

Cambridge AS & A Level · Chemistry 9701 · Notes

Reaction kinetics

AS

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What you need to know

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

8.1 Rate of reaction

1. **Explain and use the terms** rate of reaction, frequency of collisions, effective collisions and non-effective collisions.
2. **Explain how concentration and pressure change the rate**, in terms of how often effective collisions happen (no calculations needed).
3. **Calculate a rate from experimental data**, such as gas volumes, masses or concentrations measured over time, or a graph of them.

8.2 Effect of temperature and activation energy

4. **Define activation energy**, E_A : the smallest energy a collision must have to be effective.
5. **Sketch the Boltzmann distribution** of molecular energies and use it to show why the activation energy matters.
6. **Explain why a change in temperature changes the rate**, using both the Boltzmann distribution and the frequency of effective collisions.

8.3 Homogeneous and heterogeneous catalysts

7. **Explain and use the terms catalyst and catalysis**, including:
 - that with a catalyst the reaction goes by a different mechanism, one with a lower activation energy;
 - how this speeds up the reaction, shown on a Boltzmann distribution;
 - how to draw and read a reaction pathway diagram for a reaction with and without a catalyst.

The words homogeneous (same phase as the reactants) and heterogeneous (different phase) are used for catalysts at AS. How each kind works in detail (adsorption on a surface, named examples) and rate equations, orders and half-lives are A Level topics, not this one.

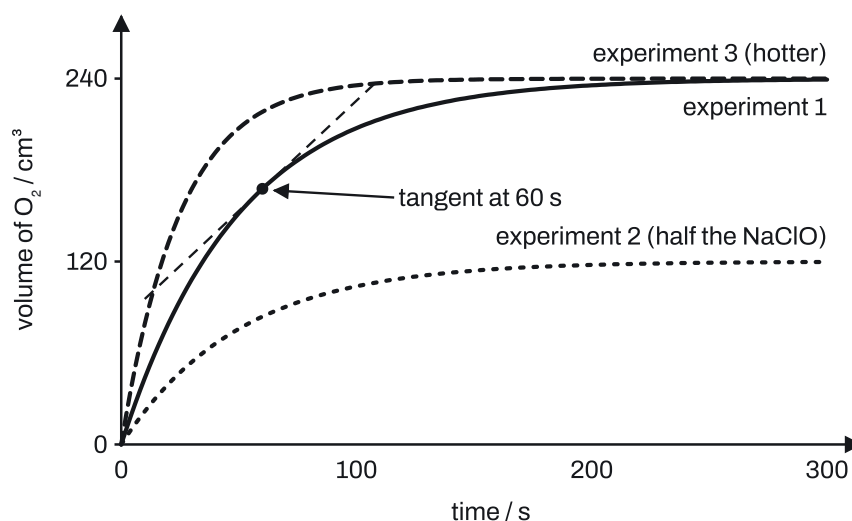
Understand it

What "rate" means

The **rate of reaction** is how fast a reactant is used up or a product is made: the change in concentration (or amount, mass or volume) **per unit time**.

$$\text{rate} = \frac{\text{change in concentration}}{\text{time taken}} \quad \text{units: mol dm}^{-3} \text{ s}^{-1}$$

If you know a gas volume, a mass or an amount instead, the rate comes out in $\text{cm}^3 \text{ s}^{-1}$, g s^{-1} or mol s^{-1} . Between two times this gives an **average rate**. On a graph of amount (or volume or concentration) against time, the **gradient** is the rate: the steeper the line, the faster the reaction. The gradient of a tangent drawn at one moment is the rate at that moment; the tangent at $t = 0$ gives the **initial rate**.



Most reactions start fast and slow down. As reactants are used up their concentrations fall, so the gradient falls. When one reactant (the **limiting** one) runs out, the line goes flat: the gradient is zero and the reaction has stopped. The reactant still left at the end was in **excess**.

Collisions

Particles can only react when they **collide**. The **frequency of collisions** is the number of collisions per unit time (per second). But most collisions do nothing: the particles just bounce apart. These are **non-effective collisions**. A collision is **effective** (successful) only if the particles hit with at least a certain minimum energy, and it is these effective collisions that make products.

So the rate depends on the **frequency of effective collisions**: how many collisions per second have enough energy to react. Anything that makes effective collisions happen more often speeds the reaction up.

Concentration and pressure

- **Higher concentration** means more particles in each dm^3 . They collide more often, so the frequency of collisions rises, and with it the frequency of effective collisions.
- **Higher pressure** of a gas does the same thing: squeezing the same gas into a smaller volume packs more molecules into each dm^3 , so they collide more often.

