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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Reactivity 2.2 Rates of Reaction and Collision Theory

Booklet 3 · Understandings 2.2.1 – 2.2.5

How fast? Measuring and calculating rates, why particles must collide with enough energy and the right orientation, and how temperature, concentration, pressure, surface area and catalysts change the rate

Complete revision notes, 15 worked examples, model answers & 36 practice questions · Standard Level & Higher Level

How the level tags work in this booklet

SL + HL Understandings 2.2.1 to 2.2.5 are common to both levels, so the whole booklet is core material.

HL The HL-only part of Reactivity 2.2 (reaction mechanisms, rate equations, orders and the Arrhenius equation, 2.2.6 onwards) is covered in a separate HL booklet. ★ marks harder examples and questions.

Inside this booklet

1. What the syllabus actually asks of you
2. 2.2.1 — Rate of reaction
3. 2.2.1 — Measuring rates
4. 2.2.2 — Collision theory
5. 2.2.3 — Factors affecting rate
6. 2.2.4 — Activation energy
7. 2.2.5 — Catalysts
8. Key points to memorise
9. Check yourself
10. Answers

1 What the syllabus actually asks of you

Reactivity 2.1 asked "how much?". Reactivity 2.2 asks "how fast?". Some reactions are over in microseconds, like the kerosene and liquid oxygen burning in a rocket engine; others, like the souring of milk or the rusting of iron, take days or years. Controlling the rate matters everywhere: in industry, where a faster reaction means more product per hour; in food storage, where we want decay to be slow; and in the atmosphere, where we want to slow the reactions that destroy ozone. This booklet covers the five SL + HL understandings: what rate means and how to measure it, the collision theory that explains it, and the five factors that change it.

Understanding	What it says	What you must be able to do	Level
2.2.1 Rate	The rate of reaction is expressed as the change in concentration of a particular reactant or product per unit time.	Determine rates of reaction. **Calculation of reaction rates from tangents of graphs of concentration, volume or mass against time should be covered.**	SL+HL
2.2.2 Collisions	Species react as a result of collisions of sufficient energy and proper orientation.	Explain the relationship between the kinetic energy of the particles and the temperature in kelvin, and the role of collision geometry.	SL+HL
2.2.3 Factors	Factors that influence the rate of a reaction include pressure, concentration, surface area, temperature and the presence of a catalyst.	Predict and explain the effects of changing conditions on the rate of a reaction.	SL+HL
2.2.4 Activation energy	Activation energy, E_a, is the minimum energy that colliding particles need for a successful collision leading to a reaction.	Construct Maxwell–Boltzmann energy distribution curves to explain the effect of temperature on the probability of successful collisions.	SL+HL
2.2.5 Catalysts	Catalysts increase the rate of reaction by providing an alternative reaction pathway with lower E_a.	Sketch and explain energy profiles with and without catalysts for endothermic and exothermic reactions. Construct Maxwell–Boltzmann curves to explain the effect of different values of E_a on the probability of successful collisions. Biological catalysts are called enzymes. **The different mechanisms of homogeneous and heterogeneous catalysts will not be assessed.**	SL+HL

Linking questions and connections for 2.2.1 – 2.2.5

- **Tool 1, 3, Inquiry 2:** concentration changes are not usually measured directly. What methods provide data to determine rates? → section 3
- **Tool 1:** what experiments use time as (i) a dependent or (ii) an independent variable? → section 3.3
- **Structure 1.1:** what is the relationship between the kinetic molecular theory and collision theory? → section 4.1
- **Tool 1:** what variables must be controlled when studying the effect of a factor on rate? → section 5.6
- **Nature of Science, Tool 3, Inquiry 3:** how can graphs provide evidence of systematic and random error? → section 5.7
- **Reactivity 2.3:** what is the relative effect of a catalyst on the rates of the forward and backward reactions? → section 7.3
- **Structure 3.1:** what features of transition elements make them useful as catalysts? → section 7.4

What the data booklet does and does not give you

It gives you: the gas constant (R = 8.31 J K^{-1} mol^{-1}), the ideal gas equation, and the molar volume at STP (22.7 dm^3 mol^{-1} at 273 K and 100 kPa).

It does not give you: the definition or units of rate; how to draw and read a tangent; the shape of the Maxwell–Boltzmann curve; or the molar volume at room temperature. At 298 K and 100 kPa, $pV = nRT$ gives 24.8 dm^3 mol^{-1}, the value used in this booklet; always use the value a question gives you.

2 Reactivity 2.2.1 — Rate of reaction SL + HL

2.1 Rate is change per unit time

In a race the fastest runner has the shortest time: rate and time are reciprocals (rate ∝ 1/time). For a reaction, what changes with time is the amount of each substance. Reactant concentrations fall and product concentrations rise, so the rate can be measured from any one of them.

Definition to learn

The **rate of reaction** is the increase in concentration of a product, or the decrease in concentration of a reactant, per unit time.

$$\text{rate} = \Delta[\text{P}] / \Delta t \quad \text{or} \quad \text{rate} = -\Delta[\text{R}] / \Delta t \qquad \text{units: } \mathbf{mol\ dm^{-3}\ s^{-1}}$$

Square brackets mean concentration in mol dm^{-3}. The minus sign for a reactant makes the rate positive: by convention a rate is always a positive value.

A graph of concentration against time is a curve, not a straight line, because the rate is **not constant**. It is greatest at the start, when the reactant concentration is highest, and falls as the reactants are used up, until the curve levels off when the reaction is complete. So there are two kinds of rate:

- an **average rate** over a time interval: the change in concentration divided by the time taken (a chord between two points);
- an **instantaneous rate** at one moment: the gradient of the **tangent** to the curve at that time. The tangent at t = 0 gives the **initial rate**, which is the usual way to compare rates under different conditions.

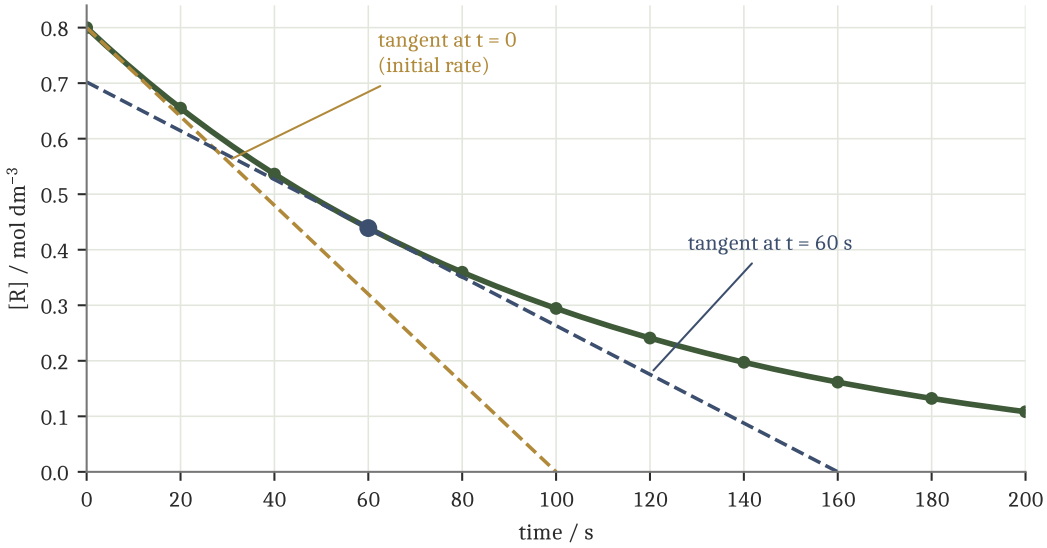


Figure 1 — Concentration of reactant R against time (worked examples 1 and 2). The gradient of the tangent gives the rate at that instant; the tangent at $t = 0$ is steepest, so the initial rate is the highest.

Worked example 1 — average rates from data

Q. The data below are for the reaction in Figure 1. Calculate the average rate over the first 20 s and between 80 s and 100 s.

time / s	0	20	40	60	80	100
[R] / mol dm^{-3}	0.800	0.655	0.536	0.439	0.359	0.294

0–20 s: rate = −(0.655 − 0.800) / (20 − 0) = 0.145 / 20 = **7.25×10^{-3} mol dm^{-3} s^{-1}**

80–100 s: rate = −(0.294 − 0.359) / (100 − 80) = 0.065 / 20 = **3.3×10^{-3} mol dm^{-3} s^{-1}**

The rate has more than halved, because the reactant concentration is lower. Note that 0.065 has only two significant figures, so the second answer does too.

