

Reaction kinetics

A2

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What you need to know

By the end of this topic you should be able to:

Rate equations, orders and rate constants

1. **Explain and use the key words:** rate equation, order of reaction (with respect to one reactant), overall order, rate constant k , half-life $t_{1/2}$, rate-determining step and intermediate.
2. **Use rate equations** of the form $\text{rate} = k[\text{A}]^m[\text{B}]^n$, where each order m or n is 0, 1 or 2.
3. **Find orders from experiments:** from the shape of a concentration–time graph, from an initial-rates table, or from half-lives.
4. **Read graphs:** concentration–time graphs (including rates from tangents) and rate–concentration graphs.
5. **Calculate an initial rate** from concentration data, and **write the rate equation** once the orders are known.
6. **Half-life:** show that a first-order reaction has a half-life that does not depend on the concentration, and use half-lives in calculations.
7. **Calculate the rate constant**, with its units, from initial rates and the rate equation, or from the half-life with
$$k = \frac{0.693}{t_{1/2}}.$$
8. **Link mechanisms and rate equations** for a reaction with several steps: suggest a mechanism that fits the rate equation and the overall equation; predict the orders from a mechanism and its slow step; write the rate equation from them; pick out an intermediate or a catalyst; and pick out the rate-determining step.
9. **Describe in words** how raising the temperature changes the rate constant, and so the rate.

Catalysts

10. **Explain** that a catalyst is homogeneous (same phase as the reactants) or heterogeneous (a different phase).
11. **Describe how a heterogeneous catalyst works** (adsorption, bond weakening, desorption), using iron in the Haber process and platinum, palladium and rhodium in car catalytic converters.
12. **Describe how a homogeneous catalyst works:** it is used up in one step and made again in a later step, using oxides of nitrogen in the oxidation of sulfur dioxide in the air, and Fe^{2+} or Fe^{3+} in the reaction of iodide ions with peroxydisulfate ions.

Collision theory, the Boltzmann distribution and the basic idea of a catalyst are in the AS note "Reaction kinetics". You do not need the Arrhenius equation or integrated rate equations here.

Understand it

The rate equation

For a reaction $A + B \rightarrow \text{products}$, experiments show how the rate depends on each concentration. The result is written as a **rate equation**:

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

- m is the **order of reaction with respect to A**: the power to which $[A]$ is raised in the rate equation. Likewise n for B.
- The **overall order** is the sum of the powers, $m + n$.
- k is the **rate constant**: the number that links the rate to the concentrations. It stays the same when concentrations change, but it **changes with temperature** (and with a catalyst).

The orders come **only from experiments**. They are not the numbers in front of the formulae in the balanced equation. For $2X + Y \rightarrow X_2Y$ the rate equation might be $\text{rate} = k[Y]$, with zero order in X. A reactant that is zero order still reacts, but its concentration does not affect the rate, so it is left out of the rate equation (or written as $[X]^0$).

What each order means

Order in A	Effect of doubling $[A]$ on the rate	Effect of tripling $[A]$
0	none ($\times 1$)	none ($\times 1$)
1	$\times 2$	$\times 3$
2	$\times 4$	$\times 9$

If several concentrations change at once, multiply the effects. For $\text{rate} = k[A][B]^2$, doubling both gives $2 \times 2^2 = 8$ times the rate.

Units of k

Rearrange the rate equation for k and put in the units. With rate in $\text{mol dm}^{-3} \text{s}^{-1}$ and concentrations in mol dm^{-3} :

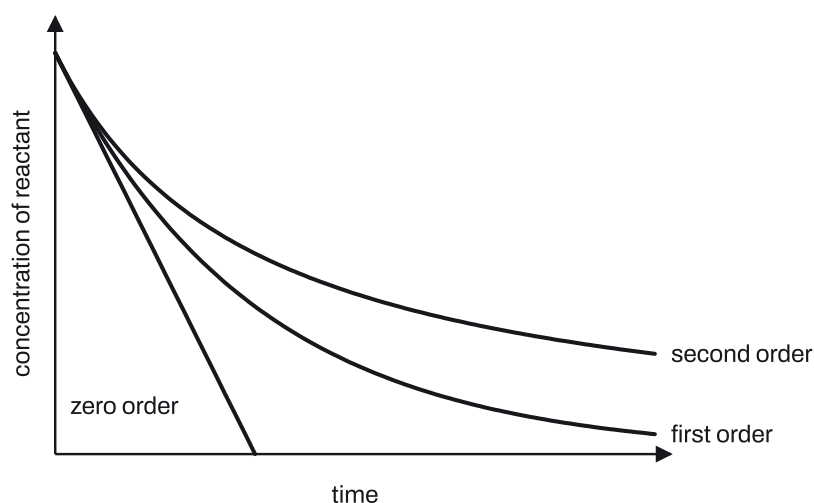
Overall order	$k =$	Units of k
0	rate	$\text{mol dm}^{-3} \text{s}^{-1}$
1	$\frac{\text{rate}}{[]}$	s^{-1}

Overall order	$k =$	Units of k
2	$\frac{\text{rate}}{[\]^2}$	$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
3	$\frac{\text{rate}}{[\]^3}$	$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

Each extra order adds one more $\text{mol}^{-1} \text{ dm}^3$. For overall order n the units are $\text{mol}^{1-n} \text{ dm}^{3(n-1)} \text{ s}^{-1}$, which also works for orders of 4 or 5. If the rate is per minute, the units end in min^{-1} instead.

