Reaction kinetics

A-Level Chemistry

Rate equations and orders

A **rate equation** 速率方程 shows how the rate depends on the concentrations of the reactants:

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

- m is the **order of reaction** 反应级数 with respect to A, and n the order with respect to B. Each is 0, 1 or 2.
- the **overall order of reaction** 总反应级数 is $m + n$.
- k is the **rate constant** 速率常数. The rate equation can only be found by experiment, not from the balanced equation.

A gas syringe measures the volume of gas made over time, which gives the rate of reaction

Finding the order

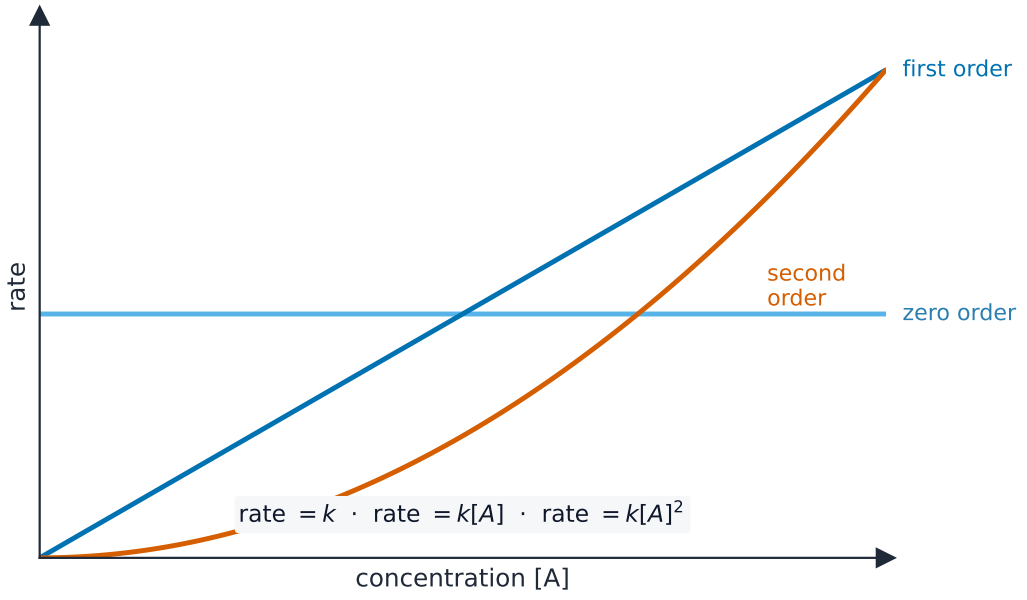
- **initial rates method**: change one concentration at a time and see how the starting rate changes. If doubling [A] doubles the rate, the order in A is 1; if it quadruples the rate, the order is 2; if the rate is unchanged, the order is 0.

Worked example. In experiments on A + B → products, doubling [A] (with [B] fixed) doubles the rate, and doubling [B] (with [A] fixed) quadruples the rate. Write the rate equation and give the overall order.

Doubling [A] doubles the rate, so first order in A. Doubling [B] quadruples (2^2) the rate, so second order in B. Hence

$$\text{rate} = k[\text{A}][\text{B}]^2, \qquad \text{overall order} = 1 + 2 = 3.$$

- **graphs**: a concentration–time graph for a first-order reaction has a constant **half-life** 半衰期 (the time for the concentration to halve). A rate–concentration graph is a straight line through the origin for first order, and a curve for second order.

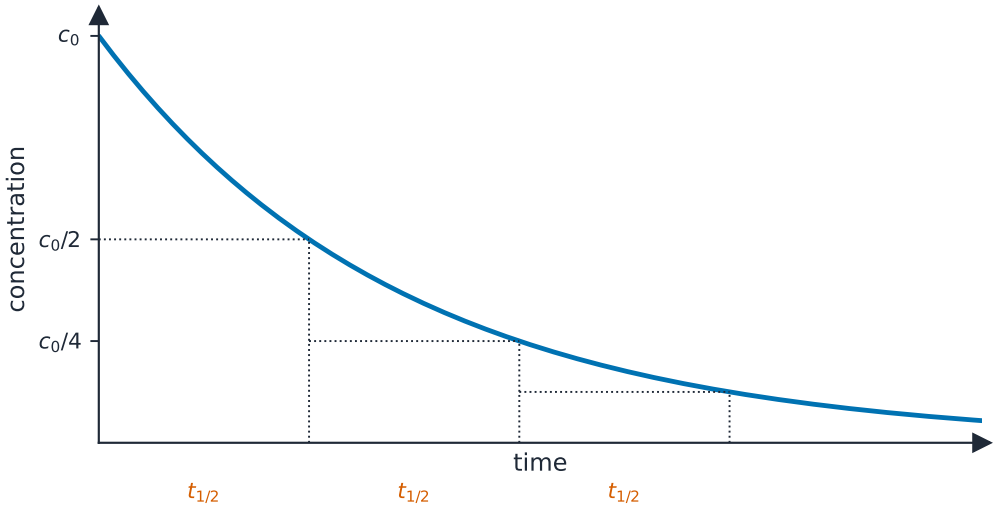


Rate against concentration: zero order is a flat line, first order a straight line through the origin, second order an upward curve

Half-life and the rate constant

For a **first-order** reaction the half-life is **constant** — it does not depend on the concentration. You can find the rate constant from it:

