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Reactivity 2.2 HL Mechanisms, Rate Equations and the Arrhenius Equation

Booklet 4 · Understandings 2.2.6 – 2.2.13

Elementary steps and the rate-determining step, rate equations and orders from experimental data, the rate constant and its units, and how the Arrhenius equation turns the temperature dependence of k into an activation energy

Complete revision notes, 18 worked examples, model answers & 37 practice questions · Higher Level

How the level tags work in this booklet

HL Everything in this booklet is HL-only content. SL students do not need it. It builds directly on Booklet 3 (Reactivity 2.2.1–2.2.5: rates, collision theory, activation energy and catalysts), which is assumed throughout.

★ marks harder, multi-step examples and questions.

Inside this booklet

1. What the syllabus actually asks of you
2. Mechanisms and molecularity
3. Energy profiles of multistep reactions
4. Rate equations and orders
5. Graphs of reaction order
6. Rate equations and mechanisms
7. The rate constant and its units
8. The Arrhenius equation
9. Key points to memorise
10. Check yourself
11. Answers

1 What the syllabus actually asks of you

Booklet 3 explained *why* rates change. This HL booklet makes the treatment quantitative. Most reactions happen in a series of simple steps, and the slowest step controls the rate. The rate equation, which can only be found by experiment, links the rate to the concentrations of the reactants and gives evidence about those steps. The rate constant, k, depends on temperature, and the Arrhenius equation uses that dependence to measure the activation energy. Expect data-analysis questions in Paper 1B and Paper 2: initial-rates tables, sketches of rate graphs, units of k, evaluating a proposed mechanism, and Arrhenius plots.

Understanding	What it says	What you must be able to do	Level
2.2.6 Mechanisms	Many reactions occur in a series of elementary steps. The slowest step determines the rate of the reaction.	Evaluate proposed reaction mechanisms and recognize reaction intermediates. Distinguish between intermediates and transition states, and recognize both in energy profiles. **Include examples where the rate-determining step is not the first step.** Mechanisms must be consistent with kinetic and stoichiometric data.	HL
2.2.7 Energy profiles	Energy profiles can be used to show the activation energy and transition state of the rate-determining step in a multistep reaction.	Construct and interpret energy profiles from kinetic data.	HL
2.2.8 Molecularity	The molecularity of an elementary step is the number of reacting particles taking part in that step.	Interpret the terms “unimolecular”, “bimolecular” and “termolecular”.	HL
2.2.9 Rate equations	Rate equations depend on the mechanism of the reaction and can only be determined experimentally.	Deduce the rate equation for a reaction from experimental data.	HL
2.2.10 Order	The order with respect to a reactant is the exponent of its concentration in the rate equation, and can describe the number of particles of it in the rate-determining step. The overall order is the sum of the orders.	Sketch, identify and analyse graphs of zero, first and second order reactions: concentration–time and rate–concentration graphs. **Only integer orders will be assessed.**	HL
2.2.11 Rate constant	The rate constant, k, is temperature dependent and its units are determined from the overall order of the reaction.	Solve problems involving the rate equation, including the units of k.	HL
2.2.12 Arrhenius	The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.	Describe the qualitative relationship between temperature and k. Analyse graphs of the Arrhenius equation, including its linear form. Both forms are in the data booklet.	HL
2.2.13 Arrhenius factor	The Arrhenius factor, A, takes into account the frequency of collisions with proper orientations.	Determine the activation energy and the Arrhenius factor from experimental data.	HL

Linking questions and connections for 2.2.6 – 2.2.13

- **Reactivity 3.4:** which mechanism in the hydrolysis of halogenoalkanes involves an intermediate? What are the rate equations and units of k for primary and tertiary halogenoalkanes with aqueous alkali? → sections 3.2 and 7.1
- **Tool 1, 3, Inquiry 2:** what measurements are needed to deduce the order with respect to a reactant? → section 4.3
- **Nature of Science:** why are reaction mechanisms only considered as "possible mechanisms"? → section 6.4
- **Reactivity 2.3:** the rate constant (lower-case k) must not be confused with the equilibrium constant (upper-case K).
- **Booklet 3:** energy profiles, collision theory and Maxwell–Boltzmann curves are used throughout.

What the data booklet does and does not give you

It gives you: the Arrhenius equation, $k = Ae^{-E_a/RT}$; its linear form, $\ln k = -E_a/RT + \ln A$; the two-temperature form, $\ln(k_1/k_2) = (E_a/R)(1/T_2 - 1/T_1)$; and $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$.

It does not give you: how to deduce orders from data; the units of k; the shapes of the rate graphs; how to write a rate equation from a mechanism; or the conversion of E_a from J mol^{-1} to kJ mol^{-1}. All of these must be learned.

2 Reactivity 2.2.6 and 2.2.8 — Mechanisms and molecularity HL

2.1 Elementary steps

An overall equation shows only the start and the end of a reaction. Most reactions that go at a measurable rate actually happen in a series of simple steps, each involving one or two particles, exactly as collision theory describes. This sequence is the **reaction mechanism**. The individual steps cannot usually be observed directly, so a mechanism is in effect a theory about what happens between reactants and products.

Definitions to learn

An **elementary step** is a single molecular event (one collision or one decomposition) in a reaction mechanism.

A **reaction intermediate** is a species that is produced in one step and used up in a later step. It does not appear in the overall equation.

The **molecularity** of an elementary step is the number of reacting particles taking part in that step: **unimolecular** (one), **bimolecular** (two) or **termolecular** (three).

The **rate-determining step** is the slowest step in a mechanism; it has the highest activation energy and determines the overall rate.

Two rules always apply. First, the steps of a mechanism must **add up to the overall equation**: species that appear on both sides cancel. Second, termolecular steps are **rare**, because the chance of three particles colliding at the same moment, with enough energy and the right orientation, is tiny. Chemists therefore prefer a sequence of bimolecular steps, applying Occam's razor: the simplest explanation that fits the evidence.

A **catalyst** can also appear in a mechanism. It is used up in an early step and regenerated in a later one, so, like an intermediate, it is absent from the overall equation; but it is present at the start, whereas an intermediate is made during the reaction.

Worked example 1 — intermediates, catalysts and the overall equation

Q. In the stratosphere, chlorine atoms destroy ozone: step 1: $Cl + O_3 \rightarrow ClO + O_2$; step 2: $ClO + O \rightarrow Cl + O_2$. Deduce the overall equation, identify the intermediate and the catalyst, and state the molecularity of each step.

add the steps: $Cl + O_3 + ClO + O \rightarrow ClO + O_2 + Cl + O_2$; cancel Cl and ClO: **$O_3 + O \rightarrow 2O_2$**

ClO is made in step 1 and used in step 2: **ClO is an intermediate**

Cl is used in step 1 and regenerated in step 2: **Cl is a catalyst**

each step has two reacting particles: **both steps are bimolecular**

Because the chlorine atom is regenerated, one atom can destroy many thousands of ozone molecules. This is why CFCs, which release chlorine atoms in the stratosphere, were banned.

2.2 The rate-determining step

When traffic planners try to speed up traffic through a city, they look for the slowest point, perhaps a crowded junction, because it limits the flow everywhere else. In the same way, the products of a multistep reaction can only appear as fast as the slowest step allows. That step is the **rate-determining step** (RDS), and the activation energy of the overall reaction is the activation energy of this step. A catalyst usually works by providing a different pathway for the rate-determining step, with a lower activation energy.

Examiner traps with mechanisms

- Steps that do not add up to the overall equation. Always check by cancelling species on both sides.
- Confusing an intermediate (made, then used) with a catalyst (used, then regenerated).
- Calling a step termolecular when it has two reacting particles of which one is written with a coefficient: $2NO \rightarrow N_2O_2$ is **bimolecular**.
- Assuming the rate-determining step is always the first step. It is the step with the highest activation energy.

3 Reactivity 2.2.6 and 2.2.7 — Energy profiles of multistep reactions HL

3.1 Intermediates and transition states

Every elementary step has its own energy barrier, so the energy profile of a two-step reaction has two peaks. Each peak is a **transition state**; the dip between them is the **intermediate**. The step with the higher barrier, measured from the species that start that step, is the rate-determining step.