Method — the rate from a tangent

1. Draw the tangent at the chosen time with a ruler: a straight line that touches the curve at that point only, with equal “gaps” either side.
2. Make the tangent as long as you can, so that both Δy and Δx are large and easy to read.
3. Choose two points far apart *on the tangent* (not on the curve) and read their coordinates.
4. Gradient = $\Delta y / \Delta x$. Give the rate as a positive value, with units: mol dm^{-3} s^{-1} for concentration, cm^3 s^{-1} for a gas volume, g s^{-1} for a mass.

Worked example 2 — instantaneous rates from tangents

Q. Use the tangents in Figure 1 to find the initial rate and the rate at 60 s.

at t = 0: the tangent passes through (0 s, 0.800) and (100 s, 0.000)

gradient = (0.000 − 0.800) / (100 − 0) = -8.00×10^{-3}, so initial rate = **8.00×10^{-3} mol dm^{-3} s^{-1}**

at t = 60 s: the tangent passes through (0 s, 0.702) and (160 s, 0.000)

gradient = (0.000 − 0.702) / (160 − 0) = -4.39×10^{-3}, so rate at 60 s = **4.39×10^{-3} mol dm^{-3} s^{-1}**

The rate at 60 s lies between the two average rates in worked example 1, as it should. A hand-drawn tangent will give a slightly different value; examiners accept a range.

2.2 Rates from gas volume and mass

Rates are often measured as the volume of gas given off or the mass lost per second. The tangent method is exactly the same; only the units change. To convert to mol dm^{-3} s^{-1}, use moles and the mole ratio exactly as in Reactivity 2.1.

Worked example 3 — from cm^3 s^{-1} to mol dm^{-3} s^{-1}

Q. Magnesium reacts with 50.0 cm^3 of hydrochloric acid at 298 K and 100 kPa: Mg(s) + 2HCl(aq) → $MgCl_2$(aq) + H_2(g). The tangent at t = 0 on a graph of gas volume against time passes through (0 s, 0 cm^3) and (25 s, 30.0 cm^3). Calculate the initial rate in cm^3 s^{-1}, then the initial rate of decrease of [HCl].

initial rate = 30.0 / 25 = **1.20 cm^3 s^{-1}** of H_2

molar volume at 298 K, 100 kPa = 24.8 dm^3 mol^{-1} = 24 800 cm^3 mol^{-1}; 1.20 / 24 800 = 4.84×10^{-5} mol H_2 s^{-1}

HCl is used twice as fast: 9.68×10^{-5} mol s^{-1}, in 0.0500 dm^3 → **1.94×10^{-3} mol dm^{-3} s^{-1}**

Worked example 4 — a rate from loss of mass

Q. Marble chips react with 50.0 cm^3 of hydrochloric acid in a flask on a balance. The reading falls from 182.45 g to 181.79 g in the first 60 s. Calculate the average rate in g s^{-1} and in mol CO_2 s^{-1}, and the average rate of decrease of [HCl].

$CaCO_3$(s) + 2HCl(aq) → $CaCl_2$(aq) + H_2O(l) + CO_2(g); the mass lost is the CO_2 that escapes

rate = (182.45 − 181.79) / 60 = 0.660 / 60 = **0.0110 g s^{-1}**; 0.0110 / 44.01 = **2.50×10^{-4} mol CO_2 s^{-1}**

HCl: $2 \times 2.50 \times 10^{-4} = 5.00 \times 10^{-4}$ mol s^{-1}, in 0.0500 dm^3 → **1.00×10^{-2} mol dm^{-3} s^{-1}**

2.3 The rate depends on which species you measure

The syllabus defines rate for “a particular reactant or product”. When the coefficients are not all equal, each species changes at a different rate, in the ratio of the coefficients. So you must always say which species a rate refers to.

Worked example 5 — rates of different species in one reaction

Q. For $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, oxygen forms at 1.5×10^{-4} mol dm^{-3} s^{-1}. Find the rate of formation of NO_2 and the rate of decrease of $[N_2O_5]$.

ratio $N_2O_5 : NO_2 : O_2 = 2 : 4 : 1$

rate of formation of $NO_2 = 4 \times 1.5 \times 10^{-4} =$ **6.0×10^{-4} mol dm^{-3} s^{-1}**

rate of decrease of $[N_2O_5] = 2 \times 1.5 \times 10^{-4} =$ **3.0×10^{-4} mol dm^{-3} s^{-1}**

Examiner traps with rates

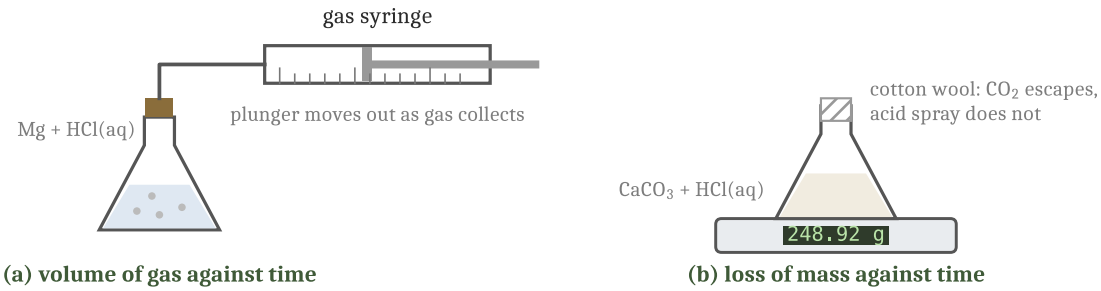
- Giving a negative rate. The gradient for a reactant is negative, but the rate is quoted as positive.
- Reading the two points for the gradient off the curve instead of off the tangent.
- Drawing a short tangent: small Δx and Δy make the reading error large.
- Missing or wrong units: mol dm^{-3} s^{-1} (not mol dm^{-3} s), or cm^3 s^{-1} and g s^{-1} for volume and mass.
- Thinking the rate is constant. It is greatest at the start and decreases as reactants are used up.
- Quoting a rate without saying which species it refers to, when the coefficients differ.

3 Reactivity 2.2.1 — Measuring rates SL + HL

3.1 Choosing a method

Concentration is rarely measured directly. Instead, we follow a property, a “signal”, that changes as the reaction proceeds and is related to concentration. The best method depends on the reaction: whether it gives off a gas, changes colour, forms a precipitate, or changes the number of ions in solution. A balanced equation tells you nothing about the rate; that can only come from experiment.

Method	Use it when	Example, and notes
volume of gas	a gas is produced; gas syringe, or an inverted burette if the gas is not very soluble in water	$Mg + 2HCl \rightarrow MgCl_2 + H_2$. Continuous readings; plot volume against time.
loss of mass	a dense gas escapes (CO_2, not H_2)	$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$. Continuous; cotton wool stops acid spray escaping.
colorimetry	a reactant or product is coloured	crystal violet (violet) + $OH^- \rightarrow$ colourless product. Absorbance is proportional to concentration, so a calibration curve converts it.
titration	a reactant or product can be titrated	$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$; I_2 titrated with thiosulfate. Samples are removed and **quenched** (stopped), so it is not continuous.
conductivity	the total number or charge of ions changes	$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$: 12 ions become none, so conductivity falls sharply.
clock reaction	an observable point is reached after a fixed amount of reaction	$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O + S(s)$: time until a cross under the flask disappears.



(a) volume of gas against time

(b) loss of mass against time

Figure 2 — Two continuous methods: (a) collecting the gas in a gas syringe; (b) following the loss of mass on a balance. Both give a curve that levels off (plateaus) when the limiting reactant is used up.

Worked example 6 — choosing a method

Q. Suggest a suitable method to follow the rate of each reaction, and explain your choice.

Reaction	Method and reason
$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$	colorimetry: purple MnO_4^- fades to almost colourless Mn^{2+}; or volume of CO_2
$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$	colorimetry: the orange-brown bromine is the only coloured species; or volume of CO_2
$CH_3COOCH_3(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + CH_3OH(aq)$	conductivity: OH^- ions conduct far better than the ethanoate ions that replace them; or titrate samples of the remaining OH^-
$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$	volume of H_2 in a gas syringe; loss of mass is unsuitable because hydrogen is so light

3.2 Clock reactions

In a **clock reaction** you measure the time, t, for a fixed amount of reaction to happen, shown by a sudden visible change. Because the same amount of reaction happens each time, the average rate over that time is proportional to $1/t$. This gives only an **average** rate, not a rate at a particular instant.

Worked example 7 — interpreting clock-reaction data

Q. Sodium thiosulfate solutions of different concentrations were mixed with the same volume of excess hydrochloric acid, and the time for a cross under the flask to disappear was recorded. Deduce how the rate depends on $[S_2O_3^{2-}]$.