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



$$t_{1/2} = \frac{\ln 2}{k} \quad \text{(constant for 1st order)}$$

A first-order reaction has a constant half-life: the concentration halves in the same time $t_{1/2}$ again and again, whatever the starting value

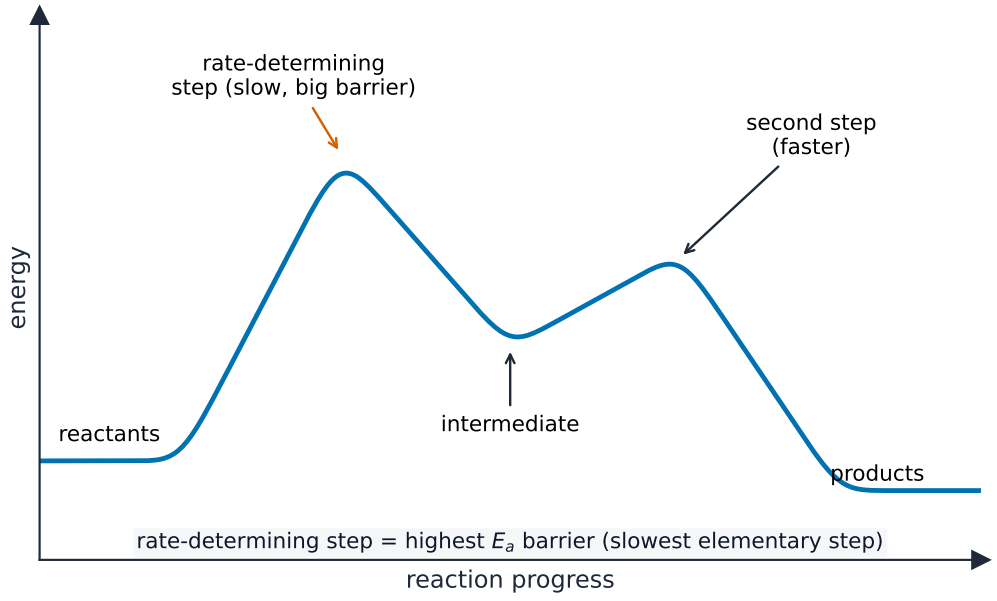
Worked example. A first-order reaction has a half-life of 120 s. Find its rate constant.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.8 \times 10^{-3}\ \text{s}^{-1}.$$

You can also find k by putting initial-rate data into the rate equation.

Reaction mechanisms

Most reactions happen in several steps. The slowest step is the **rate-determining step** 决速步骤, and it controls the overall rate. Only the species involved up to and including this step appear in the rate equation.



A two-step profile: the slower step has the bigger barrier and is rate-determining; the dip between the two barriers is an intermediate

- an **intermediate** 中间体 is a species made in one step and then used up in a later step. It is not in the overall equation.
- you can suggest a mechanism that fits both the rate equation and the overall equation, predict the order from a given mechanism, or pick out the rate-determining step.

If you compare the **initial rate** 初始速率 of different mixtures, you can deduce the rate equation, and from that work out the mechanism.

Effect of temperature

Raising the temperature increases the rate constant k (more molecules pass the activation energy), so the rate goes up.

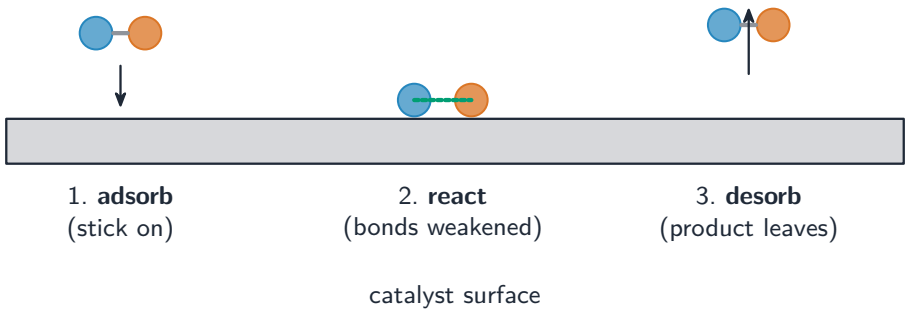
Catalysts

Catalysts 催化剂 can be homogeneous or heterogeneous.

Heterogeneous catalysts

A **heterogeneous catalyst** 多相催化剂 is in a different physical state from the reactants (usually a solid with gases). It works in three stages:

1. **adsorption** 吸附: reactant molecules stick to the catalyst surface.
2. the bonds in the reactants are weakened, so they react more easily.
3. **desorption** 脱附: the product molecules leave the surface.



A heterogeneous catalyst works in three stages: the reactants adsorb onto the surface, their weakened bonds let them react, then the product desorbs

Real heterogeneous catalysts are made as small shaped pellets, rings and perforated discs, which give a large surface area for the reactants to stick to

Examples are iron in the Haber process, and platinum, palladium and rhodium in a catalytic converter.

Homogeneous catalysts

A **homogeneous catalyst** 均相催化剂 is in the same physical state as the reactants. It is used up in one step and then reformed in a later step, so it comes back unchanged. Examples are oxides of nitrogen helping to oxidise atmospheric sulfur dioxide, and Fe^{2+} or Fe^{3+} speeding up the reaction between I^- and $S_2O_8^{2-}$.

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 rate $= k[A]^m[B]^n$ 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.