	Intermediate	Transition state (‡)
position on the profile	a minimum (dip) between two peaks	a maximum (peak) of each step
nature	a real species with fully formed bonds, e.g. a carbocation	a fleeting arrangement in which bonds are partly broken and partly formed
lifetime	exists for a finite time	exists only for an instant
can it be detected?	yes, in principle it can be detected or even isolated	no: it cannot be detected or isolated
number in a mechanism	one fewer than the number of steps	one for every step

Model answer: "Distinguish between a reaction intermediate and a transition state." (2 marks)

An intermediate is a species formed in one step and used up in a later step; it lies at an energy minimum and exists for a finite time, so it could in principle be detected or isolated [1]. A transition state is the highest-energy arrangement of atoms in a single step, with bonds partly broken and partly formed; it exists only momentarily at an energy maximum and cannot be isolated [1].

3.2 Sketching the profile from a mechanism

Worked example 2 — the energy profile of an S_N1 reaction (link to Reactivity 3.4)

Q. 2-chloro-2-methylpropane reacts with hydroxide ions in an exothermic reaction. The proposed mechanism is step 1 (slow): $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$; step 2 (fast): $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$. Sketch the energy profile.

two steps → **two peaks** (two transition states) and one dip (the carbocation intermediate, $(CH_3)_3C^+$)

step 1 is slow → its barrier (TS1) must be the **higher** one; step 2 has a small barrier

exothermic → products drawn **below** the reactants (Figure 1)

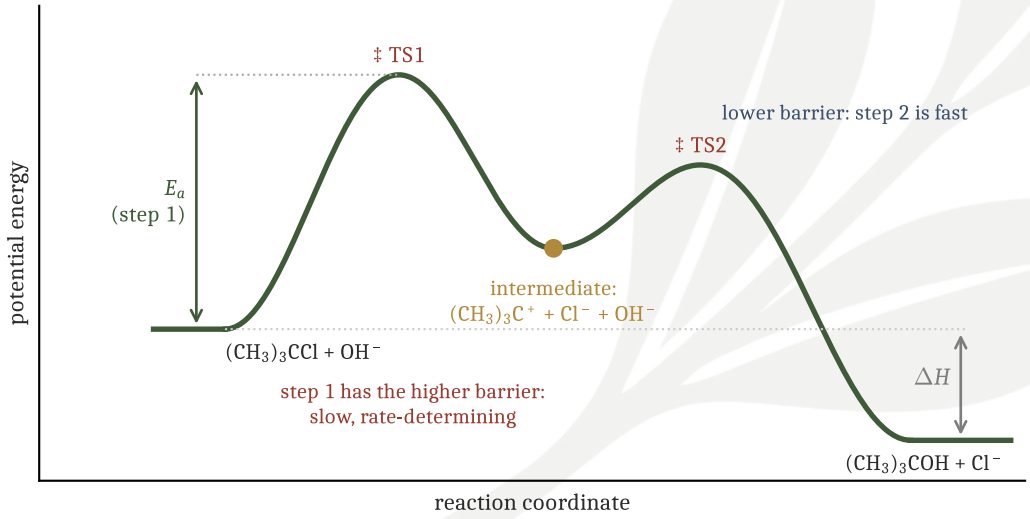


Figure 1 — Energy profile for the two-step S_N1 reaction. The two maxima are transition states; the minimum between them is the intermediate. Step 1 has the higher barrier, so it is rate-determining.

3.3 When the rate-determining step is not the first step

The syllabus specifically includes mechanisms in which a fast step comes first. On the energy profile, the second barrier is then the higher one (Figure 2). The activation energy of the overall reaction is measured from the reactants to the highest transition state.

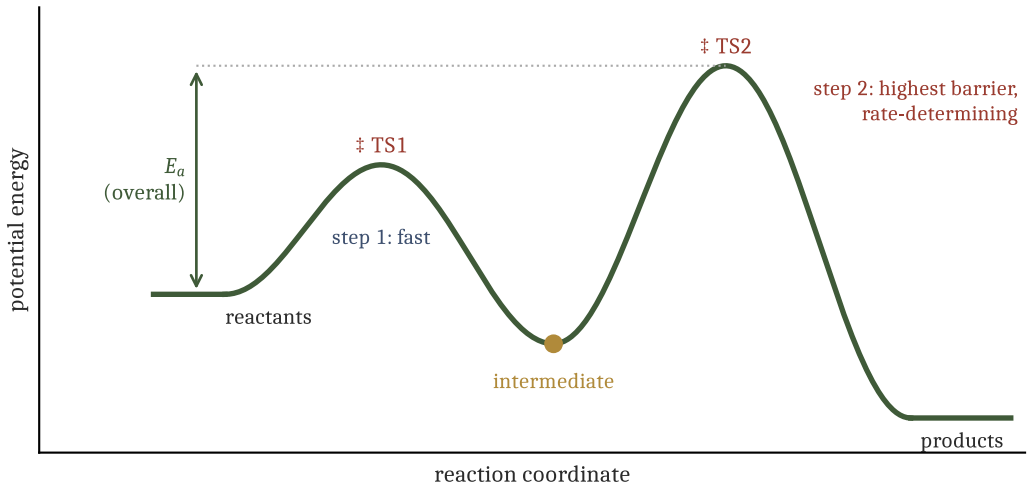


Figure 2 — A two-step reaction in which the second step is rate-determining. The first step is fast and forms the intermediate; the second has the highest barrier.

Worked example 3 — interpreting an energy profile with values

Q. Relative to the reactants (0 kJ mol^{-1}), a two-step reaction has TS1 at +60, the intermediate at +25, TS2 at +95 and the products at −40 kJ mol^{-1}. Find E_a of each step, identify the rate-determining step, and state E_a and ΔH for the overall reaction.

E_a(step 1) = 60 − 0 = **60 kJ mol^{-1}**; E_a(step 2) = 95 − 25 = **70 kJ mol^{-1}**

step 2 has the higher activation energy: **step 2 is rate-determining**

overall E_a = highest TS − reactants = **95 kJ mol^{-1}**; ΔH = −40 − 0 = **−40 kJ mol^{-1}** (exothermic)

Examiner traps with multistep energy profiles

- Labelling the dip as a transition state, or a peak as an intermediate.
- Measuring the second activation energy from the reactants instead of from the intermediate.
- Drawing the rate-determining step with the smaller barrier.
- Drawing an exothermic reaction with the products above the reactants.

4 Reactivity 2.2.9 and 2.2.10 — Rate equations and orders HL

4.1 The rate equation

Experiments show that the rate depends on the concentrations of some or all of the reactants, each raised to a power. For a reaction A + B → products:

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

Definitions to learn

The **rate equation** (also called the rate law or rate expression) gives the rate in terms of the concentrations of the reactants. It can only be determined by **experiment**.

The **order with respect to a reactant** is the power (exponent) to which its concentration is raised in the rate equation. The **overall order** is the sum of the individual orders, $m + n$.

The **rate constant**, k, is the constant of proportionality in the rate equation. It has a fixed value for a given reaction at a given temperature.

The orders are **not** the coefficients in the balanced equation. They can only be found from experimental data, because they depend on the mechanism (section 6). A reactant that is needed for the reaction but does not affect the rate is **zero order**: $[X]^0 = 1$, so it does not appear in the rate equation. Only orders of 0, 1 and 2 (and overall orders up to 3) will be assessed.