Concentration–time graphs

Plot the concentration of a reactant against time, and the **gradient** at any moment is the rate then (ignore the minus sign). To find the rate at a particular time, draw a **tangent** to the curve at that time and work out its gradient from two points far apart on the tangent. The rate at $t = 0$ is the **initial rate**.



The **half-life**, $t_{1/2}$, is the time for the concentration of a reactant to fall to half its value. The shape of the graph tells you the order:

- **Zero order:** a straight line with a constant gradient, because the rate does not depend on the concentration. Each half-life is **shorter** than the one before.
- **First order:** a curve with a **constant half-life**. It takes the same time to go from 0.0800 to $0.0400 \text{ mol dm}^{-3}$ as from 0.0400 to $0.0200 \text{ mol dm}^{-3}$.
- **Second order:** a curve whose half-lives get **longer** each time.

Why a first-order half-life is constant

In a first-order reaction the rate is proportional to the concentration. When the concentration has halved, the rate has halved too, so halving the new amount takes exactly the same time as before. The starting concentration makes no difference to $t_{1/2}$. This gives a link between k and $t_{1/2}$ that you learn and use:

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

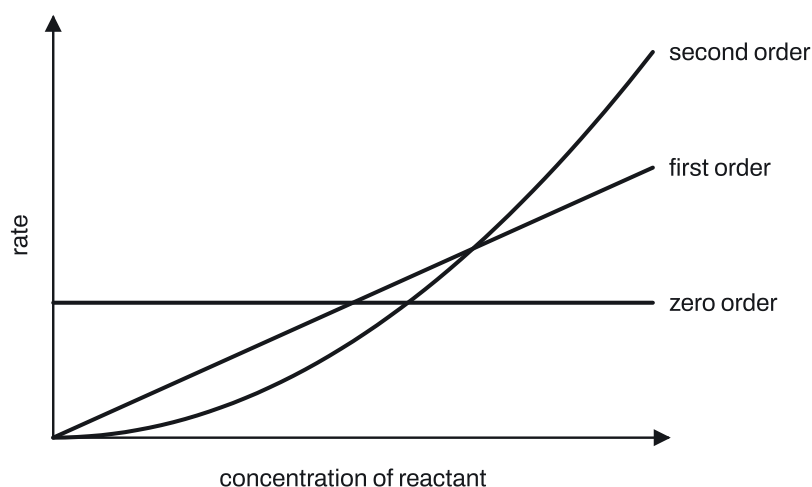
(0.693 is $\ln 2$; using $\ln 2$ is also accepted.) The units of k are then s^{-1} if $t_{1/2}$ is in seconds.

After n half-lives the fraction left is $(\frac{1}{2})^n$: one half after 1, one quarter after 2, one eighth after 3, one sixteenth after 4. So "75% has reacted" means 2 half-lives, and "87.5% has reacted" means 3.

This equation is **only** for first-order reactions. A second-order reaction has no constant half-life, so you cannot find its k this way.

Rate–concentration graphs

Plot the rate against the concentration of one reactant (others kept constant):



For a first-order reaction the line is straight through the origin and its **gradient is k** , since $\text{rate} = k[\text{A}]$.

The initial-rates method

Run the reaction several times, changing one starting concentration at a time, and measure the rate at the very start (from a tangent at $t = 0$, or from a short time interval). Comparing two experiments where only $[\text{A}]$ changes gives the order in A directly. When two concentrations change together, use an order you already know to remove its effect first.

Using a large excess

If one reactant is in large excess, its concentration hardly changes during the reaction, so it acts as a constant. For $\text{rate} = k[\text{A}][\text{B}]$ with B in large excess, the rate depends only on $[\text{A}]$:

$$\text{rate} = k'[\text{A}], \quad k' = k[\text{B}]$$

The reaction now behaves as **first order** (often called pseudo-first order). The graph of $[\text{A}]$ against time has a constant half-life, k' comes from $0.693/t_{1/2}$, and $k = k' \div [\text{B}]$. The same trick lets you study one reactant at a time.

Mechanisms and the rate-determining step

Most reactions happen in several simple steps, the **mechanism**. The steps must add up to the overall equation. Each step is a collision of one or two particles; a step that needs three or four particles to meet at once is very unlikely.

The **rate-determining step** is the slowest step in the mechanism. The whole reaction can go no faster than it, just as a queue moves at the speed of its slowest checkout. So:

- The **rate equation contains the species in the slow step**, each with the power equal to how many of that particle take part in it.
- Species that only react **after** the slow step do not appear in the rate equation: they are zero order.
- An **intermediate** is made in one step and used up in a later step. It does not appear in the overall equation.
- A **catalyst** is used up in one step and made again in a later step. It does not appear in the overall equation either, but it **can** appear in the rate equation if it takes part in the slow step.

If the slow step uses an intermediate, trace the intermediate back to what made it in a fast step before. For example:

- step 1 (fast): $A + A \rightarrow A_2$
- step 2 (slow): $A_2 + B \rightarrow \text{products}$

The slow step needs one A_2 , and each A_2 came from two A, so $\text{rate} = k[A]^2[B]$.

