

Reaction kinetics: rate equations, orders and mechanisms (A Level Chemistry notes)

These notes cover the A Level (second year) reaction kinetics topic of Cambridge International AS and A Level Chemistry (9701). At AS you explained rates qualitatively using collision theory and the Boltzmann distribution. At A Level the topic becomes quantitative: you write rate equations, deduce orders from experimental data, calculate rate constants with the correct units, use half-lives, and link rate equations to reaction mechanisms. Learn the boxed definitions word for word, and practise the data problems until the method is automatic.

1. Rate of reaction

1.1 Defining rate

Rate of reaction is the change in concentration of a reactant or product per unit time.

Units: $\text{mol dm}^{-3} \text{ s}^{-1}$.

Rate is always given as a positive number. For a reactant, the concentration falls, so rate = $-(\text{change in concentration}) \div \text{time}$. For a product, the concentration rises, so rate = $+(\text{change in concentration}) \div \text{time}$. If the equation has different stoichiometric numbers, the rates for different species are different: in $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, NO_2 forms four times as fast as O_2 , and N_2O_5 is used up twice as fast as O_2 forms.

1.2 Measuring rate

To follow a reaction, measure a property that changes with concentration over time. Common methods are:

- collecting a gas in a gas syringe and recording volume against time;
- recording the loss in mass as a gas escapes;
- colorimetry, when one species is coloured (for example iodine or manganate(VII));
- measuring electrical conductivity, when the number or type of ions changes;
- withdrawing samples at intervals, quenching them (stopping the reaction by cooling, dilution or removing the catalyst) and titrating.

From a concentration-time graph, the rate at any instant is the gradient of the tangent to the curve at that time. The initial rate is the gradient of the tangent at $t = 0$.

A clock reaction gives initial rates more simply. You measure the time, t , taken for a fixed small amount of product to form (for example, enough iodine to turn starch blue-black). Since the same amount of product forms each time, the initial rate is proportional to $1/t$.

2. Rate equations, order and the rate constant

2.1 The rate equation



For a reaction $A + B \rightarrow \text{products}$, experiments show that the rate depends on the concentrations of the reactants raised to powers:

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

Rate equation: an equation that shows how the rate of a reaction depends on the concentrations of the reactants, in the form $\text{rate} = k[A]^m[B]^n$.

Order of reaction with respect to a reactant: the power to which the concentration of that reactant is raised in the rate equation.

Overall order of reaction: the sum of the powers of the concentration terms in the rate equation ($m + n$).

Rate constant, k : the constant of proportionality in the rate equation. Its value is fixed for a given reaction at a given temperature.

The single most important fact about orders: **they can only be found by experiment**. They cannot be read from the balanced equation. For example, the reaction $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$ has the rate equation $\text{rate} = k[\text{NO}_2][\text{F}_2]$, first order in NO_2 even though two NO_2 appear in the equation. At this level, orders are 0, 1 or 2.

2.2 What each order means

Order with respect to A	Effect of doubling [A] on the rate	Effect of tripling [A] on the rate
0	no change	no change
1	doubles ($\times 2$)	triples ($\times 3$)
2	quadruples ($\times 4$)	$\times 9$

In general, if [A] is multiplied by a factor x , the rate is multiplied by x^m . A reactant that is zero order does not appear in the rate equation at all (since $[A]^0 = 1$), but it is still needed for the reaction to happen: it simply takes part after the slowest step.

2.3 Units of the rate constant

Rearrange the rate equation for k , substitute units and cancel. Rate always has units $\text{mol dm}^{-3} \text{s}^{-1}$.

Worked example 1: units of k for a second-order reaction

$$\text{rate} = k[A][B], \text{ so } k = \text{rate} \div ([A][B])$$

$$\text{Units} = (\text{mol dm}^{-3} \text{s}^{-1}) \div (\text{mol dm}^{-3} \times \text{mol dm}^{-3}) = \text{s}^{-1} \div (\text{mol dm}^{-3}) = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$$

Write this as $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Overall order	Units of k
0	$\text{mol dm}^{-3} \text{s}^{-1}$
1	s^{-1}
2	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

3	$\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$
---	---

Pattern: every increase of one in the overall order adds $\text{dm}^3 \text{mol}^{-1}$ to the units. If the time in the question is in minutes, use min^{-1} instead of s^{-1} .