$[S_2O_3^{2-}]$ / mol dm^{-3}	0.040	0.080	0.120	0.160
time, t / s	120	61	40	30
$1/t$ / s^{-1}	0.00833	0.0164	0.0250	0.0333

Doubling the concentration (0.040 → 0.080) roughly doubles $1/t$; four times the concentration gives four times $1/t$.

A graph of $1/t$ against concentration is a straight line through the origin: **rate is directly proportional to $[S_2O_3^{2-}]$**

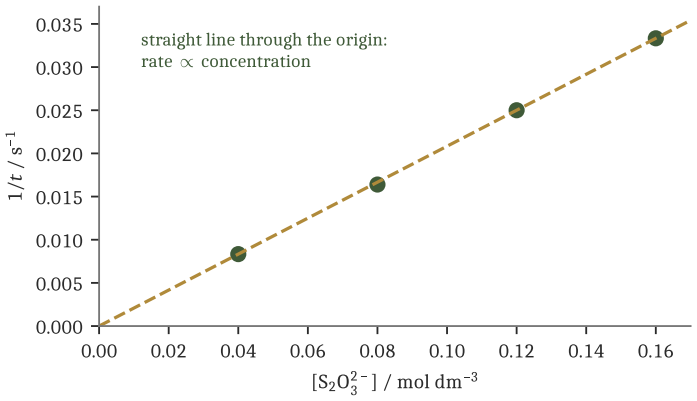


Figure 3 — Worked example 7: $1/t$ against concentration.

3.3 Time as the dependent or the independent variable

In the continuous methods (gas volume, mass, colorimetry, conductivity, titration of samples), **time is the independent variable**: you choose when to take readings and measure how the signal changes. In a clock reaction, **time is the dependent variable**: you fix the amount of change and measure how long it takes. Whichever method you use, the temperature must be controlled, for example with a thermostatted water bath, because the rate depends strongly on temperature.

Model answer: "Explain why measuring the loss of mass is not a suitable way to follow the rate of reaction of magnesium with hydrochloric acid." (2 marks)

The gas produced is hydrogen, which has a very low molar mass (2.02 g mol^{-1}) [1]. The mass lost is therefore very small compared with the total mass of the flask and contents, so the change is too small to measure accurately on a laboratory balance; collecting the gas volume is better [1].

4 Reactivity 2.2.2 — Collision theory SL + HL

4.1 Kinetic energy and temperature

The kinetic molecular theory (Structure 1.1) says that particles are in constant random motion. At any instant they have a **range** of kinetic energies, because random collisions keep transferring energy between them. Their **average** kinetic energy is directly proportional to the **absolute temperature**, in kelvin. Collision theory builds on this model: it explains reaction rates in terms of how often particles collide and how energetic those collisions are.

Definition to learn

The **temperature in kelvin** is proportional to the **average kinetic energy** of the particles in a substance.

$$T/\mathrm{K} = t/^{\circ}\mathrm{C} + 273$$

Worked example 8 — doubling the Celsius temperature does not double the energy

Q. A gas is heated from 25 °C to 50 °C. By what factor does the average kinetic energy of its particles increase?

$T_1 = 25 + 273 = 298$ K; $T_2 = 50 + 273 = 323$ K

average kinetic energy $\propto T$, so the factor = 323 / 298 = **1.08**: an increase of only 8 %, not 100 %

Yet the rate of many reactions increases about five-fold over this range. Section 6 explains why the rate rises so much more than the average energy.

4.2 The Maxwell–Boltzmann distribution

The spread of kinetic energies in a gas at one temperature is shown by the **Maxwell–Boltzmann energy distribution curve**. It plots the number of particles with each value of kinetic energy against that energy. James Clerk Maxwell and Ludwig Boltzmann developed it in the 19th century.

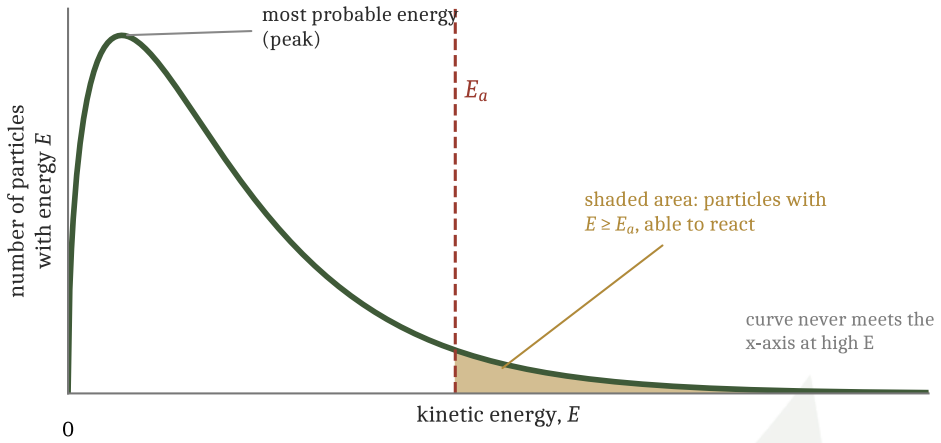


Figure 4 — The Maxwell–Boltzmann distribution. The shaded area under the curve beyond E_a represents the particles that have enough energy to react.

- The curve starts at the **origin**: no particles have zero energy.
- It is **not symmetrical**: it rises steeply to a peak (the most probable energy), then falls gradually.
- It **never touches the energy axis** at high energy: a very few particles have very high energies.
- The **area under the curve** represents the total number of particles.

4.3 What makes a collision successful

Reactions happen when particles collide, bonds break and new bonds form. But only a tiny fraction of collisions are **successful** (lead to products). Two conditions must both be met.

Definitions to learn

Collision theory: particles react only when they collide with kinetic energy **greater than or equal to the activation energy** and with the **correct orientation** (collision geometry).

The **activation energy**, E_a, is the minimum energy that colliding particles need for a successful collision leading to a reaction.

Energy. The activation energy is needed to overcome the repulsion between the electron clouds of the approaching particles and to start breaking bonds. It is an energy barrier, like a pass mark in an exam: collisions with less energy than E_a simply bounce apart. At the top of the barrier the particles form an unstable arrangement called the **transition state** (or activated complex), in which bonds are partly broken and partly formed.

Geometry. The particles must also meet with the reacting parts facing each other. For example, when a hydroxide ion attacks a halogenoalkane it must hit the carbon atom on the side opposite the halogen; a collision anywhere else does not lead to reaction, however energetic. The more complex the molecules, the smaller the fraction of collisions that have the right geometry.

So the rate depends on the **frequency of successful collisions**: how often particles collide, multiplied by the fraction of those collisions that have both enough energy and the right orientation.

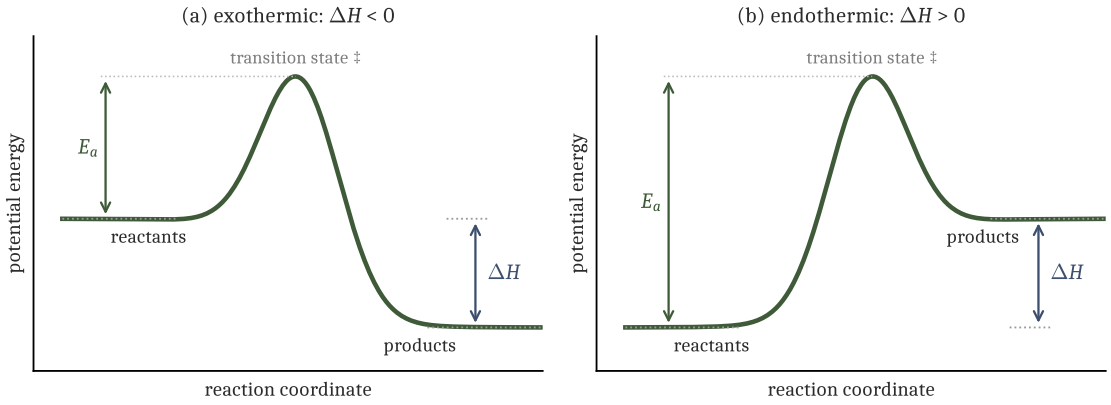


Figure 5 — Energy profiles for (a) an exothermic and (b) an endothermic reaction. E_a is measured from the reactants to the top of the barrier (the transition state, ‡). For an endothermic reaction E_a must be at least as large as ΔH.

Model answer: "Suggest why a reaction that needs three molecules to collide at the same time is usually slower than one that needs only two." (2 marks)

A collision of three particles at exactly the same moment is far less likely (less frequent) than a collision between two [1]. All three must also have the correct orientation and enough combined energy, so the frequency of successful collisions, and hence the rate, is much lower [1].