Temperature and the rate constant

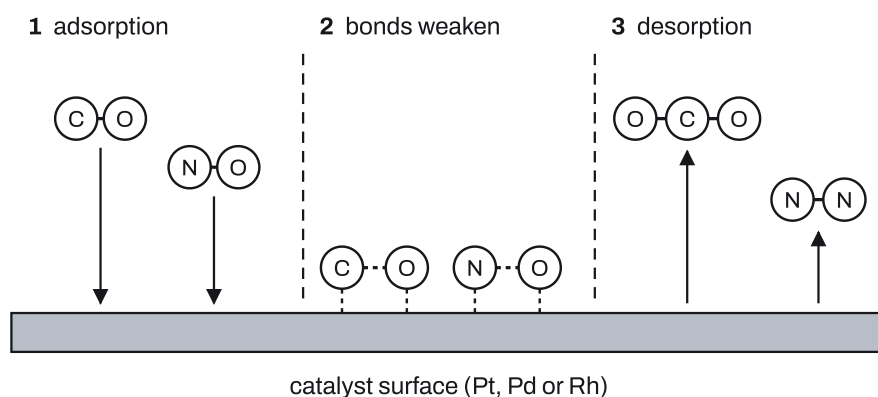
Raising the temperature **increases the rate constant**, so the rate increases for the same concentrations. The reason is the Boltzmann distribution from AS: at a higher temperature a greater proportion of molecules have energy greater than or equal to the activation energy, so effective collisions happen more often. For a first-order reaction a larger k means a **shorter** half-life.

Homogeneous and heterogeneous catalysts

A catalyst gives the reaction a different route (mechanism) with a lower activation energy, and is not used up.

- A **homogeneous** catalyst is in the **same phase** as the reactants (for example, all in aqueous solution, or all gases).
- A **heterogeneous** catalyst is in a **different phase** from the reactants, usually a solid with gases or liquids passing over it.

How a heterogeneous catalyst works



- 1. Adsorption:** the reactant molecules form weak bonds to the surface of the catalyst, at active sites.
- 2. Bond weakening:** the bonds **within** the reactant molecules weaken, so less energy is needed to break them and the reaction happens on the surface. The adsorbed molecules are also held close together.
- 3. Desorption:** the bonds between the products and the surface break and the products leave, freeing the site for more reactants.

The two syllabus examples:

- Iron in the Haber process:** solid iron with gaseous nitrogen and hydrogen, $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$. The strong $\text{N} \equiv \text{N}$ bond is weakened on the iron surface.
- Platinum, palladium and rhodium in a catalytic converter:** solid metals with exhaust gases. Oxides of nitrogen are removed, for example $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$.

If the surface is completely covered (every active site in use), adding more reactant gas cannot speed the reaction up, so the rate is zero order in that reactant.

How a homogeneous catalyst works

The catalyst reacts in one step, then is made again in a later step.

Oxides of nitrogen and sulfur dioxide in the air. Sulfur dioxide reacts only very slowly with oxygen on its own. Nitrogen dioxide speeds this up:

- $\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$ (the NO_2 is used up)
- $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ (the NO_2 is made again)

Adding them (after doubling the first) gives $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$. The same pair of steps also means NO catalyses the reaction, since it is made in one step and used in the other.

Iron ions and the iodide–peroxydisulfate reaction. $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$ is slow, because both reactants are **negative ions that repel**, which makes the activation energy high. With Fe^{2+} each step is between oppositely charged ions:

- $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}$
- $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$

Fe^{3+} works just as well: it starts with the second step. This works because iron can change easily between the +2 and +3 oxidation states, and Fe^{3+} can oxidise I^- while $\text{S}_2\text{O}_8^{2-}$ can oxidise Fe^{2+} . Another ion pair with a suitable +2/+3 couple can act in the same way.

Key facts and formulas

"Given" means it is printed in the Data Booklet or on the Paper 4 question paper. "Learn it" means you must remember it.

Formula	Status
$\text{rate} = k[\text{A}]^m[\text{B}]^n$; overall order = $m + n$	Learn it
Order 0: rate unchanged; order 1: rate $\propto [\text{A}]$; order 2: rate $\propto [\text{A}]^2$	Learn it
Units of k for overall order n : $\text{mol}^{1-n} \text{dm}^{3(n-1)} \text{s}^{-1}$ (order 1: s^{-1} ; order 2: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)	Learn it
First order: $k = \frac{0.693}{t_{1/2}}$ ($0.693 = \ln 2$)	Learn it
Fraction left after n half-lives = $\left(\frac{1}{2}\right)^n$	Learn it
Rate at time t = gradient of the tangent to the concentration–time graph	Learn it
First order: gradient of rate against $[\text{A}] = k$	Learn it
Large excess of B: $k' = k[\text{B}]$	Learn it
Molar volume of a gas at room conditions = $24.0 \text{ dm}^3 \text{ mol}^{-1}$	Given

Half-life patterns: zero order, half-lives get shorter; first order, constant; second order, get longer.

How to do it

In the Paper 4 questions we have tagged for this topic (40 questions, 2021–2025, of which 13 are repeats of a question in another paper of the same session), the types came up this often. 36 of the 40 questions mix several types, so the counts add up to 174.