3. Finding orders from initial-rates data

3.1 The method

1. Find two experiments in which only the concentration of one reactant changes and all others stay the same.
2. Work out the factor by which that concentration changes and the factor by which the rate changes.
3. Match them: rate factor = (concentration factor)^{order}.
4. Repeat for each reactant.
5. Write the rate equation, then substitute any one set of results to calculate k .

Worked example 2: deducing a rate equation

Initial rates for the reaction $\text{A} + 2\text{B} \rightarrow \text{C}$ were measured at constant temperature.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	4.0×10^{-4}
3	0.10	0.30	1.8×10^{-3}

Experiments 1 and 2: [B] is constant, [A] doubles and the rate doubles ($4.0 \div 2.0 = 2$). First order with respect to A.

Experiments 1 and 3: [A] is constant, [B] triples and the rate increases by $1.8 \times 10^{-3} \div 2.0 \times 10^{-4} = 9 = 3^2$. Second order with respect to B.

Rate equation: rate = $k[\text{A}][\text{B}]^2$. Overall order 3.

From experiment 1: $k = 2.0 \times 10^{-4} \div (0.10 \times 0.10^2) = 2.0 \times 10^{-4} \div 1.0 \times 10^{-3} = 0.20 \text{ dm}^6 \text{mol}^{-2} \text{s}^{-1}$

Prediction: with [A] = 0.30 and [B] = 0.20 mol dm^{-3} , rate = $0.20 \times 0.30 \times 0.20^2 = 2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{s}^{-1}$.

3.2 When two concentrations change at once

Sometimes no pair of experiments isolates the reactant you need. Use an order you already know to remove its effect. For example, if A is first order and both [A] and [B] double while the rate increases eightfold, then doubling [A] accounts for $\times 2$, leaving $\times 4$ for B, so B is second order.

Exam tip: show the comparison in words, for example "from experiments 1 and 3, when [B] is tripled with [A] constant, the rate increases by a factor of 9, so the reaction is second order with respect to B".

respect to B". A bare "second order" may lose the mark for reasoning.

4. Finding orders from graphs

4.1 Rate-concentration graphs

If you have several values of rate at different concentrations of one reactant (others in large excess or constant), plot rate against concentration.

- **Zero order:** a horizontal straight line. The rate does not change with concentration. The value of the rate is k .
- **First order:** a straight line through the origin. The gradient is k (when only this reactant affects the rate).
- **Second order:** an upward curve through the origin (a parabola), getting steeper as concentration increases. A plot of rate against $[A]^2$ would be a straight line through the origin.

4.2 Concentration-time graphs

If you follow one reaction over time, plot concentration of a reactant against time.

- **Zero order:** a straight line sloping downwards. The gradient is constant and equal to $-k$. The reaction stops abruptly when the reactant runs out.
- **First order:** a curve that gets less steep with time, with a **constant half-life**.
- **Second order:** also a downward curve, but steeper at first and then flattening more strongly. The half-life increases as the reaction goes on (each half-life is longer than the one before).

To use a concentration-time graph to find the order, either read off successive half-lives (constant means first order), or draw tangents at several points to get rates and then plot those rates against concentration, as in 4.1.

4.3 Using an excess of the other reactants

If all other reactants are in large excess (for example at least ten times the concentration), their concentrations hardly change during the reaction. The rate then depends only on the reactant being followed, so its order can be found from one concentration-time graph. This is called making the other reactants effectively constant.

5. Half-life and first-order reactions

Half-life, $t_{1/2}$: the time taken for the concentration of a reactant to fall to half of its initial value.

For a first-order reaction, the half-life is constant: it does not depend on the starting concentration.

For a first-order reaction: $k = 0.693 \div t_{1/2}$ (0.693 is $\ln 2$).

So for a first-order reaction, the time to go from 1.00 to 0.50 mol dm^{-3} is the same as the time to go from 0.50 to 0.25 mol dm^{-3} . After n half-lives, the fraction of reactant left is $(\frac{1}{2})^n$: one quarter after two half-lives, one eighth after three, one sixteenth after four.

For a zero-order reaction, the half-life gets shorter as the concentration falls; for a second-order

reaction it gets longer. Only the first-order case is constant, which is why a constant half-life is the standard test for first order.