Examiner traps in collision theory

- Writing that particles must have energy "greater than the average energy". The threshold is the **activation energy**.
- Forgetting orientation: energy alone is not enough.
- Using °C in arguments about kinetic energy. Average kinetic energy is proportional to temperature in **kelvin**.
- Saying "more collisions" when you mean "more **successful** collisions per unit time". Rate depends on frequency, so say *per second*.
- Drawing a Maxwell–Boltzmann curve that is symmetrical, does not start at the origin, or touches the energy axis.

5 Reactivity 2.2.3 — Factors that affect the rate SL + HL

Anything that increases the frequency of successful collisions increases the rate. Five factors do this, but in two different ways: some make collisions more frequent; others make a larger fraction of collisions successful.

Increase in…	What happens to the particles	Collision frequency	Fraction of collisions with $E \geq E_a$
concentration	more particles per unit volume	increases	unchanged
pressure (gases)	gas compressed, so more particles per unit volume	increases	unchanged
surface area (solids)	more particles exposed at the surface	increases	unchanged
temperature	particles move faster with more energy	increases (slightly)	**increases greatly**: the main effect
catalyst	alternative pathway with lower E_a	unchanged	**increases**, because E_a is lower

5.1 Concentration and pressure

At a higher concentration the particles are closer together, so they collide more often: the frequency of collisions, and of successful collisions, increases. This is also why the rate falls during a reaction: the reactants are used up, so their concentration falls. For gases, increasing the pressure (for example by reducing the volume of the container) has the same effect, because it increases the number of gas particles per unit volume.

5.2 Surface area

In a **heterogeneous** reaction, such as a solid with a solution or a gas, only the particles at the surface of the solid can collide with the other reactant. Breaking a solid into smaller pieces exposes more particles, so collisions are more frequent. Marble powder fizzes far more vigorously in acid than marble chips; small sticks catch fire more easily than a log; and fine dusts of flour, sugar or coal can explode in air. Stirring helps by keeping small solid particles spread out.

Worked example 9 — how much does subdividing increase the surface area?

Q. A 1.00 cm cube of a solid is cut into cubes of side 1.00 mm, then ground to cubes of side 0.100 mm. Calculate the total surface area each time.

one 1.00 cm cube: $6 \times (1.00\ \text{cm})^2 =$ **$6.00\ \text{cm}^2$**

1.00 mm cubes: $10 \times 10 \times 10 = 1000$ cubes, each $6 \times (0.100\ \text{cm})^2 = 0.0600\ \text{cm}^2$ → total = **$60.0\ \text{cm}^2$**

0.100 mm cubes: 10^6 cubes, each $6 \times (0.0100\ \text{cm})^2 = 6.00 \times 10^{-4}\ \text{cm}^2$ → total = **$600\ \text{cm}^2$**

The mass is unchanged, but each tenfold cut in particle size gives ten times the surface area, and so roughly ten times the initial rate.

Model answer: "Explain why powdered calcium carbonate reacts faster with hydrochloric acid than the same mass of marble chips." (2 marks)

The powder has a much larger surface area, so more calcium carbonate particles are exposed to the acid [1]. The frequency of collisions between acid particles and the solid is greater, so there are more successful collisions per unit time [1].

5.3 Temperature

Raising the temperature makes the particles move faster, so they collide slightly more often. Much more importantly, a far greater fraction of the collisions have energy equal to or greater than E_a, so the frequency of successful collisions rises steeply. As a rough rule of thumb, the rate of many reactions approximately doubles for every 10 °C rise. This is why food keeps longer in a fridge, and why mammoths frozen in Arctic permafrost for 10 000 years have been found with their flesh still intact. Section 6 shows this with the Maxwell–Boltzmann curve.

Worked example 10 — the "doubles every 10 °C" rule of thumb

Q. A reaction takes 160 s at 20 °C. Assuming that the rate doubles for every 10 °C rise, estimate the time taken at 50 °C and at 10 °C.

20 → 50 °C is three 10 °C rises: rate × 2^3 = × 8, so time = 160 / 8 = **20 s**

20 → 10 °C is one 10 °C fall: rate ÷ 2, so time = 160 × 2 = **320 s**

This is only an approximation. The exact relationship depends on E_a and is given by the Arrhenius equation (HL, Reactivity 2.2.12).

5.4 Catalysts

A catalyst provides a different route with a lower activation energy, so more collisions are successful at the same temperature. It is covered fully in section 7.

5.5 Predicting the shape of rate graphs

Questions often show a graph of gas volume (or mass loss) against time and ask how it changes when one condition is altered. Two things must be decided separately: the **initial gradient** (the rate), and the **final volume**, which depends only on the amount of the **limiting reactant** (Reactivity 2.1).

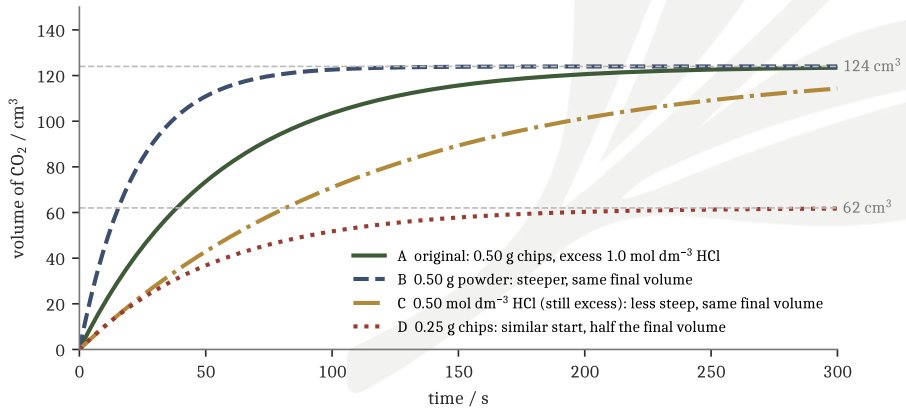


Figure 6 — Worked example 11. The initial gradient shows the rate; the plateau shows the amount of the limiting reactant.

Worked example 11 — predicting the curves ★

Q. Curve A in Figure 6 is for 0.50 g of marble chips (the limiting reactant) with excess 1.0 mol dm^{-3} HCl at 25 °C and 100 kPa. Calculate the final volume of CO_2, then predict the curve for each change.

$n(CaCO_3) = 0.50 / 100.09 = 5.00 \times 10^{-3}$ mol $= n(CO_2)$; $V = 5.00 \times 10^{-3} \times 24.8 = 0.124$ dm^3 = **124 cm^3**

B: 0.50 g of powder → steeper (larger surface area); **same final volume**, same amount of $CaCO_3$

C: 0.50 mol dm^{-3} HCl, still in excess → less steep (lower concentration); **same final volume**

D: 0.25 g of chips → about the same initial rate; **half the final volume**, 62 cm^3

A at 35 °C (not drawn) → steeper, reaches the plateau sooner; same final volume

5.6 Controlling variables

To find the effect of one factor, it must be the only thing that changes. List all the factors that affect rate, then the details of your measuring method, and keep everything except the independent variable the same.

Worked example 12 — planning a fair investigation

Q. A student investigates the effect of temperature on the rate of $Na_2S_2O_3(aq) + 2HCl(aq)$, timing how long a cross under the flask takes to disappear. Identify the variables.

Variable	In this investigation
independent	temperature of the mixture (e.g. 20, 30, 40, 50, 60 °C, using a water bath, measured in the flask)
dependent	time for the cross to disappear, t; the rate is taken as $1/t$
controlled	concentrations and volumes of both solutions (so the total volume and depth of liquid are constant); the same flask and the same cross; the same observer viewing from the same height; no catalyst

5.7 Systematic and random errors on graphs

Graphs show the type of error in a data set. **Random errors** (from the limits of the equipment, judging an end point, or changes in the surroundings) scatter points on **both sides** of the best-fit line and reduce **precision**; repeating trials reduces their effect. A **systematic error** shifts **all** points the same way, giving a line displaced above or below the expected one, and reduces **accuracy**; repeats do not remove it. Examples are a gas syringe that sticks, gas lost before the bung is inserted, or a thermometer that always reads 2 °C high. The coefficient of determination, R^2, measures how well a trend line fits: 1 means a perfect fit.

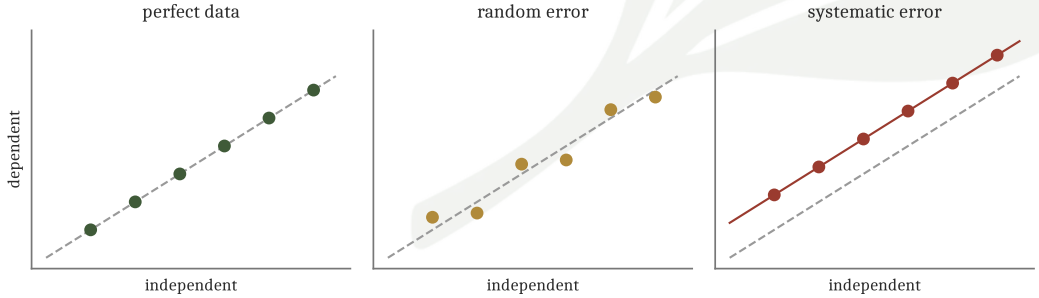


Figure 7 — Evidence of error. Random error scatters points on both sides of the line; systematic error shifts the whole line.