Question type	Questions
Calculate a rate constant and its units	18
Half-life calculations for a first-order reaction	18
State orders, write a rate equation, define the terms	15
Use a rate equation to calculate or predict a rate	15
Mechanisms, the rate-determining step and intermediates	14

Question type	Questions
Classify a catalyst as homogeneous or heterogeneous	14
Equations for homogeneous catalysis	12
Deduce orders from initial-rates data	11
How a heterogeneous catalyst works	10
Rate from the gradient of a tangent	9
Read half-lives from a graph to show first order	8
Explain whether the half-life is constant	8
Sketch or draw kinetics graphs	8
Effect of temperature on k and the rate	7
Large excess of one reactant	7

1. Calculate a rate constant and its units (18 questions)

1. **Write the rate equation** (from the question, or the one you just deduced).
2. **Rearrange for k** : $k = \frac{\text{rate}}{[\text{A}]^m [\text{B}]^n}$.
3. **Substitute one experiment's values**, the one the question names, and calculate. Give at least 2 significant figures (3 if asked).
4. **Units**: cancel the units, or use the table in "Understand it". Keep min^{-1} if the rate was per minute.

Variations you will meet:

- **High orders**. A rate equation such as $\text{rate} = k[\text{A}][\text{B}]^2[\text{C}]^2$ is fifth order overall: units $\text{mol}^{-4} \text{dm}^{12} \text{s}^{-1}$. Square each squared concentration before you divide.
- **Units only**. Just work out the power of mol dm^{-3} that has to cancel.
- **From a graph of rate against concentration** (first order): k is the gradient. Read a point on the line, such as rate 6.0×10^{-4} at $0.0300 \text{ mol dm}^{-3}$, and divide: $k = 0.020 \text{ s}^{-1}$.
- **From a rate and a concentration read off a graph**: $k = \text{rate} \div [\text{A}]$ for first order.
- **From the half-life**: see type 2.

2. Half-life calculations for a first-order reaction (18 questions)

1. **Check it is first order** (overall, or pseudo-first order because of an excess).
2. $k = \frac{0.693}{t_{1/2}}$, or $t_{1/2} = \frac{0.693}{k}$. Units of k : s^{-1} (or min^{-1}).
3. **For a time**, count the half-lives: find how many halvings take the concentration from its start to its end value, then multiply by $t_{1/2}$.

Variations you will meet:

- **Fractions.** Falling to $\frac{1}{8}$ is 3 half-lives, to $\frac{1}{16}$ is 4, to $\frac{1}{32}$ is 5. "75% used up" means 25% left: 2 half-lives.
- **Start from moles.** Turn moles into a concentration first ($\div$ volume in dm^3), then count halvings.
- **Average rate over some half-lives.** For example, starting at $0.200 \text{ mol dm}^{-3}$ with $t_{1/2} = 300 \text{ s}$, after 2 half-lives 0.0500 is left. Average rate $= \frac{0.200 - 0.0500}{600} = 2.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.
- **"Show that k is ..." or "show that $t_{1/2}$ is ...":** write $0.693 \div$ the value, then the answer to more figures than the given value.

3. State orders, write a rate equation, define the terms (15 questions)

1. **Orders table:** read the power of each concentration from the rate equation. A reactant that is in the overall equation but **missing** from the rate equation is **zero** order. The overall order is the sum.
2. **Rate equation from stated orders:** $\text{rate} = k[\dots]$. Include k , and never put products in.
3. **Definitions** (in your own words, but these ideas):
 - order with respect to a reactant: the power to which its concentration is raised in the rate equation;
 - overall order: the sum of these powers;
 - rate constant: the constant of proportionality in the rate equation;
 - half-life: the time for the concentration of a reactant to fall to half;
 - rate-determining step: the slowest step in the mechanism;
 - intermediate: a species made in one step and used up in a later one.

4. Use a rate equation to calculate or predict a rate (15 questions)

1. **A rate from numbers:** substitute k and every concentration into the rate equation. Units: $\text{mol dm}^{-3} \text{ s}^{-1}$.
2. **A change in rate:** multiply the factor for each concentration raised to its order. For $\text{rate} = k[\text{A}]^2[\text{B}]$, if $[\text{A}]$ is halved and $[\text{B}]$ is doubled, the rate is $\left(\frac{1}{2}\right)^2 \times 2 = \frac{1}{2}$ as fast.
3. **An unknown concentration:** rearrange. If two concentrations are equal to c in a third-order equation, $\text{rate} = kc^3$, so $c = \sqrt[3]{\text{rate} \div k}$.

Variations you will meet:

- **Hydrogen ions from pH.** $[\text{H}^+] = 10^{-\text{pH}}$. A pH lower by 1 means $[\text{H}^+]$ is 10 times bigger: the rate is 10 times faster if first order in H^+ , 100 times if second order.
- **A rate from a gas volume:** moles of gas $= \text{volume in cm}^3 \div 24\,000$ (room conditions), then divide by the time (and by the solution volume in dm^3 if the rate is per dm^3).