Worked example 3: half-life from concentration-time data

The decomposition of a compound X was followed at constant temperature.

Time / s	0	50	100	150
[X] / mol dm ⁻³	0.800	0.400	0.200	0.100

The concentration halves every 50 s (0.800 → 0.400 → 0.200 → 0.100), so the half-life is constant at 50 s. The reaction is first order with respect to X.

$$k = 0.693 \div 50 = 0.0139 \text{ s}^{-1} \quad (1.39 \times 10^{-2} \text{ s}^{-1})$$

$$\text{Rate when [X] = 0.400 mol dm}^{-3}: \text{rate} = k[\text{X}] = 0.01386 \times 0.400 = 5.54 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Worked example 4: using half-life to find a time

A first-order reaction has $k = 2.31 \times 10^{-3} \text{ s}^{-1}$. How long does it take for 87.5% of the reactant to be used up?

$$t_{1/2} = 0.693 \div 2.31 \times 10^{-3} = 300 \text{ s}$$

87.5% used means 12.5% (one eighth) left, which is $(\frac{1}{2})^3$, so three half-lives.

$$\text{Time} = 3 \times 300 = 900 \text{ s}$$

6. Rate-determining step and mechanisms

6.1 Multi-step reactions

Most reactions do not happen in one collision. They happen through a sequence of simpler steps, called the mechanism. Each step involves only one or two particles. Species formed in one step and used up in a later step are intermediates; they do not appear in the overall equation.

Rate-determining step: the slowest step in a reaction mechanism. It controls the overall rate of the reaction.

Think of a queue: however fast the other steps are, products cannot form faster than the slowest step allows.

6.2 Linking the rate equation to the mechanism

- The species in the rate equation are the species involved in the rate-determining step (or in fast steps before it).
- The order with respect to a reactant usually equals the number of particles of that reactant involved up to and including the rate-determining step.
- A reactant that is zero order is not involved in the rate-determining step; it reacts in a later, fast step.
- A species that appears in the rate equation but not in the overall equation is a catalyst (or forms

an intermediate before the slow step).

- The steps of a proposed mechanism must add up to the overall equation.

Worked example 5: nitrogen dioxide and fluorine

Overall: $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$. Rate equation: $\text{rate} = k[\text{NO}_2][\text{F}_2]$.

The rate-determining step must involve one NO_2 and one F_2 . A mechanism consistent with this is:

Step 1 (slow): $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$

Step 2 (fast): $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$

The fluorine atom is an intermediate. Adding the two steps gives the overall equation. The second NO_2 reacts after the slow step, so the order with respect to NO_2 is 1, not 2.

6.3 Hydrolysis of halogenoalkanes

Halogenoalkanes react with hydroxide ions: $\text{R-Br} + \text{OH}^- \rightarrow \text{R-OH} + \text{Br}^-$. The rate equation depends on the structure of the halogenoalkane and reveals the mechanism.

- **Primary, for example bromoethane:** $\text{rate} = k[\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$. Both species are in a single step: the hydroxide ion attacks the carbon as the bromide ion leaves. This is $\text{S}_{\text{N}}2$ (substitution, nucleophilic, two species in the rate-determining step).
- **Tertiary, for example 2-bromo-2-methylpropane:** $\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$. The slow step is the breaking of the C-Br bond to form a carbocation: $(\text{CH}_3)_3\text{CBr} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$. The carbocation then reacts rapidly with OH^- . This is $\text{S}_{\text{N}}1$ (one species in the rate-determining step). The hydroxide ion is zero order.

6.4 Iodination of propanone

$\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$, catalysed by acid.

$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

This tells us three things. First, iodine is zero order, so it is not involved in the rate-determining step; it reacts in a fast later step. Second, H^+ appears in the rate equation but not in the overall equation, so it is a catalyst involved in or before the slow step. Third, the rate-determining step involves one propanone molecule and one hydrogen ion (or species formed from them). The reaction can be followed by colorimetry, because the brown colour of iodine fades. Because the rate is independent of $[\text{I}_2]$, a graph of $[\text{I}_2]$ against time is a straight line when propanone and acid are in excess.

Exam tip: when asked to suggest a mechanism, check three things before you write: the slow step contains exactly the species (and numbers) in the rate equation; zero-order reactants only appear in fast steps after it; and the steps add up to the overall equation.