Reaction	Experimental rate equation	Overall order
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	rate = $k[H_2][I_2]$	2
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	rate = $k[N_2O_5]$	1
$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$	rate = $k[NO]^2[H_2]$	3
$CH_3COCH_3 + I_2 \rightarrow CH_2ICOCH_3 + HI$ (catalysed by H^+)	rate = $k[CH_3COCH_3][H^+]$	2 (zero order in I_2)

Worked example 4 — writing a rate equation from orders

Q. For $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$, the reaction is second order with respect to NO and first order with respect to Cl_2. Write the rate equation and state the overall order. How does the rate change if [NO] is tripled and $[Cl_2]$ is halved?

rate = $k[NO]^2[Cl_2]$; overall order = 2 + 1 = **3**

new rate = $3^2 \times ½$ = **4.5 times the original rate**

4.2 The initial rates method

Method — deducing orders from initial rates

1. Carry out a set of experiments, measuring the **initial rate** each time (the tangent at $t = 0$, or a clock reaction).
2. Find two experiments in which only [A] changes. Work out the factor by which [A] changes and the factor by which the rate changes.
3. rate unchanged → **zero order**; rate changes by the same factor (×2 → ×2) → **first order**; rate changes by the factor squared (×2 → ×4, ×3 → ×9) → **second order**.
4. Repeat for each reactant. If no pair has only one change, divide out the effect of the reactant whose order you already know (worked example 6).
5. Write the rate equation, then calculate k from any one experiment (section 7).

When [A] is multiplied by…	zero order	first order	second order
× 2	× 1	× 2	× 4
× 3	× 1	× 3	× 9
× ½	× 1	× ½	× ¼

Worked example 5 — orders from an initial-rates table

Q. Deduce the rate equation for A + B → C from the data, and calculate *k*.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.100	0.100	1.60×10^{-4}
2	0.200	0.100	6.40×10^{-4}
3	0.100	0.200	3.20×10^{-4}
4	0.100	0.300	4.80×10^{-4}

experiments 1 and 2: [A] × 2, [B] constant, rate × 4 = 2^2 → **second order in A**

experiments 1, 3 and 4: [B] × 2 → rate × 2; [B] × 3 → rate × 3 → **first order in B**

rate = k[A]^2[B], third order overall; from experiment 1: $k = 1.60 \times 10^{-4} / (0.100^2 \times 0.100)$ = **0.160 mol^{-2} dm^6 s^{-1}**

Worked example 6 — when two concentrations change at once ★

Q. For X + Y → products: experiment 1, [X] = [Y] = 0.10 mol dm^{-3}, rate 2.0×10^{-5}; experiment 2, [X] = 0.10, [Y] = 0.30, rate 1.8×10^{-4}; experiment 3, [X] = 0.30, [Y] = 0.20, rate 2.4×10^{-4} mol dm^{-3} s^{-1}. Deduce the rate equation.

experiments 1 → 2: only [Y] changes, × 3; rate × 9 = 3^2 → **second order in Y**

experiments 1 → 3: [X] × 3 *and* [Y] × 2. Overall the rate changes by $2.4 \times 10^{-4} / 2.0 \times 10^{-5}$ = × 12

the change in [Y] alone accounts for × 2^2 = × 4, so the change in [X] accounts for 12 ÷ 4 = × 3 → **first order in X**

rate = k[X][Y]^2; $k = 2.0 \times 10^{-5} / (0.10 \times 0.10^2)$ = 0.020 mol^{-2} dm^6 s^{-1}

Worked example 7 — using a rate equation to predict rates

Q. For the reaction in worked example 5 (rate = k[A]^2[B], rate = 1.60×10^{-4} mol dm^{-3} s^{-1} when [A] = [B] = 0.100 mol dm^{-3}), predict the initial rate when (a) [A] = 0.050, [B] = 0.400; (b) [A] = 0.300, [B] = 0.200 mol dm^{-3}.

(a) [A] × ½ → rate × ¼; [B] × 4 → rate × 4; overall × 1: **1.60×10^{-4} mol dm^{-3} s^{-1}**

(b) [A] × 3 → × 9; [B] × 2 → × 2; overall × 18: $18 \times 1.60 \times 10^{-4}$ = **2.88×10^{-3} mol dm^{-3} s^{-1}**

Check with k: $0.160 \times 0.300^2 \times 0.200 = 2.88 \times 10^{-3}$. Both methods agree.

4.3 What must be measured

To deduce the order with respect to one reactant, you need its initial concentration in several experiments, with every other concentration and the temperature kept constant, and the initial rate of each. When solutions are mixed, the volumes of

stock solutions are varied and water is added so that the **total volume is always the same**: the concentration of each species is then proportional to the volume of its stock solution used.

Worked example 8 — the iodination of propanone, from volumes of solution ★

Q. $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + HI(aq)$ is catalysed by H^+. Stock solutions: propanone 2.00, HCl 1.00 and I_2 0.0100 mol dm^{-3}. Each mixture was made up to 100 cm^3 with water. Deduce the rate equation and calculate k.

Exp.	propanone / cm^3	HCl / cm^3	I_2 / cm^3	water / cm^3	initial rate / mol dm^{-3} s^{-1}
1	10	10	10	70	2.50×10^{-6}
2	20	10	10	60	5.00×10^{-6}
3	10	20	10	60	5.00×10^{-6}
4	10	10	20	60	2.50×10^{-6}

doubling the volume of a stock doubles its concentration (total volume fixed at 100 cm^3)

1 → 2: [propanone] × 2, rate × 2 → **first order**; 1 → 3: $[H^+]$ × 2, rate × 2 → **first order**; 1 → 4: $[I_2]$ × 2, rate × 1 → **zero order**

rate = $k[CH_3COCH_3][H^+]$, second order overall

experiment 1: $[CH_3COCH_3] = 2.00 \times 10/100 = 0.200$; $[H^+] = 1.00 \times 10/100 = 0.100$ mol dm^{-3}

$k = 2.50 \times 10^{-6} / (0.200 \times 0.100) =$ **1.25×10^{-4} mol^{-1} dm^3 s^{-1}**

Two lessons: a catalyst (H^+) can appear in the rate equation, and a reactant (I_2) can be absent from it. Iodine must react only *after* the rate-determining step.

Examiner traps with rate equations

- Writing the orders from the coefficients of the overall equation. Orders come only from experiment.
- Comparing two experiments in which two concentrations change, then assigning the whole effect to one reactant.
- Using the volume of a stock solution as a concentration without checking that the total volume was kept constant.
- Leaving a zero-order reactant in the rate equation as [X]. Either omit it or write $[X]^0$.
- Confusing the rate constant k with the equilibrium constant K.

5 Reactivity 2.2.10 — Graphs of zero, first and second order HL

The order with respect to a reactant can also be identified from graphs. Concentration–time graphs show whether the rate is constant, but first and second order curves look similar. Rate–concentration graphs distinguish all three clearly.

Order	Rate equation	Concentration–time graph	Rate–concentration graph
zero	rate = k	straight line sloping down; gradient = $-k$; constant rate	horizontal line
first	rate = k[A]	curve; concentration halves in equal time intervals (constant half-life)	straight line through the origin; gradient = k

second	rate = $k[A]^2$	curve, steeper at the start, levelling off more slowly at low concentration; half-life increases	upward-curving parabola through the origin

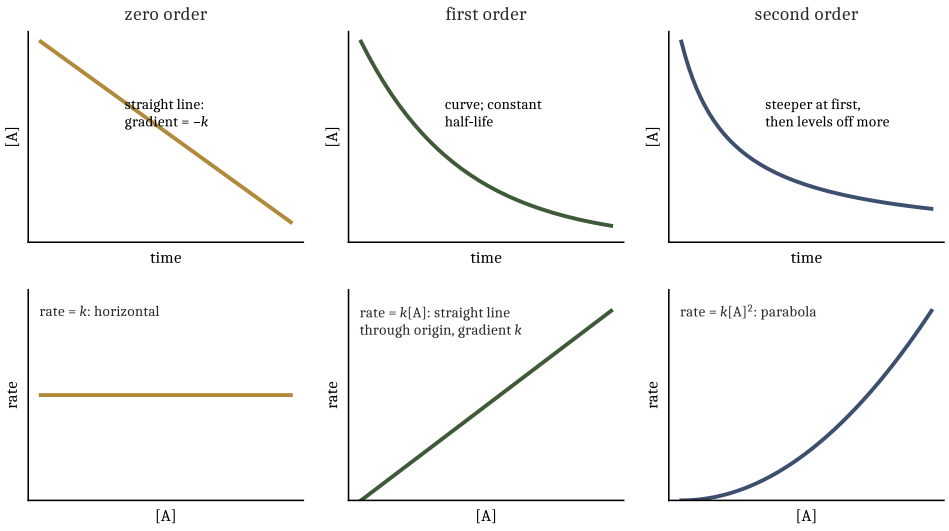


Figure 3 — Concentration–time graphs (top) and rate–concentration graphs (bottom) for a reaction that is zero, first and second order with respect to A.