5. Mechanisms, the rate-determining step and intermediates (14 questions)

Suggest a mechanism:

1. **Write the slow step first.** Its reactants are exactly the species in the rate equation, each as many times as its order. For $\text{rate} = k[\text{P}][\text{Q}]$, the slow step is $\text{P} + \text{Q} \rightarrow \dots$
2. **Make up its products** so that atoms balance, often an intermediate plus one real product.

3. **Add fast steps** that use up the intermediate and bring in any zero-order reactants, until everything **adds up to the overall equation** (cancel species that appear on both sides).
4. **Label the slow step** as rate-determining.

Pick the rate-determining step from a given mechanism: it is the step whose reactants match the rate equation, **same species, same numbers**. Say so: "step 1, because it contains one A and one B, as in the rate equation".

Variations you will meet:

- **Choose the mechanism** from several: the right one has the slow step containing only (and all of) the rate-equation species in the right numbers, and its steps add up to the overall equation.
- **Three steps, two particles each**: for a third-order rate equation, the first step joins two particles into an intermediate, and the slow second step adds the third. Count the original reactants that made the intermediate.
- **Why not one step?** A single step would need three or four particles to collide at once, which is very unlikely.
- **Identify an intermediate** (made, then used up) or a **catalyst** (used, then made again). Say which steps.
- **Deduce the rate equation from a mechanism** with the slow step marked: the species in the slow step, tracing any intermediate back.

6. Classify a catalyst as homogeneous or heterogeneous (14 questions)

1. **Compare the phases**: catalyst and reactants in the same phase → homogeneous; in different phases → heterogeneous.
2. **Give the reason** in one line, naming the phases: "heterogeneous, because the catalyst is a solid and the reactants are aqueous".

Watch for aqueous catalysts in aqueous reactions (homogeneous) and solid metals or oxides with liquids or gases (heterogeneous).

7. Equations for homogeneous catalysis (12 questions)

1. **Step 1**: the catalyst reacts with one reactant and changes (for example it is oxidised).
2. **Step 2**: the changed form reacts with the other reactant and turns back into the catalyst.
3. **Check** that the two equations add up to the overall equation and are balanced for charge.

Learn both syllabus pairs (see "Understand it"). For a new ion pair M^{2+}/M^{3+} in the iodide–peroxydisulfate reaction, copy the iron pattern: $2M^{3+} + 2I^- \rightarrow 2M^{2+} + I_2$ and $2M^{2+} + S_2O_8^{2-} \rightarrow 2M^{3+} + 2SO_4^{2-}$. "Why is it slow without a catalyst?" Two negative ions repel, so the activation energy is high.

8. Deduce orders from initial-rates data (11 questions)

1. **Find two experiments** in which only one concentration changes. State the factor it changes by and the factor the rate changes by. Conclude the order.
2. **When two change together**, divide out the known order first. If [A] (first order) $\times 2$ and [B] $\times 4$ give rate $\times 32$, then B causes $32 \div 2 = 16 = 4^2$: second order in B.
3. **Write the rate equation**, then use one experiment to find k if asked.

Always say which experiments you used, in words.

Variations you will meet:

- **Both concentrations change by the same factor in every experiment.** Then only the **overall** order can be found. If both double and the rate goes up 4 times, the possible rate equations are $k[A][B]$, $k[A]^2$ and $k[B]^2$.
- **"Show the data are consistent with the rate equation"**: work out k from each experiment and show it is the same, or check each factor.
- **Relative rates** (rate given as 1.00, 2.25 ...): the same method works; you just can't calculate k .

9. How a heterogeneous catalyst works (10 questions)

Write all three steps, which usually earn 2 marks (any two for 1):

1. reactants are **adsorbed** onto the catalyst surface;
2. bonds **within** the reactant molecules **weaken**;
3. products are **desorbed** from the surface.

Name the metals when asked: iron (Haber process); platinum, palladium and rhodium (catalytic converter). If asked why transition metals are good catalysts: they have variable oxidation states and partly filled (vacant) d orbitals that can form bonds to reactants.

10. Rate from the gradient of a tangent (9 questions)

1. **Draw a tangent** at the time (or concentration) asked for: a straight line touching the curve there and not cutting it.
2. **Make it long** and pick two points far apart on it, such as where it meets the axes.
3. **Gradient** = $\frac{\text{change in concentration}}{\text{change in time}}$. Give the rate as a positive number with units, for example $\text{mol dm}^{-3} \text{ s}^{-1}$ or $\text{mol dm}^{-3} \text{ min}^{-1}$. Show the working on the graph.

"The rate at 50 s" needs a tangent, not the average over the first 50 s.

11. Read half-lives from a graph to show first order (8 questions)

1. Read the starting concentration and find where it has halved: that time is the first half-life.

2. From there, find where it halves again: the second half-life.
3. **State both** with the values, for example "0.0800 → 0.0400 takes 50 s and 0.0400 → 0.0200 takes 50 s", and conclude: the half-life is constant, so the reaction is first order.

Mark schemes accept a small reading range. Then $k = 0.693 \div t_{1/2}$.

12. Explain whether the half-life is constant (8 questions)

- **Constant** if the reaction is first order overall, or pseudo-first order because the other reactants are in large excess (their concentrations stay constant).
- **Not constant** if the overall order is 2 (for example $\text{rate} = k[\text{A}][\text{B}]$ with similar concentrations), or zero. So $k = 0.693/t_{1/2}$ **cannot** be used for a second-order reaction.