Examiner traps with the factors

- Saying that concentration, pressure or surface area change the activation energy or the energy of the particles. They change only the **collision frequency**.
- Explaining temperature only through "more collisions". The main reason is that a larger **fraction of collisions** have $E \geq E_a$.
- Changing the final volume of gas when only the rate changes. The final amount depends only on the limiting reactant.
- Saying that pressure affects reactions in solution. Pressure matters only for reactions involving gases.
- Calling the effect of a catalyst "giving the particles more energy". It lowers E_a; the energies are unchanged.

6 Reactivity 2.2.4 — Activation energy SL + HL

6.1 The effect of temperature on the distribution

Only particles in the shaded area beyond E_a in Figure 4 can react. At a higher temperature the whole distribution spreads out to higher energies. The total number of particles has not changed, so the **area under the curve stays the same**: the peak becomes **lower** and moves to the **right**, and the curve is broader. The area beyond E_a increases greatly, even though E_a itself does not change.

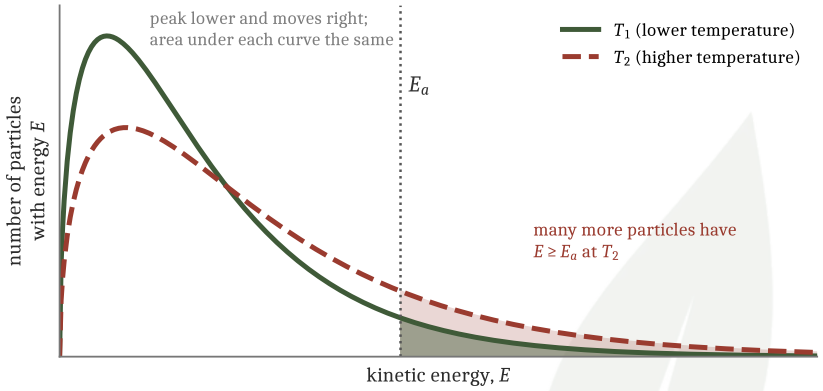


Figure 8 — Maxwell–Boltzmann curves at two temperatures, $T_2 > T_1$. The fraction of particles with $E \geq E_a$ is much greater at T_2.

Method — drawing Maxwell–Boltzmann curves in an exam

1. Label the axes: **kinetic energy** (x) and **number (or fraction) of particles** with that energy (y).
2. Start the curve at the origin; make it asymmetric with a long tail that approaches, but never meets, the x-axis.
3. For a higher temperature: peak lower and to the right, curve broader, tail above the first curve at high energy. Keep the areas roughly equal.
4. Mark E_a on the energy axis, well to the right of the peak, and shade or label the area beyond it.
5. For a catalyst: **one** curve only (the temperature is unchanged) with two E_a values marked (Figure 10).

Model answer: "Use the Maxwell–Boltzmann distribution to explain why an increase in temperature increases the rate of a reaction." (3 marks)

At a higher temperature the particles have a greater average kinetic energy, so the distribution shifts to higher energies; the peak is lower and moves to the right [1]. A much larger proportion of the particles now have energy greater than or equal to the activation energy (a larger area under the curve beyond E_a) [1]. So the frequency of successful collisions increases, and so does the rate; collisions also become slightly more frequent [1].

6.2 Reactions with different activation energies

Worked example 13 — comparing activation energies

Q. At the same temperature, reaction X has E_a = 40 kJ mol^{-1} and reaction Y has E_a = 90 kJ mol^{-1}. Predict which is faster, and explain why a mixture of methane and air does not react at room temperature even though combustion is very exothermic.

On one Maxwell–Boltzmann curve, 40 kJ mol^{-1} lies much nearer the peak than 90 kJ mol^{-1}, so a far larger fraction of particles can react in X: **X is faster**.

Methane combustion has a high E_a. At room temperature almost no collisions have enough energy, so the rate is negligible; a spark supplies the energy to start it, and the heat released then keeps it going.

ΔH tells you how much energy is released, not how fast. A mixture that is energetically unstable but reacts too slowly to notice is said to be **kinetically stable**.

Examiner traps with Maxwell–Boltzmann curves

- Drawing the higher-temperature curve with a higher peak, or with a larger area. The peak is lower; the area is the same.
- Moving E_a when the temperature changes. Temperature changes the distribution, not E_a.
- Drawing two curves to show a catalyst. A catalyst does not change the distribution; it moves E_a to the left.
- Confusing a large ΔH with a fast reaction. Rate depends on E_a, not ΔH.

7 Reactivity 2.2.5 — Catalysts SL + HL

7.1 How a catalyst works

Definition to learn

A **catalyst** is a substance that increases the rate of a chemical reaction without itself undergoing permanent chemical change. It provides an **alternative reaction pathway with a lower activation energy**.

Biological catalysts are called **enzymes**.

With a lower E_a, a larger fraction of the particles already present have enough energy to react, so the frequency of successful collisions rises without any change in temperature. In the exam analogy, a catalyst lowers the pass mark: the same stu-

dents, with the same work, but more of them pass. A catalyst does **not** change ΔH, because the reactants and products are the same; it is regenerated at the end, so only small amounts are needed and it can be reused.

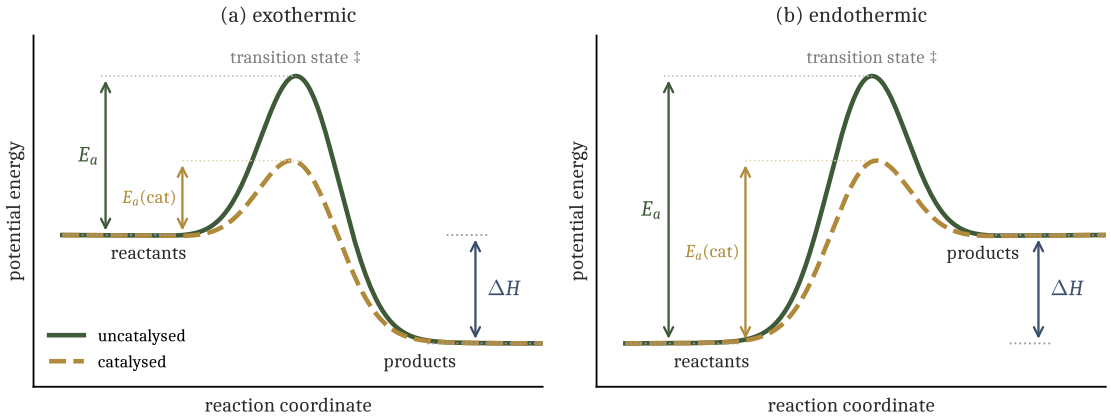


Figure 9 — Energy profiles with and without a catalyst for (a) an exothermic and (b) an endothermic reaction. The catalysed path has a lower barrier; ΔH is the same.

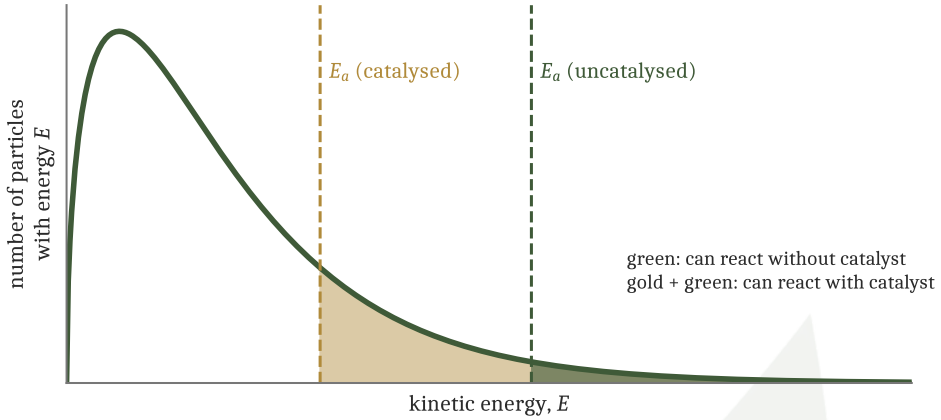


Figure 10 — The effect of a catalyst on the Maxwell–Boltzmann distribution. The curve is unchanged; the lower E_a means a much larger area beyond it.

