

Reaction kinetics (A Level)

A-Level Chemistry 9701 · Topic 26 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Orders of reaction and rate equations
2. Rate-determining step and mechanisms
3. Temperature, rate constants and the Arrhenius equation
4. Homogeneous and heterogeneous catalysts

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1 Orders of reaction and rate equations

Syllabus 26.1

A **rate equation** has the form $\text{rate} = k[A]^m[B]^n$. The powers m and n are the **orders** with respect to each reactant (0, 1 or 2 at this level) and their sum is the **overall order**. Orders are found by **experiment**, never from the stoichiometric equation. In an **initial-rates** table, doubling a concentration while the others stay fixed multiplies the rate by 1 (zero order), 2 (first order) or 4 (second order). A **first-order** reaction has a **constant half-life**, and $k = 0.693 / t_{1/2}$. The **rate constant** k changes only with temperature (or a catalyst), and its units depend on the overall order.

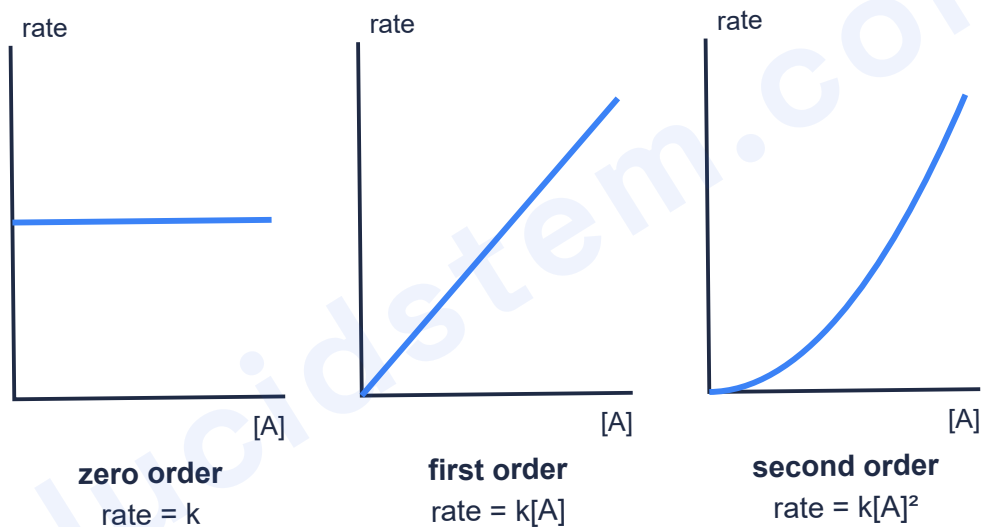


Fig. 1: rate-concentration graphs for zero-, first- and second-order reactants

Orders come from experiment.

- ✓ **Initial rates:** $\times 2$ conc. gives rate $\times 1$, $\times 2$, $\times 4$ for order 0, 1, 2.
- ✓ **Units of k :** rearrange and cancel; order 2 gives $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.
- ✓ **Constant half-life** means first order; $k = 0.693 / t_{1/2}$.
- ✓ **Rate-[A] graphs:** flat, straight through origin, upward curve.

Watch out!

Orders come from **experimental data**, not from the coefficients in the balanced equation. Doubling a concentration and seeing the rate quadruple means **second** order, not fourth. A constant half-life proves **first** order only; do not use $t_{1/2} = 0.693/k$ for other orders. Always give **units** for k , worked out from the overall order, and remember k does not change with concentration.

2 Rate-determining step and mechanisms

Syllabus 26.1

The **rate-determining step** is the **slowest step** in a mechanism. Only species that take part in the rate-determining step, or in fast steps before it, appear in the rate equation, and the **order** of each matches the number of its particles involved. A species with zero order joins the reaction **after** the slow step. An **intermediate** is made in one step and used up in a later one, so it never appears in the overall equation; a **catalyst** is used in one step and **regenerated** later, so it can appear in the rate equation but not in the overall equation. A mechanism is **consistent** with the data if its steps add up to the overall equation and its slow step matches the rate equation.