Worked example 9 — the order from rate and concentration data

Q. Rates measured at different concentrations of a single reactant gave these results. Deduce the order in each case and the value of k.

Reaction P: [A] / mol dm^{-3}	**0.0400**	**0.0300**	**0.0200**	**0.0100**
rate / mol dm^{-3} s^{-1}	2.80×10^{-4}	2.10×10^{-4}	1.40×10^{-4}	7.0×10^{-5}

Reaction Q: [B] / mol dm^{-3}	**0.100**	**0.200**	**0.300**
rate / mol dm^{-3} s^{-1}	3.0×10^{-5}	1.2×10^{-4}	2.7×10^{-4}

P: rate/[A] = 7.00×10^{-3} every time, so a plot of rate against [A] is a straight line through the origin: **first order, $k = 7.00 \times 10^{-3}$ s^{-1}**

Q: doubling [B] gives rate × 4; tripling gives × 9; rate/[B]^2 = 3.0×10^{-3} every time: **second order, $k = 3.0 \times 10^{-3}$ mol^{-1} dm^3 s^{-1}**

Worked example 10 — recognizing first order from a constant half-life

Q. [A] was 0.800, 0.566, 0.400, 0.283 and 0.200 mol dm^{-3} at 0, 50, 100, 150 and 200 s. Deduce the order with respect to A.

[A] falls from 0.800 to 0.400 in 100 s, and from 0.400 to 0.200 in the next 100 s; also 0.566 → 0.283 between 50 and 150 s

the time to halve the concentration (the **half-life**) is constant at 100 s, whatever the starting concentration: **first order**

A zero-order reaction would have a half-life that gets shorter, and a second-order one a half-life that gets longer, as the concentration falls. Radioactive decay is the best-known first-order process.

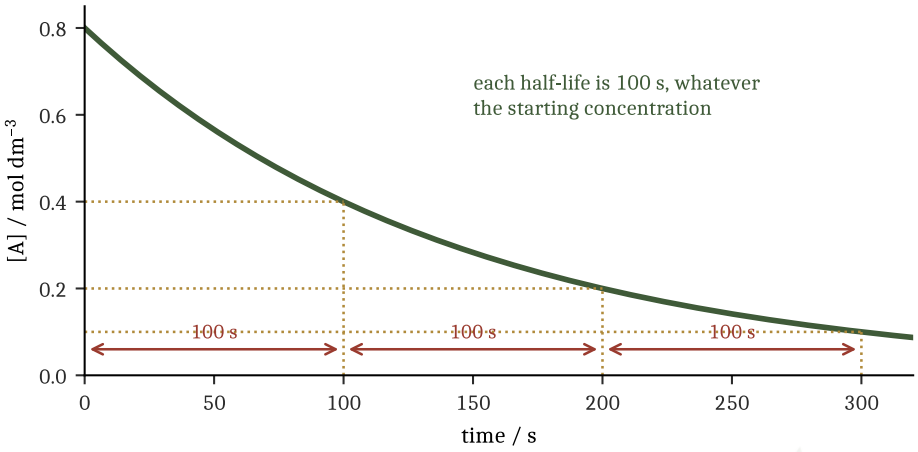


Figure 4 — Worked example 10. Successive half-lives of a first-order reaction are equal.

Examiner traps with order graphs

- Deciding between first and second order from the shape of a concentration–time curve alone. Use a rate–concentration graph, or the half-life.
- Drawing the first-order rate–concentration line so that it does not pass through the origin.
- Drawing the zero-order concentration–time graph as a curve. It is a straight line until the reactant runs out.
- Drawing a second-order rate–concentration graph as a straight line. It is a parabola.

6 Reactivity 2.2.9 — Rate equations and mechanisms HL

6.1 The rate equation of an elementary step

For a single elementary step, and *only* for an elementary step, the rate equation *can* be written from its equation: the concentration of each reacting particle appears, raised to the power of its coefficient. This follows from collision theory, because the rate of the step depends on how often those particles collide.

Elementary step	Molecularity	Rate equation for the step
A → products	unimolecular	rate = k[A]
A + B → products	bimolecular	rate = k[A][B]
2A → products	bimolecular	rate = k[A]^2

Because the rate-determining step controls the overall rate, **the overall rate equation is the rate equation of the rate-determining step**, written in terms of the reactants. So the orders tell you how many particles of each reactant (or of species formed from it) take part in, or before, the rate-determining step. A zero-order reactant takes part only after it.

6.2 When the rate-determining step is the first step

Worked example 11 — the iodide-catalysed decomposition of hydrogen peroxide

Q. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ is catalysed by iodide ions. Proposed mechanism: step 1 (slow): $H_2O_2 + I^- \rightarrow H_2O + IO^-$; step 2 (fast): $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$. Deduce the rate equation, and identify the intermediate and the catalyst.

the steps add up to $2H_2O_2 \rightarrow 2H_2O + O_2$ ✓ (IO^- and I^- cancel)

step 1 is rate-determining and bimolecular: **rate = k[H_2O_2][I^-]** (second order overall)

IO^- is the intermediate (made in step 1, used in step 2); **I^- is the catalyst** (used, then regenerated)

The catalyst appears in the rate equation because it takes part in the rate-determining step, just as H^+ did in worked example 8.

6.3 When the rate-determining step is not the first step

If a fast step comes first, the rate-determining step may involve an intermediate. An intermediate cannot appear in the overall rate equation, so replace it by the reactants that formed it in the earlier, fast step.

Worked example 12 — a fast first step ★

Q. For $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$, the proposed mechanism is step 1 (fast): $NO + Br_2 \rightarrow NOBr_2$; step 2 (slow): $NOBr_2 + NO \rightarrow 2NOBr$. Deduce the rate equation.

check: $NO + Br_2 + NOBr_2 + NO \rightarrow NOBr_2 + 2NOBr$ gives $2NO + Br_2 \rightarrow 2NOBr$ ✓

rate-determining step 2: rate = k[$NOBr_2$][NO]

$NOBr_2$ is an intermediate, formed from one NO and one Br_2 in step 1, so [$NOBr_2$] depends on [NO][Br_2]

substitute: **rate = k[NO]^2[Br_2]**, third order overall

The rate equation is third order, yet no step is termolecular: the two NO molecules and one Br_2 molecule all take part *up to* the rate-determining step, but in two separate collisions.

6.4 Evaluating a proposed mechanism

Method — is this mechanism possible?

1. **Stoichiometry:** do the steps add up to the overall equation?
2. **Kinetics:** does the rate equation predicted from the rate-determining step (after substituting for any intermediate) match the experimental rate equation?
3. **Plausibility:** are all steps unimolecular or bimolecular (termolecular steps are unlikely)?

A mechanism that fails test 1 or 2 must be rejected. One that passes is only **consistent** with the evidence.

Worked example 13 — choosing between mechanisms

Q. $H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HCl(g)$ has the experimental rate equation rate = $k[H_2][ICl]$. Evaluate three proposed mechanisms.

Mechanism	Evaluation
I: one step, $H_2 + 2ICl \rightarrow I_2 + 2HCl$	rate = $k[H_2][ICl]^2$ ✗; also termolecular. **Rejected.**
II: $H_2 + ICl \rightarrow HI + HCl$ (slow); $HI + ICl \rightarrow I_2 + HCl$ (fast)	adds up √; RDS gives rate = $k[H_2][ICl]$ √; both steps bimolecular. **Consistent.**
III: $ICl + ICl \rightarrow I_2 + Cl_2$ (slow); $Cl_2 + H_2 \rightarrow 2HCl$ (fast)	adds up √; but RDS gives rate = $k[ICl]^2$ ✗. **Rejected.**

Model answer: "Explain why a mechanism that agrees with the experimental rate equation is described only as a 'possible' mechanism." (2 marks)

The elementary steps cannot usually be observed directly; kinetic and stoichiometric data can only show that a mechanism is consistent with the evidence [1]. Another mechanism could fit the same data equally well, so the mechanism cannot be proved, only supported or disproved by further evidence, such as detecting an intermediate [1].