13. Sketch or draw kinetics graphs (8 questions)

- **Concentration of a reactant against time:** a falling curve, steep at first and levelling off (first or second order); a falling straight line (zero order). A **product's** concentration rises and levels off.
- **Rate against concentration:** horizontal line (zero order), straight line through the origin (first), upward curve through the origin (second).
- **Rate against time** for a zero-order reaction: a horizontal line.
- **Plotting a first-order decay:** mark the start value, then half of it after one $t_{1/2}$, a quarter after two, an eighth after three, and join with a smooth curve.
- A zero-order line **drawn from an initial rate:** a straight line with that gradient.

14. Effect of temperature on k and the rate (7 questions)

1. Say that **both** k and the rate **increase**.
2. If asked to explain: a greater proportion of molecules have energy greater than or equal to E_A , so there are more frequent effective collisions.

15. Large excess of one reactant (7 questions)

1. **Why use an excess?** The excess reactant's concentration stays (almost) constant, so it does not affect the rate during the experiment. The reaction behaves as first (or zero) order in the other reactant.
2. **So** the half-life of the other reactant is constant and k' can come from $0.693 \div t_{1/2}$; divide by the excess concentration to get k .
3. **"Can k be calculated from this graph?"** Not unless you know the concentrations of the excess reactants in the rate equation.

Following a reaction: measure something that changes with the concentration at intervals, for example the volume of a gas made, the colour (with a colorimeter), or the pH.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Sulfuryl chloride decomposes in the gas phase: $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$. The reaction is first order with respect to SO_2Cl_2 . At a certain temperature $k = 2.20 \times 10^{-5} \text{ s}^{-1}$.

- (a) Write the rate equation and explain why the units of k are s^{-1} . **[2]**
- (b) Calculate the half-life of the reaction at this temperature. **[1]**
- (c) The initial concentration of SO_2Cl_2 is $0.0800 \text{ mol dm}^{-3}$. Calculate the initial rate, and the time taken for the concentration to fall to $0.0100 \text{ mol dm}^{-3}$. **[3]**
- (d) State the effect of raising the temperature on k and on the half-life. **[1]**

(a) $\text{rate} = k[\text{SO}_2\text{Cl}_2]$ **B1**. $k = \frac{\text{rate}}{[\text{SO}_2\text{Cl}_2]}$, so the units are $\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$. **B1**

(b) $t_{1/2} = \frac{0.693}{2.20 \times 10^{-5}} = 3.15 \times 10^4 \text{ s}$ **B1**

(c) Initial rate $= 2.20 \times 10^{-5} \times 0.0800 = 1.76 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$. **B1**

$0.0800 \rightarrow 0.0400 \rightarrow 0.0200 \rightarrow 0.0100$ is 3 half-lives. **M1**

Time $= 3 \times 3.15 \times 10^4 = 9.45 \times 10^4 \text{ s}$ **A1**

(d) k increases, so the half-life decreases. **B1**

Example 2

Iodine monochloride reacts with hydrogen: $2\text{ICl(g)} + \text{H}_2\text{(g)} \rightarrow \text{I}_2\text{(g)} + 2\text{HCl(g)}$. The initial rate was measured in three experiments at the same temperature.

Experiment	$[\text{ICl}] / \text{mol dm}^{-3}$	$[\text{H}_2] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.0150	0.0100	3.60×10^{-5}
2	0.0450	0.0100	1.08×10^{-4}

Experiment	[ICl] / mol dm ⁻³	[H ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
3	0.0300	0.0400	2.88×10^{-4}

(a) Deduce the order with respect to each reactant and write the rate equation. Explain your reasoning. **[3]**

(b) Use experiment 1 to calculate k , with its units. **[2]**

(c) Calculate the initial rate when [ICl] = 0.0200 mol dm⁻³ and [H₂] = 0.0250 mol dm⁻³. **[1]**

(d) The reaction takes place in two steps. Suggest equations for the two steps, identify the rate-determining step and name the intermediate. **[3]**

(a) Experiments 1 and 2: [ICl] $\times 3$, [H₂] the same, rate $\times 3$, so first order with respect to ICl. **M1**

Experiments 1 and 3: [ICl] $\times 2$ and [H₂] $\times 4$, rate $\times 8$. The ICl accounts for $\times 2$, leaving $8 \div 2 = 4$ for the $\times 4$ in [H₂], so first order with respect to H₂. **M1**

$$\text{rate} = k[\text{ICl}][\text{H}_2] \quad \mathbf{A1}$$

$$\mathbf{(b)} \quad k = \frac{3.60 \times 10^{-5}}{0.0150 \times 0.0100} = 0.240 \quad \mathbf{M1}, \text{ units mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad \mathbf{A1}$$

$$\mathbf{(c)} \quad \text{rate} = 0.240 \times 0.0200 \times 0.0250 = 1.20 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1} \quad \mathbf{B1}$$

(d) The slow step must contain one ICl and one H₂:

- step 1 (slow, rate-determining): $\text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl}$ **M1**
- step 2 (fast): $\text{HI} + \text{ICl} \rightarrow \text{HCl} + \text{I}_2$ **M1**