7. Catalysis

Catalyst: a substance that increases the rate of a reaction without itself undergoing any permanent chemical change. It provides an alternative reaction pathway with a lower activation energy.

Homogeneous catalysis: the catalyst is in the same phase as the reactants.

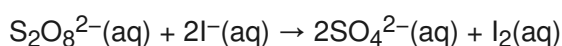
Heterogeneous catalysis: the catalyst is in a different phase from the reactants.

Lowering the activation energy means a greater proportion of collisions have energy equal to or greater than the activation energy, so the frequency of successful collisions increases. In terms of the rate equation, a catalyst increases the value of k . A catalyst does not change the enthalpy change of the reaction or the position of equilibrium.

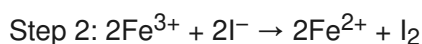
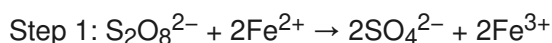
7.1 Homogeneous catalysis

Homogeneous catalysts usually work by taking part in the reaction to form an intermediate, and then being regenerated in a later step. Transition metal ions are good at this because they can change easily between oxidation states.

Iron ions in the reaction of peroxodisulfate with iodide. The overall reaction is:

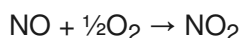
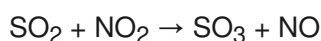


Uncatalysed, this is slow because both reactants are negative ions, which repel each other, so the activation energy is high. With Fe^{2+} ions added:



Each step involves oppositely charged ions, which attract, so each has a lower activation energy. Fe^{2+} is regenerated in step 2. Fe^{3+} also catalyses the reaction, because the two steps then occur in the opposite order.

Oxides of nitrogen in the atmosphere. Nitrogen dioxide catalyses the oxidation of sulfur dioxide, contributing to acid rain:



The NO_2 is regenerated, so it is a catalyst; all species are gases, so this is homogeneous catalysis.

7.2 Heterogeneous catalysis

Most heterogeneous catalysts are solids (often transition metals or their compounds) catalysing reactions of gases or liquids. They work at their surface in a series of stages.

1. **Adsorption:** reactant molecules form weak bonds with atoms on the catalyst surface (at active sites).
2. **Weakening of bonds:** bonds within the reactant molecules are weakened, and the molecules are held close together in a favourable orientation.
3. **Reaction:** new bonds form between the adsorbed species.
4. **Desorption:** the product molecules leave the surface, freeing the active sites for new reactants.

A good heterogeneous catalyst adsorbs strongly enough to weaken bonds in the reactants, but not so strongly that the products cannot desorb.

Examples:

- Iron in the Haber process: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$.
- Platinum, palladium and rhodium in catalytic converters, which remove pollutants from car exhausts, for example $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$.
- Vanadium(V) oxide in the Contact process: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$.

Solid catalysts are used in finely divided form or spread thinly on a support (such as the ceramic honeycomb in a catalytic converter) to give a large surface area. They can be poisoned when impurities, such as lead or sulfur compounds, adsorb strongly and block the active sites.

8. The effect of temperature on the rate constant

The rate equation shows how rate depends on concentration at a fixed temperature. Changing the temperature does not change the concentrations, so its effect on rate must appear through the rate constant: **increasing the temperature increases the value of k** , and therefore the rate.

The explanation uses the Boltzmann distribution from AS:

- At a higher temperature, the molecules have a greater average kinetic energy, so they move faster and collide more often.
- More importantly, the Boltzmann distribution shifts to the right and flattens, so a much greater proportion of molecules have energy equal to or greater than the activation energy, E_a .
- So the frequency of successful collisions increases greatly, and k increases.

For many reactions near room temperature, a rise of 10 K roughly doubles the rate, but this is only a rough guide; the exact effect depends on the activation energy. Reactions with a larger activation energy are more sensitive to temperature changes.

Exam tip: a catalyst and a temperature rise both increase k , but in different ways. A catalyst lowers E_a (the energy barrier moves to the left on the Boltzmann diagram). A temperature rise changes the distribution of energies (the curve changes, the barrier stays the same). Neither changes the orders of reaction for a simple reaction, and a rate constant is only quoted with its temperature.