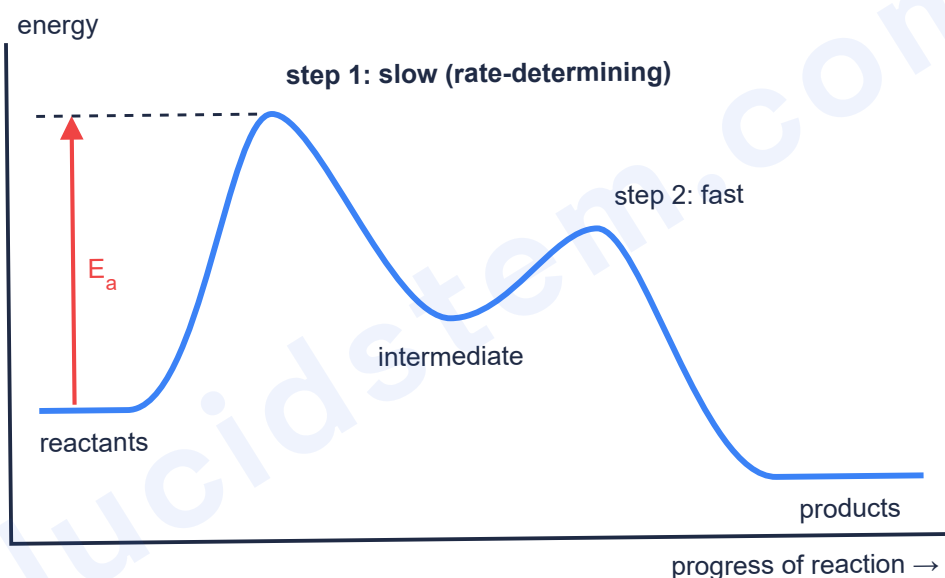


Fig. 1: energy profile of a two-step reaction; step 1 has the larger activation energy, so it is the slow, rate-determining step

The slow step writes the rate equation.

- ✓ **Rate-determining step:** the slowest step.
- ✓ **Orders** = number of each particle in (or before) the slow step.
- ✓ **Zero order:** joins after the slow step.
- ✓ **Intermediate** made then used; **catalyst** used then regenerated.

Watch out!

The rate equation tells you about the **slow step**, not the overall equation, so do not copy coefficients from the overall equation. A reactant that is **zero order** is still needed: it reacts in a fast step **after** the rate-determining step. An **intermediate** is formed then used up; a **catalyst** is used then regenerated. Do not call the transition state an intermediate: a transition state is a peak on the energy profile, an intermediate sits in a dip.

3 Temperature, rate constants and the Arrhenius equation

Syllabus 26.2

The **rate constant** k increases with temperature because a larger fraction of collisions have energy $\geq E_a$. The **Arrhenius equation** is $k = Ae^{-E_a/RT}$, where A is the **pre-exponential factor** (linked to collision frequency and orientation), T is in **kelvin** and $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$. Taking logs gives $\ln k = \ln A - E_a/RT$, a straight line when $\ln k$ is plotted against $1/T$; the **gradient** $= -E_a/R$ and the intercept is $\ln A$. A larger E_a means a steeper line, so the rate is **more sensitive** to temperature.

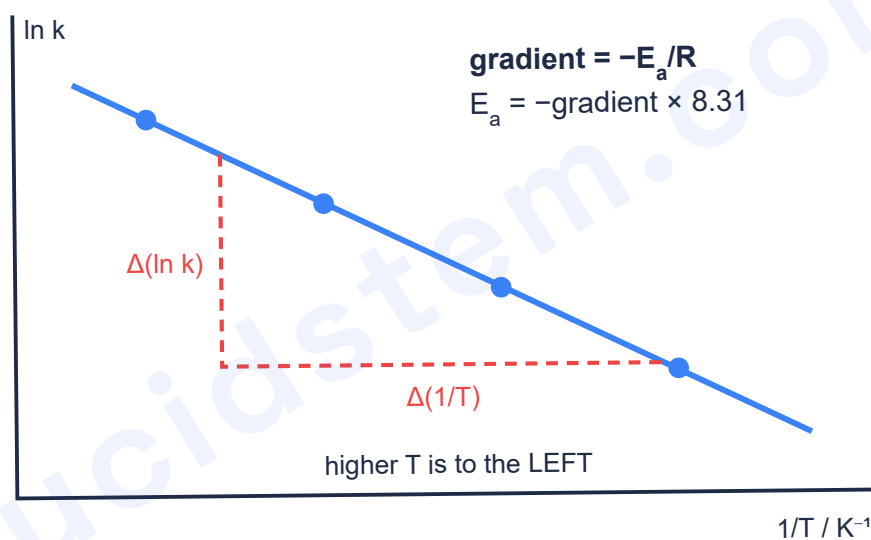


Fig. 1: an Arrhenius plot; the gradient of $\ln k$ against $1/T$ equals $-E_a/R$

Kelvin, $\ln k$ and a negative gradient.