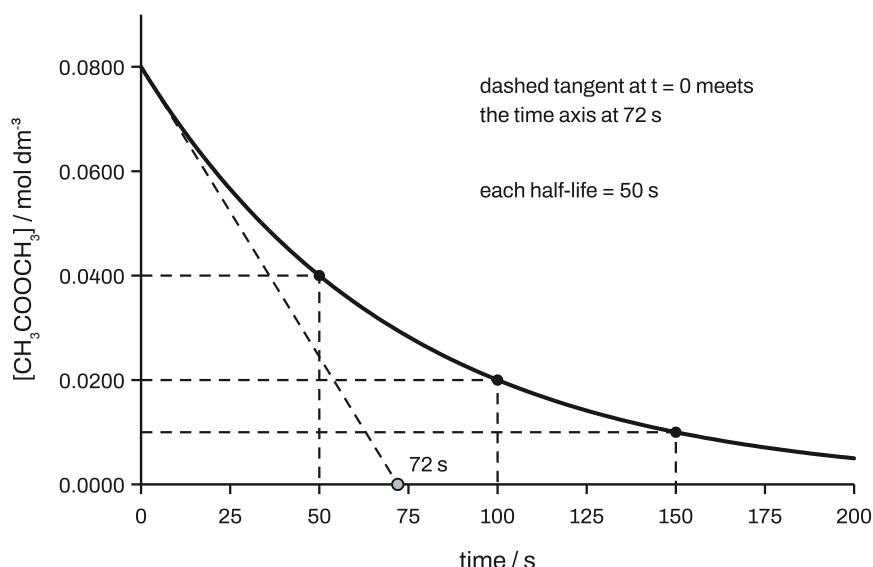
The steps add up to the overall equation. HI is the intermediate: it is made in step 1 and used up in step 2. **A1**

Example 3

Methyl ethanoate is hydrolysed by aqueous sodium hydroxide:



In one experiment [OH⁻] = 0.500 mol dm⁻³, a large excess, and the initial [CH₃COOCH₃] is 0.0800 mol dm⁻³. The graph shows the results.



(a) Explain why the graph shows a constant half-life, although the reaction is second order overall. [1]

(b) Use the graph to show that the half-life is constant. [1]

(c) Calculate the pseudo-first-order rate constant k' and use it to find k . [2]

(d) Use the tangent drawn on the graph to find the initial rate, and show that it agrees with your k' . [2]

(a) $[\text{OH}^-]$ is in large excess, so it stays effectively constant; the rate depends only on $[\text{CH}_3\text{COOCH}_3]$, so the reaction behaves as first order. **B1**

(b) $0.0800 \rightarrow 0.0400$ takes 50 s and $0.0400 \rightarrow 0.0200$ takes a further 50 s ($0.0200 \rightarrow 0.0100$ also 50 s): the half-life is constant, 50 s. **B1**

(c) $k' = \frac{0.693}{50} = 0.01386 = 0.0139 \text{ s}^{-1}$ **M1**

$k' = k[\text{OH}^-]$, so $k = \frac{0.01386}{0.500} = 0.0277 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ **A1**

(d) The tangent falls from $0.0800 \text{ mol dm}^{-3}$ to 0 in 72 s. Gradient = $\frac{0.0800}{72} = 1.11 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$. **M1**

Check: rate = $k'[\text{CH}_3\text{COOCH}_3] = 0.01386 \times 0.0800 = 1.11 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, the same. **A1**

Example 4

Nitrogen dioxide reacts with carbon monoxide: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$. The rate equation is rate = $k[\text{NO}_2]^2$, and at a certain temperature $k = 0.540 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

(a) State the order with respect to NO_2 , to CO, and the overall order. [1]

(b) Calculate the initial rate when $[\text{NO}_2] = 0.0200 \text{ mol dm}^{-3}$ and $[\text{CO}] = 0.0500 \text{ mol dm}^{-3}$. [1]

(c) Predict the effect on the initial rate of tripling $[\text{NO}_2]$ and halving $[\text{CO}]$ at the same time. [1]

(d) Suggest a two-step mechanism consistent with the rate equation. Identify the rate-determining step and the intermediate. **[3]**

(e) Explain whether the half-life of NO_2 is constant when both gases start at similar concentrations. **[1]**

(a) NO_2 : 2; CO: 0; overall: 2 **B1**

(b) $\text{rate} = 0.540 \times 0.0200^2 = 2.16 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ **B1**

(c) $3^2 = 9$; CO is zero order so halving it has no effect: the rate is 9 times faster. **B1**

(d) The slow step must contain two NO_2 and no CO:

- step 1 (slow, rate-determining): $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ **M1**
- step 2 (fast): $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ **M1**

Adding them and cancelling one NO_2 and the NO_3 gives the overall equation. NO_3 is the intermediate. **A1**

(e) Not constant: the reaction is second order in NO_2 , and only first-order reactions have a constant half-life. **B1**