Worked example 14 — reading an energy profile ★

Q. For a reaction, ΔH = −95 kJ mol^{-1} and E_a = 180 kJ mol^{-1}. A catalyst lowers E_a for the forward reaction to 75 kJ mol^{-1}. Calculate E_a for the reverse reaction with and without the catalyst, and comment.

E_a(reverse) = E_a(forward) − ΔH (the barrier measured from the products)

uncatalysed: 180 − (−95) = **275 kJ mol^{-1}**; catalysed: 75 − (−95) = **170 kJ mol^{-1}**

Both barriers fall by the same amount, 105 kJ mol^{-1}, and ΔH is unchanged.

Because the forward and reverse rates increase by the same factor, a catalyst does not change the position of equilibrium or the yield. It only means that equilibrium is reached sooner (Reactivity 2.3).

Worked example 15 — showing that a catalyst is not used up

Q. 25.0 cm^3 of 0.400 mol dm^{-3} hydrogen peroxide decomposes, $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$, at 298 K and 100 kPa. With 0.50 g of manganese(IV) oxide the oxygen is released in about 2 minutes instead of several hours. Calculate the final volume of oxygen, and state what you would find if the solid were filtered off, dried and weighed afterwards.

$n(H_2O_2) = 0.400 \times 0.0250 = 0.0100$ mol → $n(O_2) = 0.00500$ mol; $V = 0.00500 \times 24.8 =$ **0.124 dm^3 (124 cm^3)**, with or without MnO_2

The recovered MnO_2 still has a mass of **0.50 g**: it is chemically unchanged and can be reused.

The catalyst changes how fast the 124 cm^3 is released, not how much is released.

7.2 Catalysts in industry, the body and the environment

- **Industry:** without catalysts many processes would be far too slow, or would need such high temperatures that they would not be economic. Iron in the Haber process and vanadium(V) oxide in the Contact process are examples. Finding the best catalyst is an active area of research, and industrial recipes are often kept secret.
- **Catalytic converters:** platinum, palladium and rhodium on a ceramic honeycomb convert CO, NO and unburnt hydrocarbons into CO_2, N_2 and H_2O, for example $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$. They reduce harmful emissions by about 90 %.
- **Enzymes:** every biological reaction is controlled by an enzyme, each specific to one reaction. Pepsin in the stomach, for example, catalyses the breakdown of proteins into peptides. Enzymes are also used in biological detergents, cheese-making and biosensors.
- **Green Chemistry:** catalysts can replace reagents that would otherwise be used up, often make reactions more selective, work in small amounts and can be reused, and allow lower temperatures. All of this reduces waste and energy use.
- **Ozone depletion:** chlorine radicals from CFCs and nitrogen oxides catalyse the breakdown of ozone in the stratosphere. International treaties to phase out CFCs have been essential.

7.3 Catalysts and equilibrium

A catalyst lowers the activation energy of the forward and the reverse reactions by the same amount (worked example 14), so both rates increase by the same factor. It therefore has no effect on the position of equilibrium or on the yield. This is developed in Reactivity 2.3.

7.4 Homogeneous and heterogeneous catalysts

A **homogeneous** catalyst is in the same phase as the reactants, such as chlorine radicals with ozone in the gas phase. A **heterogeneous** catalyst is in a different phase, usually a solid with gases or liquids, such as V_2O_5 with SO_2 and O_2. Heterogeneous catalysts are easier to separate and reuse. Transition metals and their compounds are common catalysts because they have variable oxidation states and can form weak bonds to reactant molecules using their 3d and 4s electrons (Structure 3.1). The detailed mechanisms of the two types will not be assessed.

Model answer: "Explain how a catalyst increases the rate of a reaction." (2 marks)

A catalyst provides an alternative reaction pathway with a lower activation energy [1]. So a greater proportion of the particles have energy greater than or equal to E_a, and the frequency of successful collisions increases [1].

Examiner traps with catalysts

- Saying a catalyst "lowers the activation energy" without saying it does so by providing an **alternative pathway**.
- Saying a catalyst changes ΔH, the yield or the position of equilibrium. It changes none of them.
- Saying a catalyst is "not involved" in the reaction. It takes part, but is regenerated, so it is not permanently changed.
- Drawing the catalysed energy profile starting or ending at different energies from the uncatalysed one.
- Drawing a second Maxwell–Boltzmann curve to show a catalyst.

8 Key points to memorise

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

A Definitions

- **Rate of reaction:** the increase in concentration of a product, or decrease in concentration of a reactant, per unit time; mol dm^{-3} s^{-1}.
- **Initial rate:** the gradient of the tangent at $t = 0$. **Instantaneous rate:** the gradient of the tangent at any time.
- **Temperature in kelvin** is proportional to the average kinetic energy of the particles.
- **Activation energy, E_a:** the minimum energy that colliding particles need for a successful collision leading to a reaction.
- **Collision theory:** particles react when they collide with $E \geq E_a$ and the correct orientation.
- **Catalyst:** increases the rate without permanent chemical change, by providing an alternative pathway with a lower E_a. Biological catalysts are **enzymes**.

B Equations and graph skills

- rate = $\Delta[P]/\Delta t = -\Delta[R]/\Delta t$; average rate from a chord, instantaneous rate from a tangent; always positive.
- Gas and mass rates: cm^3 s^{-1} and g s^{-1}. Convert with $n = V/V_m$ or $n = m/M$, then the mole ratio and $c = n/V$.
- Different species change at rates in the ratio of their coefficients.
- Clock reactions: rate $\propto 1/t$ (an average rate). $T/K = t/°C + 273$.
- E_a(reverse) = E_a(forward) − ΔH.

C Explanations you will be asked for

- Rate is greatest at the start and falls because the reactant concentration falls.
- Concentration, pressure and surface area increase the **collision frequency**; they do not change E_a or the energy distribution.
- Temperature: mainly a larger **fraction** of particles with $E \geq E_a$; the Maxwell–Boltzmann peak is lower and moves right, with the area unchanged.
- Catalyst: lower E_a via an alternative pathway, so a larger fraction of collisions succeed; ΔH, yield and equilibrium position unchanged.
- The final amount of product depends only on the limiting reactant; the rate does not change it.
- Random error scatters points either side of the line; systematic error shifts the whole line.

9 Check yourself

Use A_r values from the data booklet (H 1.01, C 12.01, O 16.00, Mg 24.31, Ca 40.08, Zn 65.38), $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$ and, where needed, a molar volume of 24.8 $\text{dm}^3\ \text{mol}^{-1}$ at 298 K and 100 kPa. Marks are shown in brackets; allow about 1.2 minutes per mark. Full answers are in section 10.

Part A — Multiple choice SL + HL

1. Which are the units of rate of reaction?

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

2. What does the gradient of the tangent to a graph of product concentration against time give?

A the rate at that instant
B the average rate of the reaction
C the activation energy
D the final concentration of product

3. The concentration of a reactant falls from 0.500 to 0.320 mol dm^{-3} in 40 s. What is the average rate?

A 4.50×10^{-3} **B** 8.00×10^{-3} **C** 1.25×10^{-2} **D** 7.20

(all in $\text{mol dm}^{-3}\ \text{s}^{-1}$)

4. Which method is least suitable for following the rate of $\text{Mg(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$?

A measuring the loss in mass
B collecting the gas in a gas syringe
C timing how long the magnesium takes to disappear
D collecting the gas in an inverted burette

5. In a clock reaction, the time t for a fixed amount of reaction is measured. Which is correct?

A Time is the independent variable and rate $\propto t$.
B Time is the dependent variable and the average rate $\propto 1/t$.
C The method gives the instantaneous rate at $t = 0$.
D The method can only be used for reactions that produce a gas.

6. For $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, N_2O_5 is used up at $2.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$. What is the rate of formation of NO_2?

A 1.0×10^{-4} **B** 2.0×10^{-4} **C** 4.0×10^{-4} **D** 8.0×10^{-4}

7. The average kinetic energy of the particles in a gas is directly proportional to

A the temperature in °C
B the temperature in K
C the square of the temperature in K
D the activation energy

8. What does the total area under a Maxwell–Boltzmann distribution curve represent?

A the activation energy
B the total number of particles
C the average kinetic energy
D the number of successful collisions

9. Which change increases the *fraction* of collisions that have energy greater than or equal to E_a, without adding anything to the mixture?

A increasing the concentration
B increasing the pressure
C increasing the temperature
D grinding a solid reactant

10. Which must be true for a collision to lead to a reaction? I. energy ≥ E_a II. correct orientation III. the particles have equal masses

A I and II only **B** I and III only **C** II and III only **D** I, II and III

11. How does a catalyst increase the rate of a reaction?

A It gives the reactant particles more kinetic energy.
B It provides an alternative pathway with a lower activation energy.
C It makes ΔH more negative.
D It increases the collision frequency.