Model answer: "The reaction is zero order with respect to iodine. Explain what this suggests about the mechanism." (2 marks)

Changing $[I_2]$ does not change the rate, so iodine does not take part in the rate-determining step [1]. It must react in a fast step that comes after the rate-determining step [1].

Examiner traps linking mechanisms and rate equations

- Writing the overall rate equation from the overall equation instead of from the rate-determining step.
- Leaving an intermediate in the overall rate equation. Replace it with the reactants that formed it.
- Claiming that a mechanism is "proved" because it fits the rate equation.
- Forgetting that a catalyst can appear in the rate equation, although it is not in the overall equation.

7 Reactivity 2.2.11 — The rate constant and its units HL

7.1 Units of k depend on the overall order

The rate always has units of concentration per unit time, mol dm^{-3} s^{-1}. So the units of k must make the rate equation balance: k = rate ÷ (concentration)$^{\text{overall order}}$.

Overall order	example rate equation	units of k	example
0	rate = k	mol dm^{-3} s^{-1}	$2NH_3 \rightarrow N_2 + 3H_2$ on hot platinum
1	rate = k[A]	s^{-1}	tertiary halogenoalkane + OH^-: rate = k[RX]
2	rate = k[A][B]	mol^{-1} dm^3 s^{-1}	primary halogenoalkane + OH^-: rate = k[RX][OH^-]
3	rate = k[A]^2[B]	mol^{-2} dm^6 s^{-1}	$2NO + O_2 \rightarrow 2NO_2$

A quick rule: for overall order n, the units of k are mol^{1-n} $dm^{3(n-1)}$ s^{-1}. If the rate is given per minute, replace s^{-1} by min^{-1}. The value of k does not depend on concentration, but it does depend on **temperature** (section 8) and is increased by a catalyst.

Worked example 14 — the value and units of k

Q. For rate = k[A][B], the rate is 3.6×10^{-3} mol dm^{-3} min^{-1} when [A] = 0.20 and [B] = 0.15 mol dm^{-3}. Calculate k in min-based and in second-based units.

k = rate / ([A][B]) = 3.6×10^{-3} mol dm^{-3} min^{-1} / (0.20×0.15 mol^2 dm^{-6})

= **0.12 mol^{-1} dm^3 min^{-1}**; ÷ 60 = **2.0×10^{-3} mol^{-1} dm^3 s^{-1}**

Working out the units by cancelling, as here, is safer than memorizing the table.

Worked example 15 — using k to find the rate part-way through

Q. For rate = k[X]^2, k = 0.350 mol^{-1} dm^3 s^{-1} and [X] starts at 0.400 mol dm^{-3}. Calculate the initial rate and the rate when 25 % of X has reacted.

initial rate = 0.350×0.400^2 = **0.0560 mol dm^{-3} s^{-1}**

after 25 % has reacted, [X] = 0.75×0.400 = 0.300 mol dm^{-3}; rate = 0.350×0.300^2 = **0.0315 mol dm^{-3} s^{-1}**

Examiner traps with k

- Missing or wrong units for k: they depend on the overall order.
- Thinking k changes with concentration. It changes only with temperature (and with a catalyst).
- Mixing minutes and seconds between the rate and the units of k.

8 Reactivity 2.2.12 and 2.2.13 — The Arrhenius equation HL

8.1 Temperature changes k

Raising the temperature does not change the concentrations, so its effect on rate must be through the rate constant. ***k* increases with temperature**, roughly exponentially (Figure 5a). The higher the activation energy, the more sharply k rises: with a large E_a, a small rise in temperature greatly increases the small fraction of particles that can react. This is why the "rate doubles every 10 °C" rule of thumb is only true for E_a of about 50 kJ mol^{-1} (worked example 18).

The Arrhenius equation (in the data booklet)

$$k = Ae^{-E_a/RT} \qquad \ln k = -E_a/RT + \ln A$$

$e^{-E_a/RT}$ is the fraction of collisions with energy ≥ E_a. The **Arrhenius factor** (frequency factor, pre-exponential factor), A, takes into account the frequency of collisions with the proper orientation. A is constant for a reaction and has the same units as k. Use T in kelvin, R = 8.31 J K^{-1} mol^{-1} and E_a in **J** mol^{-1}.

8.2 The Arrhenius plot

The linear form has the shape $y = mx + c$, with $y = \ln k$ and $x = 1/T$. So a graph of ln k against $1/T$ is a straight line with **gradient = $-E_a/R$** and **y-intercept = ln A**.

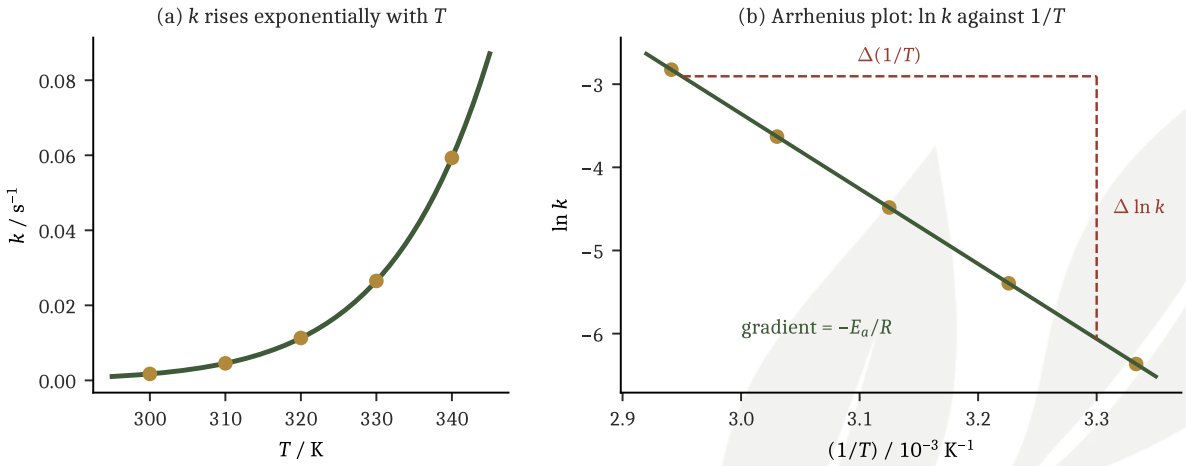


Figure 5 — (a) The rate constant rises steeply with temperature. (b) The Arrhenius plot of the same data (worked example 16) is a straight line with gradient $-E_a/R$.

Worked example 16 — E_a and A from an Arrhenius plot

Q. Use the data to determine the activation energy and the Arrhenius factor for this first-order reaction.

T / K	300	310	320	330	340
k / s^{-1}	1.72 × 10^{-3}	4.54 × 10^{-3}	1.13 × 10^{-2}	2.65 × 10^{-2}	5.93 × 10^{-2}
$(1/T)$ / 10^{-3} K^{-1}	3.333	3.226	3.125	3.030	2.941
ln k	−6.37	−5.39	−4.48	−3.63	−2.83

plot ln k against $1/T$ and draw the best-fit line (Figure 5b)

two points on the line: (2.950 × 10^{-3}, −2.90) and (3.300 × 10^{-3}, −6.06)

gradient = (−6.06 − (−2.90)) / (3.300 − 2.950) × 10^{-3} = −3.16 / 3.50 × 10^{-4} = −9.03 × 10^{3} K

E_a = −gradient × R = 9.03 × 10^{3} × 8.31 = 7.50 × 10^{4} J mol^{-1} = **75.0 kJ mol^{-1}**

ln A = ln k + E_a/RT; at 300 K: −6.37 + 9.03 × 10^{3}/300 = 23.7, so A = $e^{23.7}$ = **2.0 × 10^{10} s^{-1}**

If the plot shows the y-axis at $1/T$ = 0, read ln A directly as the intercept. Usually it does not, so calculate it from a point on the line as here. Note that A has the same units as k.

