# Reaction kinetics (A Level)

Rate equations, orders, rate constants and half-life, multi-step mechanisms and the rate-determining step, the effect of temperature on k, and how homogeneous and heterogeneous catalysts work.

## 26.1 Simple rate equations, orders of reaction and rate constants

A **rate equation** links the rate to the concentrations of reactants. For $A + B \longrightarrow$ products:

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

- The **order of reaction** with respect to a reactant is the power to which its concentration is raised ($m$ or $n$; 0, 1 or 2). The **overall order** is $m + n$.
- The **rate constant**, $k$, is the constant of proportionality. Its units depend on the overall order: zero order mol dm$^{-3}$ s$^{-1}$, first order s$^{-1}$, second order mol$^{-1}$ dm$^3$ s$^{-1}$.
- The orders can only be found **by experiment**, not from the balanced equation.

### Finding the order

- **Initial rates method:** vary one concentration at a time. If doubling $[A]$ doubles the rate, first order; if it quadruples the rate, second order; if there is no effect, zero order.
- **Concentration–time graph:** a **straight line** (constant gradient) shows zero order. A curve with a **constant half-life** shows first order. The half-life, $t_{1/2}$, is the time for the concentration to halve.
- **Rate–concentration graph:** a horizontal line is zero order, a straight line through the origin is first order, and a curve through the origin (rate against $[A]$) is second order.

The **half-life of a first-order reaction is independent of concentration**, and

$$k = \frac{0.693}{t_{1/2}} \quad (\ln 2 = 0.693)$$

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The initial rates for $A + B \longrightarrow C$: experiment 1, $[A]$ 0.10, $[B]$ 0.10, rate 2.0×10$^{-4}$; experiment 2, $[A]$ 0.20, $[B]$ 0.10, rate 4.0×10$^{-4}$; experiment 3, $[A]$ 0.10, $[B]$ 0.20, rate 8.0×10$^{-4}$ (mol dm$^{-3}$ s$^{-1}$). Find the rate equation and $k$.

Doubling $[A]$ doubles the rate: first order in A. Doubling $[B]$ quadruples it: second order in B. Rate $= k[A][B]^2$. From experiment 1, $k = 2.0 \times 10^{-4}/(0.10 \times 0.10^2) = 0.20$ mol$^{-2}$ dm$^6$ s$^{-1}$.

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## Mechanisms and the rate-determining step

Many reactions take place in several steps. The slowest is the **rate-determining step**. The **rate equation** includes only the species that appear in the rate-determining step (and the steps before it). An **intermediate** is formed in one step and used up in a later one; it does not appear in the overall equation. A **catalyst** is used up in one step and reformed in a later step.

> **A mechanism must (1) add up to the overall equation and (2) agree with the rate equation. The order of a reactant is the number of molecules of it in the rate-determining step (with any earlier steps considered).**

For $2NO + O_2 \rightarrow 2NO_2$ with rate $= k[NO]^2[O_2]$, one compatible model is a fast pre-equilibrium $2NO \rightleftharpoons N_2O_2$, followed by slow $N_2O_2 + O_2 \rightarrow 2NO_2$. Substituting the intermediate concentration from the pre-equilibrium gives the observed dependence. A rate law does not uniquely prove a mechanism. For $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$, a single bimolecular SN2 step is consistent with rate $= k[CH_3Br][OH^-]$.

## Temperature and the rate constant

A temperature rise increases the **rate constant** $k$, because more molecules have energy of at least $E_a$ (see the Boltzmann distribution), so the rate increases. $k$ is constant at a given temperature.

## Analysing an initial-rate table

Choose a pair of experiments in which only one relevant concentration changes. Divide their rate equations so the constant and unchanged concentrations cancel. If concentration changes by a factor $f$ and rate by $r$, then $r = f^m$ for the order being investigated. When both concentrations change, establish one order from another comparison before separating their effects.

**Worked example:** doubling A and doubling B together increases rate eightfold. Another pair shows that doubling A alone doubles rate. A is first order, accounting for a factor of two; B must account for the remaining factor four, so B is second order. The overall order is three, although the balanced equation need not have those coefficients.

Calculate $k$ from a complete row, then check another row. For rate $= k[A]^2$, $k = (\text{mol dm}^{-3}\text{s}^{-1})/(\text{mol dm}^{-3})^2$, giving dm³ mol⁻¹ s⁻¹. For $k[A][B]^2$ the unit becomes dm⁶ mol⁻² s⁻¹. Deriving units from the expression avoids memorising the wrong unit for an unfamiliar overall order.

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> Doubling A quadruples rate while tripling B has no effect. Find the rate law and overall order.

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**Answer:** Rate $= k[A]^2[B]^0 = k[A]^2$. It is second order overall and zero order in B under the experimental conditions. B may still be chemically consumed; zero order does not mean absent from the overall reaction.

## Half-life and graphical evidence

For first-order behaviour, each halving takes the same time: 0.800 to 0.400, then 0.400 to 0.200 mol dm$^{-3}$ occur in equal intervals. A curve that simply bends downwards is not sufficient proof of first order; check consecutive half-lives or appropriate rate–concentration evidence. Zero-order concentration decreases linearly, so its half-life becomes shorter as initial concentration falls.