12. When the temperature of a gas is increased, the peak of its Maxwell–Boltzmann curve

A becomes higher and moves to lower energy
B becomes higher and moves to higher energy
C becomes lower and moves to higher energy
D stays at the same height and energy

13. Which conditions give the highest initial rate for $CaCO_3$ with excess hydrochloric acid?

A chips, 1.0 mol dm^{-3}, 20 °C
B powder, 1.0 mol dm^{-3}, 20 °C
C powder, 2.0 mol dm^{-3}, 40 °C
D chips, 2.0 mol dm^{-3}, 40 °C

14. Why does increasing the pressure increase the rate of a reaction between gases?

A The particles have more kinetic energy.
B The activation energy is lowered.
C There are more particles per unit volume, so collisions are more frequent.
D A larger fraction of collisions have the correct orientation.

15. Which statement about a catalyst in a reversible reaction is correct?

A It increases the rate of the forward reaction only.
B It increases the rates of the forward and reverse reactions equally.
C It increases the yield of product.
D It increases the activation energy of the reverse reaction.

16. On a graph, all the data points lie close to a straight line that is parallel to, but above, the expected line. What does this show?

A a large random error
B a systematic error
C no error at all
D an incorrect independent variable

Part B — Structured questions SL + HL

17. The concentration of reactant A was measured during a reaction at constant temperature.

time / s	0	50	100	150	200	250	300
[A] / mol dm^{-3}	0.0500	0.0389	0.0303	0.0236	0.0184	0.0143	0.0112

(a) Plot a graph of [A] against time and draw a smooth curve. [2]

(b) Draw a tangent and determine the rate at 100 s. [2]

(c) Explain why the rate decreases as the reaction proceeds. [1]

18. Using the data in question 17, calculate the average rate between 0 and 50 s and between 200 and 250 s, and comment on the difference. [3]

19. Zinc reacts with 40.0 cm^3 of hydrochloric acid at 298 K and 100 kPa: $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$. The initial rate of hydrogen production, from a tangent, is 0.85 cm^3 s^{-1}.

(a) Calculate the initial rate of production of hydrogen in mol s^{-1}. [2]

(b) Calculate the initial rate of decrease of [HCl] in mol dm^{-3} s^{-1}. [2]

(c) Explain why initial rates are used to compare reactions under different conditions. [1]

20. Marble chips were added to excess hydrochloric acid in a flask on a balance, with cotton wool in the neck.

time / s	0	30	60	90	120	180	240
mass / g	250.00	249.40	249.10	248.98	248.92	248.90	248.90

(a) Calculate the average rate over the first 30 s in g s^{-1} and in mol CO_2 s^{-1}. [2]

(b) Explain why the mass stops changing after 180 s. [1]

(c) State the purpose of the cotton wool. [1]

(d) Calculate the mass of calcium carbonate that reacted. [1]

21. For $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$, ammonia is used up at 0.24 mol dm^{-3} s^{-1}. Calculate the rate of use of O_2 and the rates of formation of NO and H_2O. [3]

22. Suggest a suitable method for following the rate of each reaction, giving a reason.

(a) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ (b) $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$ (c) $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$ (d) $(CH_3)_3CCl(l) + H_2O(l) \rightarrow (CH_3)_3COH(aq) + H^+(aq) + Cl^-(aq)$ [4]

23. Different volumes of 0.150 mol dm^{-3} $Na_2S_2O_3(aq)$ were made up to 50.0 cm^3 with water, and 10.0 cm^3 of HCl(aq) was added each time. The time for the cross to disappear was recorded.

volume of $Na_2S_2O_3$ / cm^3	50.0	40.0	30.0	20.0	10.0
time, t / s	22	28	37	56	111

(a) Calculate the concentration of thiosulfate in the 50.0 cm^3 and $1/t$ for each experiment. [1]

(b) Deduce the relationship between rate and thiosulfate concentration, explaining your reasoning. [2]

(c) Explain why water was added to keep the total volume constant. [1]

(d) Explain why $1/t$ can be used as a measure of the rate. [1]

24. Collision theory.

(a) State the two conditions needed for a collision to lead to a reaction. [2]

(b) Explain why most collisions do not lead to reaction, even at high temperature. [1]

(c) Explain why increasing the concentration increases the rate, although the activation energy is unchanged. [1]

25. A gas is heated from 0 °C to 100 °C.

(a) Calculate the factor by which the average kinetic energy of its particles increases. [1]

(b) The rate of a reaction of this gas increases by a factor of about 200. Explain why the rate increases so much more than the average kinetic energy. [2]

26. Sketch, on one set of labelled axes, Maxwell–Boltzmann distribution curves for a gas at temperatures T_1 and T_2, where $T_2 > T_1$. Mark the activation energy and use your sketch to explain why the rate is greater at T_2. [5]

27. Sketch an energy profile for an endothermic reaction with and without a catalyst. Label the axes, ΔH and both activation energies. [4]

28. ★ For a reaction, E_a = 92 kJ mol^{-1} and ΔH = +38 kJ mol^{-1}. A catalyst lowers the forward E_a to 54 kJ mol^{-1}.

(a) Calculate the activation energy of the reverse reaction without the catalyst. [1]

(b) Calculate the activation energy of the reverse reaction with the catalyst. [1]

(c) State the effect of the catalyst on ΔH. [1]

(d) Explain why the catalyst does not change the position of equilibrium. [1]

29. ★ 0.240 g of magnesium ribbon reacts with 50.0 cm^3 of 1.00 mol dm^{-3} HCl at 25 °C and 100 kPa, and the hydrogen is collected.

(a) Show that magnesium is the limiting reactant, and calculate the final volume of hydrogen. [2]

For each change, state the effect on the initial rate and on the final volume of hydrogen:

(b) 0.240 g of magnesium powder [1]

(c) 0.120 g of magnesium ribbon [1]

(d) 50.0 cm^3 of 0.500 mol dm^{-3} HCl [1]

(e) the original mixture at 35 °C [1]

30. A bag of flour burns slowly, but fine flour dust in the air of a flour mill can explode.

(a) Explain the difference in rate. [2]

(b) Suggest one way of reducing the risk of a dust explosion. [1]

31. Catalytic converters in cars contain platinum and rhodium on a ceramic honeycomb.

(a) Write an equation for the reaction of carbon monoxide with nitrogen monoxide to form carbon dioxide and nitrogen. [1]

(b) Explain why the metals are spread thinly over a honeycomb. [1]

(c) Suggest why the converter does not work well until the engine has warmed up. [1]

(d) State whether this is homogeneous or heterogeneous catalysis, and why. [1]

(e) Explain why the platinum does not need to be replaced after each journey. [1]

32. A student plans to investigate how the concentration of hydrochloric acid affects the rate of its reaction with magnesium ribbon, by collecting the hydrogen in a gas syringe. Identify the independent and dependent variables, two controlled variables, and one source of random error. [4]

33. In repeated gas-syringe experiments, a student's points are scattered on both sides of the best-fit line, and the whole line lies below the expected one. Identify the two types of error shown, and suggest one cause of the second. [3]

34. (a) State the name given to biological catalysts. (b) Suggest why reactions in the body are fast enough at only 37 °C. [2]

35. ★ 25.0 cm^3 of 0.400 mol dm^{-3} H_2O_2 was decomposed with a MnO_2 catalyst at 298 K and 100 kPa.

time / s	0	20	40	60	90	120	180	240
volume of O_2 / cm^3	0	38	65	84	102	112	120	121

(a) Calculate the expected final volume of oxygen. [2]

(b) Calculate the average rate over the first 20 s in $cm^3\ s^{-1}$. [1]

(c) Convert your answer to (b) into the average rate of decrease of $[H_2O_2]$ in mol $dm^{-3}\ s^{-1}$. [2]

(d) Suggest why the measured final volume was less than expected. [1]

36. ★ The decolorisation of crystal violet, CV^+, by OH^- is followed with a colorimeter. A calibration line gives absorbance = 4.20×10^4 $dm^3\ mol^{-1} \times [CV^+]$. The absorbance falls from 0.840 to 0.630 in the first 60 s.