8.3 Rate constants at two temperatures

Subtracting the linear form at two temperatures gives the two-point form, also in the data booklet:

$$\ln(k_1/k_2) = (E_a/R)(1/T_2 - 1/T_1)$$

Worked example 17 — E_a from two rate constants

Q. A reaction has k = 2.45 × 10^{-4} s^{-1} at 25 °C and 1.12 × 10^{-3} s^{-1} at 45 °C. Calculate E_a.

T_1 = 298 K, T_2 = 318 K; ln(2.45 × 10^{-4} / 1.12 × 10^{-3}) = ln(0.2188) = −1.520

1/318 − 1/298 = −2.111 × 10^{-4} K^{-1}

E_a = 8.31 × (−1.520) / (−2.111 × 10^{-4}) = 5.98 × 10^{4} J mol^{-1} = **59.8 kJ mol^{-1}**

Keep the signs consistent: k_1 must go with T_1. If E_a comes out negative, a pair has been swapped.

Worked example 18 — predicting k, and the “doubles every 10 °C” rule ★

Q. (a) A reaction with E_a = 88.0 kJ mol^{-1} has k = 3.10 × 10^{-5} s^{-1} at 300 K. Calculate k at 330 K. (b) Calculate the activation energy for which k exactly doubles between 298 K and 308 K.

(a) ln(k_{330}/k_{300}) = (88 000/8.31)(1/300 − 1/330) = 10 590 × 3.030 × 10^{-4} = 3.209

k_{330}/k_{300} = $e^{3.209}$ = 24.8, so k_{330} = 24.8 × 3.10 × 10^{-5} = **7.67 × 10^{-4} s^{-1}**

(b) ln 2 = (E_a/8.31)(1/298 − 1/308) ⇒ E_a = 8.31 × 0.693 / 1.090 × 10^{-4} = **52.9 kJ mol^{-1}**

A 30 K rise makes this reaction about 25 times faster, far more than the “× 8” the rule of thumb would suggest, because its E_a is well above 53 kJ mol^{-1}.

Model answer: “Explain why the rate constant of a reaction with a high activation energy is more sensitive to temperature than one with a low activation energy.” (2 marks)

Only particles with energy ≥ E_a can react; for a high E_a this is a very small fraction in the tail of the Maxwell–Boltzmann distribution [1]. A rise in temperature increases this small fraction by a much larger factor, so k rises more steeply; in the Arrhenius equation, a larger E_a gives a steeper Arrhenius plot [1].

Examiner traps with the Arrhenius equation

- Using °C instead of K, or kJ mol^{-1} instead of J mol^{-1} with R = 8.31.
- Forgetting the minus sign: E_a = −gradient × R, and the gradient is negative.
- Reading the intercept from a graph whose x-axis does not start at $1/T = 0$.
- Giving A without units. A has the same units as k.
- Saying that a higher temperature lowers E_a. E_a is unchanged; k increases.

9 Key points to memorise

Everything below is either wording that examiners look for or knowledge you must carry into the exam yourself.

A Definitions

- **Elementary step:** a single molecular event in a mechanism. **Molecularity:** the number of reacting particles in it: uni-, bi- or termolecular.
- **Rate-determining step:** the slowest step; it has the highest activation energy.
- **Intermediate:** formed in one step and used in a later one; at an energy minimum; can in principle be isolated. **Transition state:** at an energy maximum; bonds partly broken and formed; cannot be isolated.
- **Order with respect to a reactant:** the power of its concentration in the rate equation. **Overall order:** the sum of the orders.
- **Rate constant, *k*:** the constant in the rate equation; fixed at a given temperature.
- **Arrhenius factor, *A*:** takes into account the frequency of collisions with proper orientation; same units as k.

B Equations

- rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$; zero order: × 1; first: × factor; second: × factor^2.
- Units of k: order 0, mol dm^{-3} s^{-1}; 1, s^{-1}; 2, mol^{-1} dm^3 s^{-1}; 3, mol^{-2} dm^6 s^{-1}.
- $k = Ae^{-E_a/RT}$; $\ln k = -E_a/RT + \ln A$; gradient of $\ln k$ against $1/T = -E_a/R$; intercept = $\ln A$.
- $\ln(k_1/k_2) = (E_a/R)(1/T_2 - 1/T_1)$; T in K, E_a in J mol^{-1}.

C Explanations you will be asked for

- Orders can only be found by experiment; they are not the coefficients of the overall equation.
- The overall rate equation is that of the rate-determining step, with any intermediate replaced by the reactants that formed it.
- A zero-order reactant reacts after the rate-determining step; a catalyst can appear in the rate equation.
- A mechanism must add up to the overall equation and agree with the rate equation; it can be supported, never proved.
- Termolecular steps are rare because three-particle collisions are very unlikely.
- Graphs: zero order, straight-line [A]–t; first order, rate–[A] straight line through origin and constant half-life; second order, rate–[A] parabola.
- k increases with temperature; the larger E_a, the more sensitive k is to temperature.

10 Check yourself

Use $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$ and $T/\text{K} = t/°\text{C} + 273$. Marks are shown in brackets; allow about 1.2 minutes per mark. Full answers are in section 11.

Part A — Multiple choice HL

1. Which statement about the rate-determining step is correct?

A It is always the first step of a mechanism.
B It is the step with the highest activation energy.
C It is the step with the most reacting particles.
D It is always the last step of a mechanism.

2. Which species could, in principle, be detected or isolated during a reaction?

A an intermediate
B a transition state
C an activated complex
D none of these

3. What is the molecularity of the elementary step $2NO_2 \rightarrow NO_3 + NO$?

A zero
B unimolecular
C bimolecular
D termolecular

4. For rate = $k[X]^2[Y]$, what are the overall order and the units of k?

A 2; $\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$
B 3; $\text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$
C 3; $\text{mol}^2\ \text{dm}^{-6}\ \text{s}^{-1}$
D 2; s^{-1}

5. For rate = $k[X]^2[Y]$, by what factor does the rate change if both [X] and [Y] are doubled?

A × 2
B × 4
C × 6
D × 8

6. Experiment 1: [P] = 0.10, [Q] = 0.10, rate 2.0×10^{-3}; experiment 2: [P] = 0.20, [Q] = 0.10, rate 4.0×10^{-3}; experiment 3: [P] = 0.20, [Q] = 0.20, rate 4.0×10^{-3}. What is the rate equation?

A rate = k[P]
B rate = k[P][Q]
C rate = k[P]^2
D rate = k[Q]

7. Which graph shows that a reaction is first order with respect to A?

A rate against [A]: a horizontal line

B rate against [A]: a straight line through the origin

C rate against [A]: a parabola through the origin

D [A] against time: a straight line with negative gradient

8. A graph of [A] against time is a straight line with a negative gradient. What is the order with respect to A?

A zero **B** first **C** second **D** third

9. A mechanism is: step 1 (slow) A + B → C; step 2 (fast) C + B → D. What is the rate equation?

A rate = k[A][B] **B** rate = k[A][B]^2 **C** rate = k[C][B] **D** rate = k[A]

10. Which change alters the value of the rate constant, k?

A increasing the concentration of a reactant **B** increasing the temperature

C increasing the volume of solution **D** removing a product

11. What is the gradient of a graph of ln k against $1/T$?

A E_a/R **B** $-E_a/R$ **C** $-E_a/RT$ **D** ln A

12. What are the units of the Arrhenius factor, A, for a second-order reaction?

A no units **B** s^{-1}

C $mol^{-1}\ dm^3\ s^{-1}$ **D** $J\ mol^{-1}$

13. What does the Arrhenius factor, A, take into account?

A the activation energy **B** the enthalpy change

C the frequency of collisions with proper orientation **D** the temperature

14. How does a catalyst affect k and E_a?

A k increases; E_a decreases **B** k increases; E_a unchanged

C k unchanged; E_a decreases **D** both unchanged

15. Two reactions are heated from 300 K to 310 K. Which has the larger percentage increase in k?

A the reaction with the larger activation energy

B the reaction with the smaller activation energy

C the reaction with the larger Arrhenius factor

D both increase by the same percentage

16. Mechanism: step 1, $SO_2 + NO_2 \rightarrow SO_3 + NO$; step 2, $NO + \frac{1}{2}O_2 \rightarrow NO_2$. Which species is the catalyst?