Quick check

1. State what is meant by (a) the order of reaction with respect to a reactant (b) the rate constant.
[2]
2. The reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ was studied at constant temperature.

Experiment	$[\text{NO}] / \text{mol dm}^{-3}$	$[\text{Cl}_2] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.010	0.010	1.2×10^{-4}
2	0.020	0.010	4.8×10^{-4}
3	0.010	0.030	3.6×10^{-4}
4	0.030	0.020	to be calculated

- (a) Deduce the order with respect to each reactant, explaining your reasoning. (b) Write the rate equation. (c) Calculate k and give its units. (d) Calculate the initial rate in experiment 4. [7]
3. Give the units of k for each rate equation: (a) $\text{rate} = k$ (b) $\text{rate} = k[A]^2$ (c) $\text{rate} = k[A]^2[B]$. [3]
4. Describe the shape of a graph of rate against concentration for a reactant that is (a) zero order (b) first order (c) second order. [3]
5. The concentration of reactant P was measured over time: 0 s, $0.240 \text{ mol dm}^{-3}$; 400 s, $0.120 \text{ mol dm}^{-3}$; 800 s, $0.060 \text{ mol dm}^{-3}$; 1200 s, $0.030 \text{ mol dm}^{-3}$. (a) Show that the reaction is first order with respect to P. (b) Calculate k . (c) Calculate the rate when $[P] = 0.120 \text{ mol dm}^{-3}$. [4]
6. A first-order reaction has a rate constant of $4.62 \times 10^{-3} \text{ s}^{-1}$. (a) Calculate its half-life. (b) Calculate the time taken for the concentration to fall to 12.5% of its initial value. [3]
7. For a reaction of Q, catalysed by a metal surface, $[Q]$ fell from $0.100 \text{ mol dm}^{-3}$ to 0.085, 0.070 and $0.055 \text{ mol dm}^{-3}$ at 30 s, 60 s and 90 s. Deduce the order with respect to Q, and calculate k with units. [3]
8. The reaction $2A + B \rightarrow A_2B$ has the rate equation $\text{rate} = k[A][B]$. Suggest a two-step mechanism consistent with this rate equation, and identify the rate-determining step and the intermediate. [3]
9. The hydrolysis of 2-bromo-2-methylpropane by aqueous hydroxide ions has the rate equation $\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$. (a) Explain why $[\text{OH}^-]$ does not appear. (b) Write equations for the two steps of the mechanism, labelling the slow step. (c) State the effect on the rate of doubling $[\text{OH}^-]$. [4]
10. The acid-catalysed iodination of propanone has the rate equation $\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$. (a) What does this tell you about the role of iodine in the mechanism? (b) Explain how the rate equation shows that H^+ is a catalyst. (c) Describe what a graph of $[\text{I}_2]$ against time would look like, with propanone and acid in large excess. [4]
11. Peroxodisulfate ions react slowly with iodide ions. (a) Explain why the uncatalysed reaction is slow. (b) Write two equations to show how Fe^{2+} ions catalyse the reaction. (c) State the type of catalysis and explain why Fe^{3+} ions also work. [5]
12. (a) Describe the stages by which a solid catalyst speeds up a reaction between gases. (b) Explain why increasing the temperature increases the rate constant of a reaction. [6]

1. (a) The power to which the concentration of that reactant is raised in the rate equation. (b) The constant of proportionality in the rate equation; its value is fixed for a reaction at a given temperature.
2. (a) Experiments 1 and 2: $[\text{Cl}_2]$ is constant and $[\text{NO}]$ doubles; the rate increases from 1.2×10^{-4} to 4.8×10^{-4} , a factor of $4 = 2^2$, so second order with respect to NO. Experiments 1 and 3: $[\text{NO}]$ is constant and $[\text{Cl}_2]$ triples; the rate increases from 1.2×10^{-4} to 3.6×10^{-4} , a factor of 3, so first order with respect to Cl_2 . (b) $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$. (c) From experiment 1: $k = 1.2 \times 10^{-4} \div (0.010^2 \times 0.010) = 1.2 \times 10^{-4} \div 1.0 \times 10^{-6} = 120 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ (third order overall). (d) $\text{rate} = 120 \times 0.030^2 \times 0.020 = 120 \times 9.0 \times 10^{-4} \times 0.020 = 2.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ (2.16×10^{-3}).
3. (a) Zero order: $k = \text{rate}$, so $\text{mol dm}^{-3} \text{ s}^{-1}$. (b) Second order: $k = \text{rate} \div [\text{A}]^2 = (\text{mol dm}^{-3} \text{ s}^{-1}) \div (\text{mol dm}^{-3})^2 = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. (c) Third order: $k = \text{rate} \div [\text{A}]^2[\text{B}] = (\text{mol dm}^{-3} \text{ s}^{-1}) \div (\text{mol dm}^{-3})^3 = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.
4. (a) A horizontal straight line: the rate is the same at every concentration. (b) A straight line through the origin: rate is directly proportional to concentration. (c) A curve through the origin that