- ✓ $k = Ae^{-E_a/RT}$; $\ln k = \ln A - E_a/RT$.
- ✓ **Plot** $\ln k$ against $1/T$ (T in K).
- ✓ $E_a = -\text{gradient} \times 8.31$, in J mol^{-1} .
- ✓ **Only T and catalysts** change k .

Watch out!

Always use T in **kelvin** and R in $\text{J K}^{-1} \text{ mol}^{-1}$, so E_a comes out in J mol^{-1} ; divide by 1000 for kJ. The gradient is **negative**; $E_a = -\text{gradient} \times R$ is positive. Plot **$\ln k$** , not k , and **$1/T$** , not T . Increasing concentration does **not** change k ; only temperature and catalysts do.

4 Homogeneous and heterogeneous catalysts

Syllabus 26.3

A catalyst increases the rate by providing an **alternative route with a lower activation energy**, and is **regenerated** at the end. A **homogeneous** catalyst is in the **same phase** as the reactants and works by forming an **intermediate**, so its energy profile has two humps with a dip between them. Transition-metal ions are good homogeneous catalysts because they change **oxidation state** easily: Fe^{2+} or Fe^{3+} catalyses $\text{S}_2\text{O}_8^{2-} + 2\text{I}^-$, and NO_2 catalyses the oxidation of SO_2 in the air. A **heterogeneous** catalyst is in a **different phase**, usually a solid with gaseous reactants, and works by **adsorption**, reaction on the surface and **desorption**. Adsorption must be **neither too strong nor too weak**. **Enzymes** are protein catalysts with highly specific active sites.

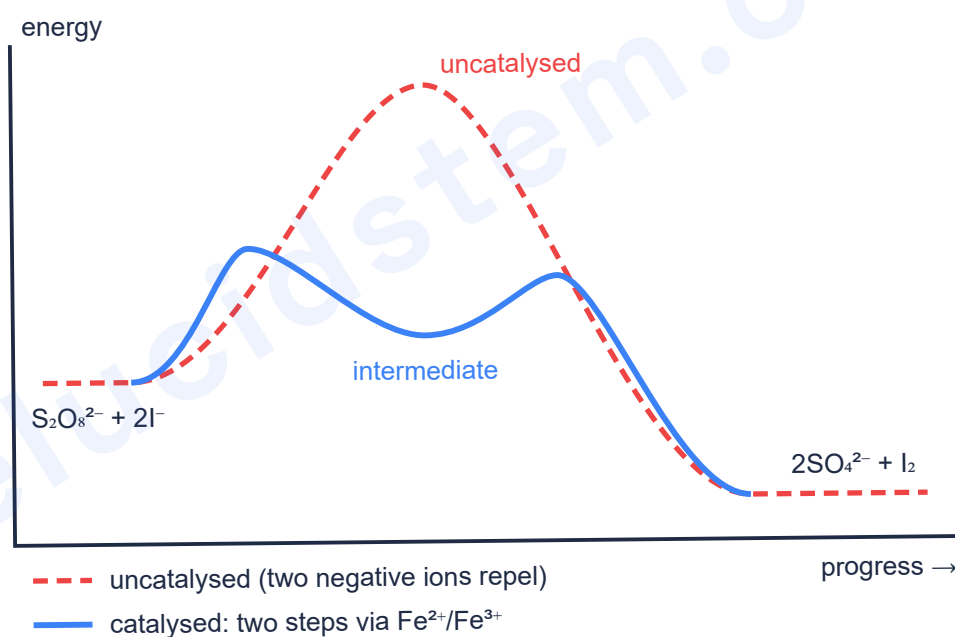


Fig. 1: energy profiles for the reaction of peroxodisulfate with iodide, uncatalysed and catalysed by Fe^{2+} ions

New route, lower barrier, regenerated.

- ✓ **Homogeneous:** same phase; works via an intermediate.
- ✓ **$\text{Fe}^{2+}/\text{Fe}^{3+}$:** two steps between oppositely charged ions.
- ✓ **Heterogeneous:** adsorption, reaction, desorption.
- ✓ **Adsorption** neither too strong nor too weak.

Watch out!

A catalyst lowers E_a by providing a **different mechanism**; it does not give molecules more energy and does not change ΔH or the position of equilibrium.

Homogeneous means the **same phase**, not the same substance. In heterogeneous catalysis, **stronger adsorption is not always better**: products must be able to desorb. The catalysed profile has **two humps** with an intermediate in the dip.