A SO_2 **B** NO_2 **C** NO **D** SO_3

Part B — Structured questions HL

17. A proposed mechanism is step 1 (slow): $NO_2 + NO_2 \rightarrow NO_3 + NO$; step 2 (fast): $NO_3 + CO \rightarrow NO_2 + CO_2$.

(a) Deduce the overall equation. [1]

(b) Identify the intermediate. [1]

(c) State the molecularity of step 1. [1]

(d) Deduce the rate equation. [1]

(e) Explain why changing [CO] does not change the rate. [1]

18. Sketch the energy profile for an exothermic two-step reaction in which the second step is rate-determining. Label the axes, both transition states, the intermediate, the activation energy of the overall reaction and ΔH. [5]

19. $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ is second order with respect to NO and first order with respect to H_2.

(a) Write the rate equation and state the overall order. [2]

(b) Deduce the effect on the rate of doubling [NO] and halving $[H_2]$ at the same time. [1]

(c) State the units of k (rate in mol dm^{-3} s^{-1}). [1]

20. The following data are for $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ at a fixed temperature.

Experiment	[NO] / mol dm^{-3}	$[Cl_2]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.5×10^{-5}
2	0.20	0.10	1.0×10^{-4}
3	0.20	0.20	2.0×10^{-4}
4	0.30	0.40	?

(a) Deduce the order with respect to NO and to Cl_2, and write the rate equation. [3]

(b) Calculate k, with units. [2]

(c) Calculate the initial rate in experiment 4. [1]

21. ★ For C + D → products: experiment 1, [C] = 0.20, [D] = 0.20, rate 3.0×10^{-4}; experiment 2, [C] = 0.40, [D] = 0.20, rate 6.0×10^{-4}; experiment 3, [C] = 0.60, [D] = 0.40, rate 3.6×10^{-3} mol dm^{-3} s^{-1}.

(a) Deduce the order with respect to C. [1]

(b) Deduce the order with respect to D, showing your reasoning. [2]

(c) Write the rate equation. [1]

22. Sketch, on separate labelled axes, a concentration–time graph and a rate–concentration graph for a reactant A when the reaction is (a) zero order, (b) first order and (c) second order with respect to A. [6]

23. For a single reactant E, the rate was 1.25×10^{-5}, 5.00×10^{-5} and 1.125×10^{-4} mol dm^{-3} s^{-1} at [E] = 0.050, 0.100 and 0.150 mol dm^{-3}.

(a) Deduce the order with respect to E, explaining your reasoning. [2]

(b) Calculate k, with units, and describe the shape of a graph of rate against [E]. [2]

24. [F] was 0.120, 0.0849, 0.0600, 0.0424 and 0.0300 mol dm^{-3} at 0, 40, 80, 120 and 160 s.

(a) Use half-lives to deduce the order with respect to F. [2]

(b) Predict [F] at 240 s. [1]

25. ★ For $2A + B \rightarrow A_2B$, the proposed mechanism is step 1 (fast): $A + A \rightarrow A_2$; step 2 (slow): $A_2 + B \rightarrow A_2B$.

(a) Deduce the rate equation, explaining each step of your reasoning. [2]

(b) State the molecularity of each step. [1]

(c) Explain why a single termolecular step, $2A + B \rightarrow A_2B$, is unlikely. [1]

26. $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ has the experimental rate equation rate = $k[NO]^2[H_2]$. Two mechanisms are proposed.

Mechanism I: a single step, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$. Mechanism II: $2NO \rightarrow N_2O_2$ (fast); $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow); $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast). Evaluate each mechanism. [4]

27. State the units of k for (a) rate = k; (b) rate = k[A]; (c) rate = k[A][B]^2. The rate is in mol dm^{-3} s^{-1}. [3]

28. For rate = k[A][B], the rate is 6.0×10^{-5} mol dm^{-3} min^{-1} when [A] = 0.0250 and [B] = 0.0400 mol dm^{-3}. Calculate k in units based on minutes, and convert it to units based on seconds. [3]

29. For rate = k[X]^2, k = 0.180 mol^{-1} dm^3 s^{-1} and [X] starts at 0.250 mol dm^{-3}. Calculate the initial rate and the rate when 20 % of X has reacted. [3]

30. ★ $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ was studied using stock solutions of BrO_3^- (0.0400), Br^- (0.200) and H^+ (0.400 mol dm^{-3}), each mixture made up to 50.0 cm^3 with water.

Exp.	BrO_3^- / cm^3	Br^- / cm^3	H^+ / cm^3	water / cm^3	initial rate / mol dm^{-3} s^{-1}
1	10.0	10.0	10.0	20.0	1.64×10^{-5}
2	20.0	10.0	10.0	10.0	3.28×10^{-5}
3	10.0	20.0	10.0	10.0	3.28×10^{-5}
4	10.0	10.0	20.0	10.0	6.56×10^{-5}

(a) Explain why water was added to each mixture. [1]

(b) Calculate the concentration of each reactant in experiment 1. [1]

(c) Deduce the order with respect to each reactant. [2]

(d) Write the rate equation and state the overall order. [1]

(e) Calculate k, with units. [1]

31. Primary halogenoalkanes react with aqueous hydroxide ions by a one-step mechanism; tertiary halogenoalkanes react by a two-step mechanism with a slow first step that forms a carbocation. Write the rate equation for each, and state the units of k for each. [3]

32. ★ The rate constant of a second-order reaction was measured at five temperatures.

T / K	290	300	310	320	330
k / mol^{-1} dm^3 s^{-1}	6.68×10^{-3}	2.08×10^{-2}	6.00×10^{-2}	0.162	0.413

(a) Calculate $1/T$ and ln k for each, and plot an Arrhenius graph. [2]

(b) Determine the gradient and hence the activation energy in kJ mol^{-1}. [2]

(c) Determine the Arrhenius factor, with units. [1]

33. A reaction has $k = 4.20 \times 10^{-3}$ s^{-1} at 300 K and 1.85×10^{-2} s^{-1} at 320 K. Calculate the activation energy. [3]

34. A reaction has E_a = 62.0 kJ mol^{-1} and $k = 1.5 \times 10^{-3}$ s^{-1} at 298 K. Calculate k at 318 K. [3]

35. Temperature and the rate constant.

(a) Explain why the rate constant increases with temperature. [2]

(b) Explain why k for a reaction with a high E_a is more sensitive to temperature. [1]

(c) State the effect of a catalyst on E_a and on k. [1]

36. ★ The "rate doubles for every 10 °C rise" rule of thumb.

(a) Calculate the activation energy for which k exactly doubles between 298 K and 308 K. [2]

(b) Calculate the factor by which k increases over the same range when E_a = 100 kJ mol^{-1}. [1]

(c) Comment on the usefulness of the rule. [1]

37. ★ An Arrhenius plot for a second-order reaction, drawn with the x-axis starting at $1/T = 0$, has a y-intercept of 24.6. Calculate the Arrhenius factor, with units. [2]

Part A: 16 marks · Part B: 84 marks · Total: 100 marks (about 2 hours)

11 Answers

Part A

1. B.

2. A. Transition states (activated complexes) cannot be isolated.

3. C. Two reacting particles.

4. B.

5. D. $2^2 \times 2 = 8$.

6. A. [P] × 2 → rate × 2 (first); [Q] × 2 → no change (zero).

7. B.

8. A.

9. A. Rate equation of the slow first step.

10. B.

11. B.

12. C. Same units as k.

13. C.

14. A.

15. A.

16. B. NO_2 is used in step 1 and regenerated in step 2; NO is the intermediate.

Part B

17. (a) $NO_2 + CO \rightarrow NO + CO_2$ [1]. (b) NO_3 [1]. (c) Bimolecular [1]. (d) rate = $k[NO_2]^2$ [1]. (e) CO reacts only in step 2, after the rate-determining step [1].