gets steeper as concentration increases (rate proportional to concentration squared).

5. (a) The concentration halves from 0.240 to 0.120 in 400 s, from 0.120 to 0.060 in a further 400 s, and from 0.060 to 0.030 in a further 400 s. The half-life is constant at 400 s, which shows the reaction is first order. (b) $k = 0.693 \div 400 = 1.73 \times 10^{-3} \text{ s}^{-1}$. (c) $\text{rate} = k[\text{P}] = 1.73 \times 10^{-3} \times 0.120 = 2.08 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.

6. (a) $t_{1/2} = 0.693 \div 4.62 \times 10^{-3} = 150 \text{ s}$. (b) 12.5% = one eighth = $(\frac{1}{2})^3$, so three half-lives: $3 \times 150 = 450 \text{ s}$.

7. The concentration falls by $0.015 \text{ mol dm}^{-3}$ in every 30 s interval, so it decreases linearly with time and the rate is constant. The reaction is zero order with respect to Q. $k = \text{rate} = 0.015 \div 30 = 5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. (Zero order is common for surface-catalysed reactions when the surface is saturated with reactant.)

8. The slow step must involve one A and one B. Step 1 (slow, rate-determining): $\text{A} + \text{B} \rightarrow \text{AB}$. Step 2 (fast): $\text{AB} + \text{A} \rightarrow \text{A}_2\text{B}$. AB is the intermediate. The steps add up to $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$, and the second A reacts after the slow step, so the order with respect to A is 1.

9. (a) The hydroxide ion is not involved in the rate-determining step; it reacts only in a fast step after it, so its concentration does not affect the rate (zero order). (b) Step 1 (slow): $(\text{CH}_3)_3\text{CBr} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$. Step 2 (fast): $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH}$. This is the $\text{S}_{\text{N}}1$ mechanism. (c) No effect on the rate.

10. (a) Iodine is zero order, so it is not involved in the rate-determining step; it reacts in a later, fast step. (b) H^+ appears in the rate equation, so it is involved in (or before) the rate-determining step, but it does not appear in the overall equation $(\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI})$, so it is regenerated: it is a catalyst. (c) A straight line sloping downwards: $[\text{I}_2]$ falls at a constant rate, because the rate does not depend on $[\text{I}_2]$ and the concentrations of propanone and H^+ stay effectively constant.

11. (a) Both $\text{S}_2\text{O}_8^{2-}$ and I^- are negative ions, so they repel each other; the activation energy is high and few collisions are successful. (b) $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}$, then $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$. Each step is between oppositely charged ions, so it has a lower activation energy, and Fe^{2+} is regenerated. (c) Homogeneous catalysis, because the catalyst and reactants are all in aqueous solution. Fe^{3+} also works because it can react with I^- first (forming Fe^{2+} and I_2), and the Fe^{2+} formed then reacts with $\text{S}_2\text{O}_8^{2-}$ to regenerate Fe^{3+} : the same two steps in reverse order.

12. (a) The reactant molecules are adsorbed onto active sites on the catalyst surface, forming weak bonds with it. This weakens bonds within the reactant molecules and holds them close together in a suitable orientation. The reaction takes place on the surface, forming new bonds. The products are then desorbed, leaving the active sites free. (b) At a higher temperature the molecules have more kinetic energy and collide more often. More importantly, the Boltzmann distribution shifts to higher energies, so a much greater proportion of molecules have energy equal to or greater than the activation energy. The frequency of successful collisions increases, so the rate constant k increases (the concentrations are unchanged, so the whole effect appears in k).