders
- 2 Order graphs
- 3 Half-life & rate constant
- 4 Reaction mechanisms
- 5 Catalysts



measures gas made over time

1

Rate equations

Rate equations and orders

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

Worked example

doubling [A] doubles the rate (order 1); doubling [B] quadruples it (order 2) $\Rightarrow$ rate = $k[A][B]^2$, **overall order 3**

The **order** 反应级数 and **rate constant** 速率常数 k are found by **experiment**, not from the equation.

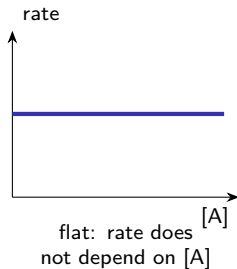


A catalyst raises k by offering a route with a lower activation energy

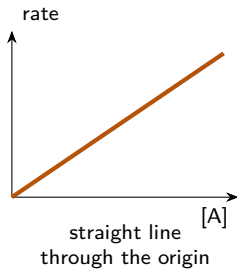
Order graphs

Rate against concentration:

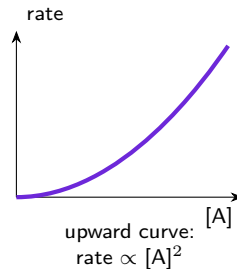
zero order



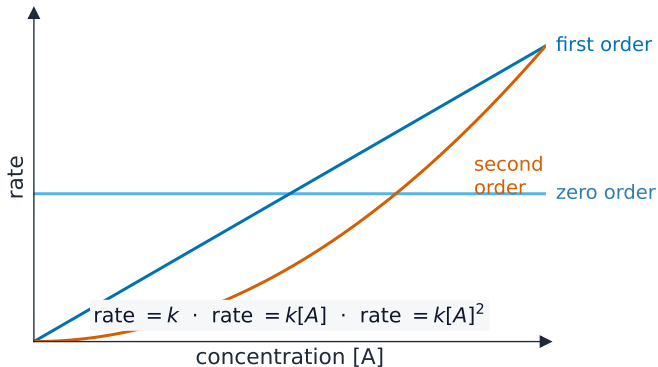
first order



second order



Order graphs, in detail



Rate against concentration: zero order is a flat line, first order a straight line through the origin, second order an upward curve

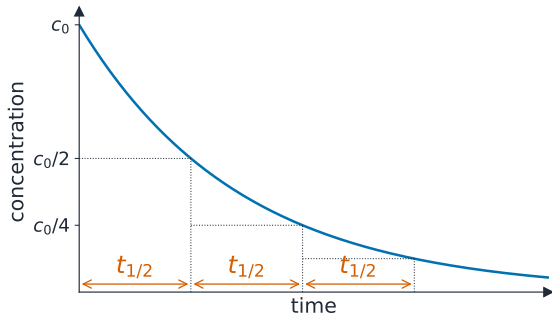
Half-life and the rate constant

A **first-order** reaction has a **constant half-life** 恒定半衰期 $t_{1/2}$.

$$k = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = 120 \text{ s}$$

$$k = \frac{0.693}{120} = 5.8 \times 10^{-3} \text{ s}^{-1}$$



Half-life and the rate constant, continued

For a first-order reaction the **half-life** 半衰期 is constant:

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$$

A constant half-life on a concentration–time graph **proves** first order. Zero-order half-life gets shorter as concentration falls; second-order half-life gets longer.

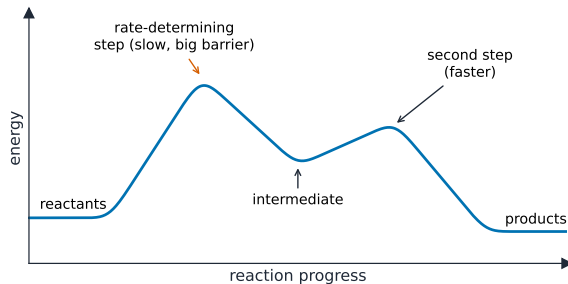
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Mechanisms and catalysts

Reaction mechanisms

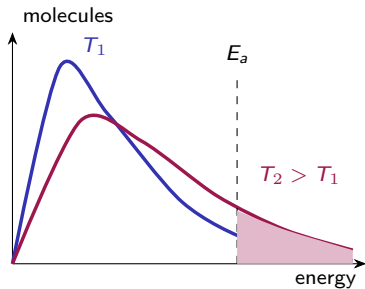
The slowest step is the **rate-determining step** 决速步骤 – it controls the overall rate.

Only species up to & including it appear in the rate equation.
An **intermediate** 中间体 is made then used up – not in the overall equation.



rate-determining step = highest E_a barrier (slowest elementary step)

Effect of temperature



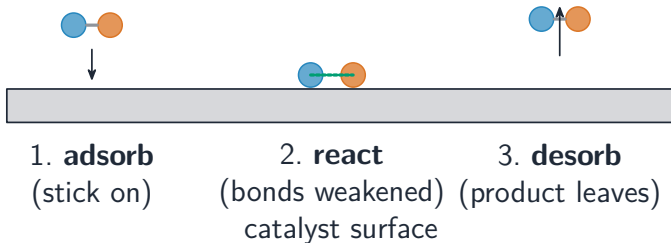
- Raising T : more molecules pass E_a (shaded)
- So the **rate constant** k increases
- So the **rate** goes up, at the same concentrations

Catalysts

A **heterogeneous catalyst** 多相催化剂 works in three stages:

- **adsorption** 吸附 onto the surface
- weakened bonds react
- **desorption** 脱附 of the product

A **homogeneous** 均相 one is reformed unchanged.



The two kinds of catalyst, and the rate vocabulary

heterogeneous

多相催化剂

a **different** physical state from the reactants – iron in the Haber process, and platinum, palladium and rhodium in a catalytic converter

how it works

reactants adsorb onto the surface, react there, and desorb

homogeneous

catalyst 均相催化剂

the **same** physical state as the reactants; it is **used up in one step and remade in a later one**

order of

reaction 反应级数

the power to which a concentration is raised in the rate equation

the overall order 总级数

the sum of the individual orders

the initial

rate 初始速率

measured at $t = 0$, before any product can interfere – which is why it is used to find orders

Order is found **by experiment**, never from the balanced equation. That is the single most-tested point in this topic.

Exam tips

- Find **orders** from initial-rate data: doubling a concentration that doubles the rate is first order, quadruples it is second order, no change is zero order.
- Write $\text{rate} = k[\text{A}]^m[\text{B}]^n$ and work out the **units of** k from it.
- The **rate-determining step** contains the species (and orders) in the rate equation – use this to test a mechanism.
- A **constant half-life** means first order.

3

Recap

Topic 26 – key takeaways

1

Rate equation

rate = $k[A]^m[B]^n$; found by experiment

2

Orders

0 flat, 1 straight, 2 curved

3

Half-life

first order: constant $t_{1/2}$; $k = 0.693/t_{1/2}$

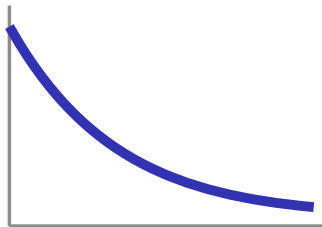
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Mechanism

the rate-determining step controls the rate

Check yourself

- 1 How is a rate equation found?
- 2 What graph shape is a first-order rate-conc plot?
- 3 What is special about a first-order half-life?
- 4 Which step controls the overall rate?



Answers 1. by experiment 2. a straight line through the origin 3. it is constant
4. the rate-determining step