(a) Calculate the initial $[CV^+]$. [1]

(b) Calculate $[CV^+]$ after 60 s. [1]

(c) Calculate the average rate over the first 60 s. [1]

(d) Suggest why a wavelength of about 590 nm is used. [1]

(e) Explain why the cuvette holder is kept at constant temperature. [1]

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

10 Answers

Part A

1. C.

2. A.

3. A. $(0.500 - 0.320)/40 = 4.50 \times 10^{-3}$.

4. A. Hydrogen is too light to give a measurable loss of mass.

5. B.

6. C. NO_2 forms twice as fast as N_2O_5 is used (4 : 2).

7. B.

8. B.

9. C. A, B and D increase only the collision frequency.

10. A.

11. B. A catalyst does not change the energy of the particles or ΔH.

12. C.

13. C. Largest surface area, highest concentration, highest temperature.

14. C.

15. B.

16. B. All points displaced the same way.

Part B

17. (a) Suitable scales, axes labelled with units [1]; points plotted correctly with a smooth curve [1]. (b) Tangent drawn at 100 s [1]; rate = 1.5×10^{-4} mol $dm^{-3}\ s^{-1}$ (accept $1.3–1.7 \times 10^{-4}$) [1]. (c) The concentration of A falls, so collisions become less frequent [1].

18. 0–50 s: (0.0500 − 0.0389)/50 = 2.22 × 10^{-4} mol dm^{-3} s^{-1} [1]; 200–250 s: (0.0184 − 0.0143)/50 = 8.2 × 10^{-5} mol dm^{-3} s^{-1} [1]; the later rate is less than half the initial rate because the concentration of A is lower [1].

19. (a) 0.85/24 800 [1] = 3.4 × 10^{-5} mol s^{-1} [1]. (b) HCl used at 2 × 3.43 × 10^{-5} = 6.86 × 10^{-5} mol s^{-1} [1]; ÷ 0.0400 dm^3 = 1.7 × 10^{-3} mol dm^{-3} s^{-1} [1]. (c) At the start, the concentrations are known exactly and are the same in every experiment (no reactant has yet been used up), so only the chosen factor differs [1].

20. (a) (250.00 − 249.40)/30 = 0.020 g s^{-1} [1]; 0.020/44.01 = 4.5 × 10^{-4} mol CO_2 s^{-1} [1]. (b) The calcium carbonate (the limiting reactant) has all been used up, so no more CO_2 is produced [1]. (c) It lets CO_2 escape but stops acid spray (liquid) being lost, which would add to the mass loss [1]. (d) CO_2 lost = 1.10 g = 0.0250 mol, so $CaCO_3$ = 0.0250 × 100.09 = 2.50 g [1].

21. O_2: 0.24 × 5/4 = 0.30 mol dm^{-3} s^{-1} [1]; NO: 0.24 mol dm^{-3} s^{-1} [1]; H_2O: 0.24 × 6/4 = 0.36 mol dm^{-3} s^{-1} [1].

22. (a) Volume of O_2 collected in a gas syringe (a gas is produced) [1]. (b) Colorimetry: the blue colour of Cu^{2+} fades [1]. (c) Clock method/light sensor: time for the sulfur precipitate to hide a cross (solution becomes opaque) [1]. (d) Conductivity (or pH): ions are formed from neutral molecules, so the conductivity rises [1].

23. (a) [$S_2O_3^{2-}$] = 0.150, 0.120, 0.090, 0.060, 0.030 mol dm^{-3}; $1/t$ = 0.0455, 0.0357, 0.0270, 0.0179, 0.00901 s^{-1} [1]. (b) [$S_2O_3^{2-}$]/($1/t$) is constant (about 3.3) [1], so a graph of $1/t$ against concentration is a straight line through the origin: rate is directly proportional to concentration [1]. (c) So that the concentration of thiosulfate is the only variable changed (the HCl concentration and the depth of liquid stay the same) [1]. (d) The same amount of sulfur must form to hide the cross each time, so the average rate = fixed amount ÷ t, which is proportional to $1/t$ [1].

24. (a) Energy greater than or equal to the activation energy [1]; the correct orientation (collision geometry) [1]. (b) Most collisions have energy below E_a, or the wrong orientation [1]. (c) There are more particles per unit volume, so collisions, and therefore successful collisions, are more frequent [1].

25. (a) 373/273 = 1.37 [1]. (b) The distribution shifts to higher energy, so the *fraction* of particles with energy ≥ E_a increases greatly [1]; this fraction rises far faster than the average energy, because E_a lies in the tail of the distribution [1].

26. Axes labelled: kinetic energy (x), number of particles (y) [1]; T_1 curve from the origin, asymmetric, not touching the x-axis [1]; T_2 curve with lower peak moved to the right, similar area [1]; E_a marked and the areas beyond it identified [1]; at T_2 more particles have $E \geq E_a$, so there are more successful collisions per unit time [1].

27. Axes: potential energy and reaction coordinate/progress [1]; products higher than reactants, ΔH labelled as positive [1]; uncatalysed hump with E_a labelled from reactants to the top [1]; lower catalysed hump with the same reactants and products, E_a(cat) labelled [1].

28. (a) 92 − 38 = 54 kJ mol^{-1} [1]. (b) 54 − 38 = 16 kJ mol^{-1} [1]. (c) No effect: ΔH is still +38 kJ mol^{-1} [1]. (d) Both activation energies are lowered by the same amount (38 kJ mol^{-1}), so the forward and reverse rates increase by the same factor [1].

29. (a) n(Mg) = 0.240/24.31 = 9.87 × 10^{-3} mol needs 0.0197 mol HCl; 0.0500 mol is present, so Mg is limiting [1]; $V(H_2)$ = 9.87 × 10^{-3} × 24.8 = 0.245 dm^3 = 245 cm^3 [1]. (b) Faster initial rate; same final volume [1]. (c) About the same initial rate; final volume halved, 122 cm^3 [1]. (d) Slower initial rate; same final volume, because the 0.0250 mol HCl is still in excess [1]. (e) Faster initial rate; same final volume [1].

30. (a) The dust has a vast surface area, so oxygen molecules can collide with a huge number of flour particles at once [1]; the frequency of successful collisions, and the rate of the exothermic reaction, become so great that heat and gas are produced explosively [1]. (b) Any one: good ventilation or dust extraction; avoid sparks and naked flames; keep the dust damp [1].

31. (a) $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$ [1]. (b) It gives a very large surface area of catalyst for the gases to contact, using little expensive metal [1]. (c) At low temperature few molecules have energy ≥ E_a, even for the catalysed pathway, so the rate is too low [1]. (d) Heterogeneous: the solid catalyst is in a different phase from the gaseous reactants [1]. (e) A catalyst is regenerated and not permanently changed, so it is not used up [1].

32. Independent: concentration of HCl [1]; dependent: volume of hydrogen at time intervals, or the initial rate [1]; controlled, any two: temperature, volume of acid, length/mass of Mg ribbon (surface area), cleaning the ribbon, same apparatus [1]; random error, any one: reading the syringe, starting the timer, judging when the reaction starts [1].

33. Scatter about the line: random error [1]; the whole line displaced below: systematic error [1]; cause, any one: gas escaping before the bung is inserted; a leak; a plunger that sticks; a syringe that is not zeroed [1].

34. (a) Enzymes [1]. (b) Enzymes provide pathways with very low activation energies, so many collisions are successful even at 37 °C [1].

35. (a) $n(H_2O_2) = 0.400 \times 0.0250 = 0.0100$ mol → 0.00500 mol O_2 [1]; × 24 800 = 124 cm^3 [1]. (b) 38/20 = 1.9 $cm^3\ s^{-1}$ [1]. (c) 1.9/24 800 = 7.66×10^{-5} mol $O_2\ s^{-1}$; H_2O_2 used at twice this, 1.53×10^{-4} mol s^{-1} [1]; ÷ 0.0250 dm^3 = 6.1×10^{-3} mol $dm^{-3}\ s^{-1}$ [1]. (d) Any one: some O_2 dissolved in the water; gas escaped before the bung was fitted; the H_2O_2 solution had partly decomposed before use [1].

36. (a) $0.840/4.20 \times 10^4 = 2.00 \times 10^{-5}$ mol dm^{-3} [1]. (b) $0.630/4.20 \times 10^4 = 1.50 \times 10^{-5}$ mol dm^{-3} [1]. (c) $(2.00 - 1.50) \times 10^{-5}/60 = 8.3 \times 10^{-8}$ mol $dm^{-3}\ s^{-1}$ [1]. (d) It is the wavelength that crystal violet absorbs most strongly, giving the greatest sensitivity [1]. (e) Rate depends on temperature, so a change in temperature during the run would change the rate [1].

Where this fits in Reactivity 2

- **Booklets 1 and 2** — Reactivity 2.1: how much? Equations, reacting quantities, yield and atom economy. **Booklet 3 (this booklet)** — Reactivity 2.2.1–2.2.5: how fast? Rates, collision theory, factors, activation energy, catalysts.
- **Next (HL):** Reactivity 2.2.6 onwards: mechanisms, rate equations, orders and the Arrhenius equation. **Then:** Reactivity 2.3: how far? Equilibrium.

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