Common mistakes

- **Taking orders from the balanced equation.** Orders come only from experiments; a coefficient of 2 does not mean second order.
- **Leaving out k , or writing an equilibrium-style fraction** (products over reactants) instead of a rate equation.
- **Mixing up the units of rate and of k ,** or writing units that can't be read clearly. Write them with negative powers, for example $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and check by cancelling.
- **Not saying which experiments you compared,** or leaving the reasoning as marks on the table. Examiners want sentences: "experiments 1 and 3: $[\text{A}] \times 2$, rate $\times 4$, so second order".
- **Forgetting to remove a known order** when two concentrations change together.
- **An average rate instead of the rate at an instant.** "At 100 s" means a tangent at 100 s.
- **Weak evidence for a constant half-life.** Quoting two times such as "50 s and 100 s" is not enough; give each halving with its start and end concentration and the time it took.
- **Using $k = 0.693/t_{1/2}$ for a reaction that is not first order.**
- **Slow step with the wrong numbers.** If the rate equation has one of each reactant, the slow step must have exactly one of each, no more.
- **Mechanism steps that don't add up** to the overall equation, or that have three or more particles colliding in one step.
- **Describing a heterogeneous catalyst instead of how it works,** saying bonds **between** molecules weaken (it is bonds **within** them), or leaving out desorption.
- **Temperature answers that miss the rate constant.** Say k increases as well as the rate; when explaining, mention the greater proportion of molecules with energy $\geq E_A$.

- **Excess-reagent answers that don't say the concentration stays constant.**
- **Unit slips in time:** dividing by 60 (or not) when converting between seconds and minutes.

How to get the marks

- **"Deduce the rate equation, explain your reasoning":** one mark per order with the experiments and the factors stated, then a mark for the rate equation. A wrong order used correctly later still earns follow-through marks.
- **"Calculate k ":** usually 2 marks, one for the value (at least 2 s.f., or 3 s.f. when asked) and one for the units.
- **"Show that":** the answer is given, so write the calculation in full, for example $t_{1/2} = 0.693 \div k = \dots$ with the numbers in, and give more figures than printed.
- **"Suggest a mechanism":** equations, not words. One mark usually needs the steps to add up to the overall equation; another needs the slow step to match the rate equation, labelled as rate-determining.
- **"Explain" a type of catalysis:** the type **and** the reason (same or different phase from the reactants, naming them).
- **"Describe the mode of action":** all three steps for full marks.
- **"Describe the effect of temperature":** both k and the rate increase; one mark often needs both.
- **Graph work:** draw the tangent or the half-life lines on the graph itself; the working marks are for what you draw.
- **"State"** needs only the answer; **"predict"** needs a clear answer (such as " $\times 27$ "); **"explain"** needs the reason.

Quick check

1. The rate equation for a reaction is $\text{rate} = k[\text{P}][\text{Q}]^2[\text{R}]$. Give the overall order and the units of k (rate in $\text{mol dm}^{-3} \text{s}^{-1}$).
2. Cyclopropane isomerises to propene in a first-order reaction with $k = 6.70 \times 10^{-4} \text{s}^{-1}$. Calculate the half-life, and the time for 87.5% of the cyclopropane to react.
3. For $\text{rate} = k[\text{C}]^2[\text{D}]$, $[\text{C}]$ is halved and $[\text{D}]$ is tripled. By what factor does the rate change?
4. A reaction $\text{A} + \text{B} \rightarrow \text{AB}$ has this mechanism: step 1 (slow) $\text{A} + \text{C} \rightarrow \text{AC}$; step 2 (fast) $\text{AC} + \text{B} \rightarrow \text{AB} + \text{C}$. Write the rate equation, and identify the catalyst and the intermediate.
5. In the Contact process, solid vanadium(V) oxide catalyses $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$. State the type of catalysis, with a reason, and describe how the catalyst works.

Answers

- Overall order $1 + 2 + 1 = 4$. $k = \frac{\text{rate}}{[\]^4}$, so units $= \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol}^4 \text{dm}^{-12}} = \text{mol}^{-3} \text{dm}^9 \text{s}^{-1}$.
- $t_{1/2} = \frac{0.693}{6.70 \times 10^{-4}} = 1034 \text{ s} = 1.03 \times 10^3 \text{ s}$. 87.5% reacted leaves 12.5% $= \frac{1}{8}$: 3 half-lives, so time $= 3 \times 1034 = 3.10 \times 10^3 \text{ s}$.
- $\left(\frac{1}{2}\right)^2 \times 3 = \frac{3}{4}$: the rate falls to 0.75 times its value.
- The slow step contains one A and one C, so rate $= k[\text{A}][\text{C}]$ (zero order in B). C is the catalyst: used in step 1 and made again in step 2. AC is the intermediate: made in step 1 and used up in step 2.
- Heterogeneous: the catalyst is a solid and the reactants are gases. SO_2 and O_2 are adsorbed onto the surface; the bonds within them weaken, so they react; the SO_3 is desorbed, freeing the surface.

Past questions to try

- 9701/43/O/N/22 Q2**: iron-ion catalysis, a rate from a rate equation, and counting half-lives from moles.
- 9701/42/M/J/24 Q5**: orders from an initial-rates table where two concentrations change, then k with units and a two-step mechanism.
- 9701/43/O/N/23 Q1**: a two-step mechanism, then plotting a first-order decay and drawing a tangent.
- 9701/42/O/N/22 Q2**: whether the half-life is constant, zero-order graphs and a heterogeneous catalyst.