18. Axes: potential energy and reaction coordinate [1]; two peaks labelled as transition states, with the second higher than the first [1]; dip between them labelled intermediate [1]; overall E_a from reactants to the higher (second) peak [1]; products below reactants with ΔH labelled (negative) [1].

19. (a) rate = $k[NO]^2[H_2]$ [1]; third order [1]. (b) $2^2 \times ½$ = rate doubles [1]. (c) $mol^{-2}\ dm^6\ s^{-1}$ [1].

20. (a) Experiments 1 → 2: [NO] × 2, rate × 4: second order in NO [1]; 2 → 3: $[Cl_2]$ × 2, rate × 2: first order in Cl_2 [1]; rate = $k[NO]^2[Cl_2]$ [1]. (b) $k = 2.5 \times 10^{-5}/(0.10^2 \times 0.10) = 0.025$ [1] $mol^{-2}\ dm^6\ s^{-1}$ [1]. (c) $0.025 \times 0.30^2 \times 0.40 = 9.0 \times 10^{-4}$ mol $dm^{-3}\ s^{-1}$ [1].

21. (a) 1 → 2: [C] × 2, rate × 2: first order [1]. (b) 1 → 3: overall rate × 12; [C] × 3 accounts for × 3, so [D] × 2 accounts for × 4 [1]: second order in D [1]. (c) rate = $k[C][D]^2$ [1].

22. One mark for each correct, labelled sketch: zero order, [A]–time straight line down [1], rate–[A] horizontal [1]; first order, [A]–time curve [1], rate–[A] straight line through origin [1]; second order, [A]–time steeper curve levelling off more [1], rate–[A] parabola through origin [1].

23. (a) Doubling [E] (0.050 → 0.100) multiplies the rate by 4, and tripling it multiplies the rate by 9 [1]: second order [1]. (b) $k = 5.00 \times 10^{-5}/0.100^2 = 5.0 \times 10^{-3}$ $mol^{-1}\ dm^3\ s^{-1}$ [1]; an upward-curving parabola through the origin [1].

24. (a) [F] halves from 0.120 to 0.0600 in 80 s and from 0.0600 to 0.0300 in the next 80 s (also 0.0849 → 0.0424 in 80 s) [1]; constant half-life, so first order [1]. (b) 240 s is three half-lives: 0.120/8 = 0.0150 mol dm^{-3} [1].

25. (a) The slow step gives rate = $k[A_2][B]$; A_2 is an intermediate formed from two A, so $[A_2]$ depends on $[A]^2$ [1]; rate = $k[A]^2[B]$ [1]. (b) Both steps are bimolecular [1]. (c) Three particles colliding at once with enough energy and the correct orientation is extremely improbable [1].

26. Mechanism I would give rate = $k[NO]^2[H_2]^2$, which does not match [1], and needs four particles to collide at once, which is very unlikely: rejected [1]. Mechanism II adds up to the overall equation [1], and the slow step gives rate = $k[N_2O_2][H_2] = k[NO]^2[H_2]$ after substituting for the intermediate N_2O_2, so it is consistent with the data [1].

27. (a) mol $dm^{-3}\ s^{-1}$ [1]. (b) s^{-1} [1]. (c) $mol^{-2}\ dm^6\ s^{-1}$ [1].

28. $k = 6.0 \times 10^{-5}/(0.0250 \times 0.0400)$ [1] = 0.060 $mol^{-1}\ dm^3\ min^{-1}$ [1]; ÷ 60 = 1.0×10^{-3} $mol^{-1}\ dm^3\ s^{-1}$ [1].

29. Initial rate = $0.180 \times 0.250^2 = 0.0113$ mol $dm^{-3}\ s^{-1}$ [1]; after 20 % reacted, [X] = 0.200 mol dm^{-3} [1]; rate = $0.180 \times 0.200^2 = 7.20 \times 10^{-3}$ mol $dm^{-3}\ s^{-1}$ [1].

30. (a) To keep the total volume constant, so that the concentration of each reactant is proportional to the volume of its stock solution and only one concentration changes at a time [1]. (b) $[BrO_3^-] = 0.00800$, $[Br^-] = 0.0400$, $[H^+] = 0.0800$ mol dm^{-3} [1]. (c) BrO_3^-: first order; Br^-: first order [1]; H^+: doubling gives rate × 4, second order [1]. (d) rate = $k[BrO_3^-][Br^-][H^+]^2$; fourth order overall [1]. (e) $k = 1.64 \times 10^{-5}/(0.00800 \times 0.0400 \times 0.0800^2) = 8.0$ mol^{-3} dm^9 s^{-1} [1].

31. Primary: rate = k[RX][OH$^-$], units mol^{-1} dm^3 s^{-1} [1]; tertiary: rate = k[RX], units s^{-1} [1]; the tertiary rate-determining step (formation of the carbocation) involves only the halogenoalkane [1].

32. (a) $1/T = 3.448, 3.333, 3.226, 3.125, 3.030 \times 10^{-3}$ K^{-1}; $\ln k = -5.01, -3.87, -2.81, -1.82, -0.88$ [1]; points plotted with a straight best-fit line [1]. (b) Gradient = -9.86×10^3 K (accept -9.6 to -10.1×10^3) [1]; $E_a = 9.86 \times 10^3 \times 8.31 = 8.2 \times 10^4$ J mol^{-1} = 82 kJ mol^{-1} [1]. (c) $\ln A = \ln k + E_a/RT$, e.g. $-3.87 + 9.86 \times 10^3/300 = 29.0$; $A = e^{29.0} \approx 4 \times 10^{12}$ mol^{-1} dm^3 s^{-1} [1].

33. $\ln(4.20 \times 10^{-3}/1.85 \times 10^{-2}) = -1.483$ [1]; $1/320 - 1/300 = -2.083 \times 10^{-4}$ K^{-1} [1]; $E_a = 8.31 \times 1.483/2.083 \times 10^{-4} = 5.91 \times 10^4$ J mol^{-1} = 59.1 kJ mol^{-1} [1].

34. $\ln(k_{318}/k_{298}) = (62\,000/8.31)(1/298 - 1/318) = 7461 \times 2.111 \times 10^{-4} = 1.575$ [1]; ratio = $e^{1.575} = 4.83$ [1]; $k = 4.83 \times 1.5 \times 10^{-3} = 7.2 \times 10^{-3}$ s^{-1} [1].

35. (a) At a higher temperature a much greater fraction of collisions have energy ≥ E_a [1]; in $k = Ae^{-E_a/RT}$, increasing T makes $e^{-E_a/RT}$ larger, so k increases [1]. (b) With a high E_a, the reacting fraction lies far in the tail of the distribution, which grows by a larger factor when T rises (steeper Arrhenius plot) [1]. (c) E_a decreases and k increases [1].

36. (a) $E_a = R \ln 2/(1/298 - 1/308)$ [1] = $8.31 \times 0.693/1.090 \times 10^{-4} = 52.9$ kJ mol^{-1} [1]. (b) $e^{(100\,000/8.31)(1.090 \times 10^{-4})} = \times 3.7$ [1]. (c) It is only a rough guide that applies to reactions with E_a near 50 kJ mol^{-1}; reactions with higher or lower E_a are more or less sensitive to temperature [1].

37. $\ln A = 24.6$, so $A = e^{24.6}$ [1] = 4.8×10^{10} mol^{-1} dm^3 s^{-1} [1].

Where this fits in Reactivity 2

- **Booklets 1 and 2** — Reactivity 2.1: how much? **Booklet 3** — Reactivity 2.2.1–2.2.5 (SL + HL): rates and collision theory. **Booklet 4 (this booklet)** — Reactivity 2.2.6–2.2.13 (HL): mechanisms, rate equations and the Arrhenius equation. Together, Booklets 3 and 4 complete Reactivity 2.2.
- **Next:** Reactivity 2.3: how far? Equilibrium, where the equilibrium constant K (upper case) comes from the stoichiometry, unlike the rate constant k. **Later:** Reactivity 3.4 uses rate equations to tell the S_N1 and S_N2 mechanisms apart.

These notes are a free resource, shared for any IB student who finds them useful.

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