**Worked example:** a reactant falls from 0.160 to 0.0200 mol dm$^{-3}$ in 90.0 s through three equal 30.0 s half-lives. Thus $k = 0.693/30.0 = 0.0231$ s$^{-1}$. After five half-lives, the remaining fraction is $(1/2)^5 = 1/32$, so 96.875% has reacted. The concentration approaches zero rather than reaching it after one or two half-lives.

For an initial rate, draw the tangent at zero and calculate its gradient with a large triangle. A later average gradient is smaller for a slowing reaction and should not be substituted silently for the initial slope. Keep time units consistent when converting half-life to $k$.

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> A first-order reaction has a half-life of 2.00 min. Find $k$ in s$^{-1}$ and the fraction remaining after 6.00 min.

**Answer:** $t_{1/2} = 120$ s, so $k = 0.00578$ s$^{-1}$. Three half-lives leave $1/8 = 12.5\%$ of the initial reactant.

## Testing a proposed mechanism

Add the elementary steps and cancel intermediates and regenerated catalysts. The resulting overall equation must balance. Then ask whether the proposed rate-determining step, with any preceding equilibria, predicts the experimental concentration dependence. Molecularity describes species in an **elementary step**, whereas reaction order is an experimental property of a rate law; they are not generally interchangeable for an overall equation.

**Worked example:** slow $A + B \rightarrow X$, followed by fast $X + B \rightarrow P$, gives overall $A + 2B \rightarrow P$. The simple slow-step model predicts rate $= k[A][B]$, not $k[A][B]^2$. X is an intermediate because it is produced then consumed. The second B affects the overall stoichiometry without appearing in the slow-step rate expression.

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> A proposed mechanism begins with slow $A \longrightarrow X$ and then fast $X + B \longrightarrow P$. Is it consistent with an observed first-order dependence on both A and B?

**Answer:** Not in this simple model. Its rate-determining first step predicts dependence on A alone, whereas the measured rate also depends on B. Agreement with the overall equation by itself is insufficient.

At fixed temperature, changing reactant concentration changes rate but not $k$ for an unchanged mechanism. Raising temperature generally increases $k$ by increasing the fraction of particles able to overcome the barrier. Adding a catalyst changes the mechanism, so the applicable rate law and constant may change as well.

## 26.2 Homogeneous and heterogeneous catalysts

A **homogeneous** catalyst is in the **same phase** as the reactants; a **heterogeneous** catalyst is in a **different phase**.

### Heterogeneous catalysis

The mode of action: (1) reactant molecules are **adsorbed** onto active sites on the metal surface; (2) bonds in the reactants are **weakened** (and brought close together in the correct orientation); (3) the products are **desorbed**, freeing the site.

- **Iron in the Haber process:** $N_2 + 3H_2 \rightleftharpoons 2NH_3$.
- **Palladium, platinum and rhodium** in a car's catalytic converter, which converts $NO$ and $CO$ to $N_2$ and $CO_2$.

A catalyst can be **poisoned** (sulfur or lead block the active sites), and a large surface area increases efficiency.

### Homogeneous catalysis

The catalyst is **used in one step and reformed in a later step**, with a different pathway of lower activation energy.

- **Atmospheric oxides of nitrogen** in the oxidation of $SO_2$: $SO_2 + NO_2 \longrightarrow SO_3 + NO$, then $2NO + O_2 \longrightarrow 2NO_2$.
- $Fe^{2+}$ **or** $Fe^{3+}$ in the reaction $2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$. Both ions are negative, so they repel and the uncatalysed reaction is slow. The iron ions provide a path: $S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$, then $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$. This works because $E^{\ominus}(Fe^{3+}/Fe^{2+})$ lies between the two half-reactions.

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## Explaining the catalytic cycle

In the iron-catalysed iodide/peroxodisulfate reaction, iron(II) reduces peroxodisulfate and becomes iron(III); iron(III) then oxidises iodide and returns to iron(II). Add the equations to show that both iron species cancel. Beginning with iron(III) still permits the cycle because the iodide step first produces iron(II). The catalyst's oxidation state changes temporarily, but its total amount can be regenerated.

For atmospheric nitrogen oxides, multiply $SO_2 + NO_2 \rightarrow SO_3 + NO$ by two before adding $2NO + O_2 \rightarrow 2NO_2$. The overall result is $2SO_2 + O_2 \rightarrow 2SO_3$. Nitrogen oxides are recycled, explaining how a relatively small amount can facilitate oxidation of much more sulfur dioxide.

For a heterogeneous catalyst, adsorption must be strong enough to activate the reactants but not so strong that products remain permanently attached. Desorption frees active sites for further turnover. Powdering increases accessible area; poisoning blocks sites, reducing activity without necessarily changing the catalyst's total mass.

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> Why is “the catalyst is never involved in the reaction” an incorrect description?

**Answer:** It can react in intermediate steps, adsorb reactants or change oxidation state. It is regenerated overall and provides a different pathway with a lower activation barrier; it need not remain chemically unchanged at every stage.

**Chapter check:** infer orders from data, derive the units of $k$, check half-life constancy, and test a mechanism against both the overall equation and measured rate law. Link catalytic redox cycles to **standard potentials**.

### References and further reading

Scope follows section 26 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide’s Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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