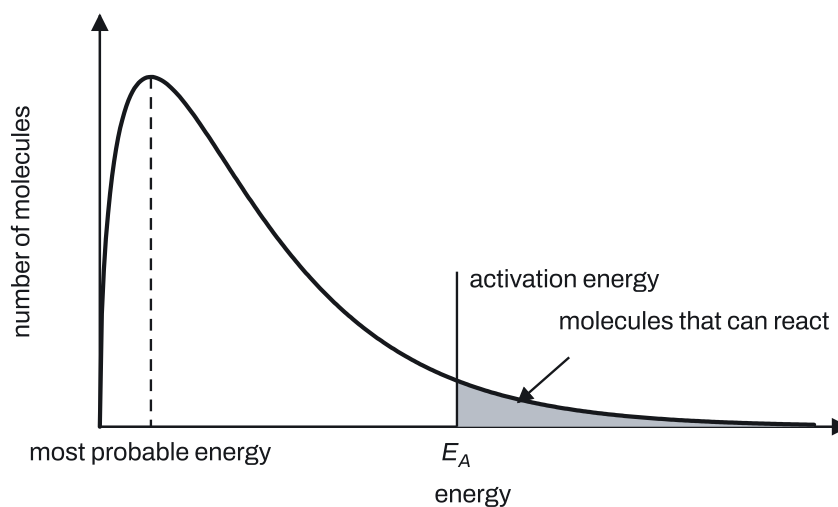
Notice what does **not** change: the particles have the same energies as before, so the **fraction** of collisions that are effective stays the same. There are simply more collisions per second, so more effective ones per second. (For a solid, a larger **surface area**, such as a powder instead of lumps, works the same way: more particles are exposed, so there are more collisions per second.)

Activation energy

The **activation energy**, E_A , is the **minimum energy needed for a collision to be effective**. Bonds have to start breaking before new ones can form, and that takes energy. A reaction with a large E_A is slow because few collisions have that much energy; weaker bonds to break usually mean a smaller E_A and a faster reaction.

The Boltzmann distribution

In a gas the molecules do not all have the same energy. At any moment a few are slow, most have middling energies and a few are very fast. A graph of the **number of molecules** with each energy against **energy** is the **Boltzmann distribution**.



Its features, which examiners check when you sketch one:

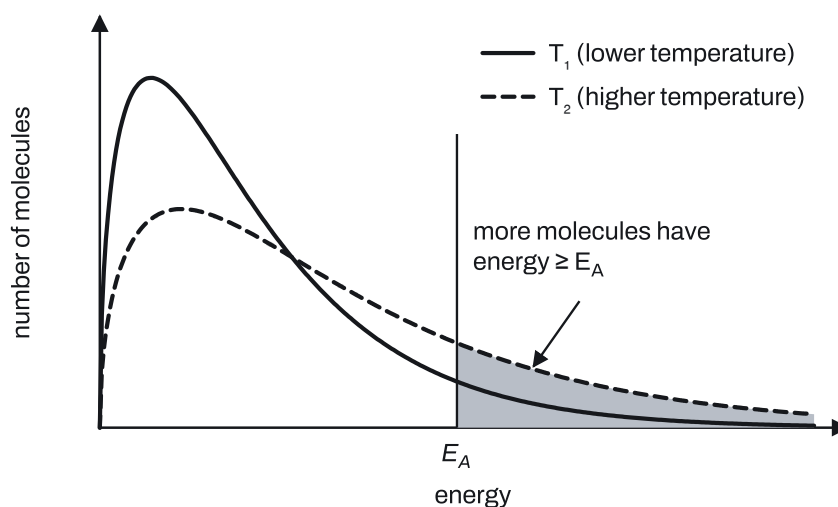
- It **starts at the origin**: no molecule has zero energy.
- It rises to a **peak**. The energy at the peak is the **most probable energy**; the height of the peak is the number of molecules that have it.
- It is **not symmetrical**: the right-hand side is a long tail.

- The tail gets **closer and closer to the energy axis but never touches or crosses it**: there is no top limit to the energy a molecule can have.
- The **area under the curve** is the total number of molecules.
- The **area under the curve to the right of E_A** is the number of molecules with energy **greater than or equal to** the activation energy: the ones that can react when they collide.

If you add more of the same gas at the same temperature, every point of the curve is scaled up by the same factor: the peak is taller but at the **same** energy. Squeezing a fixed sample into a smaller volume at the same temperature does not change the curve at all, because the molecules' energies depend only on temperature.

Temperature

Heating a gas gives its molecules more energy on average, so the curve **spreads out to the right**:



- The peak is **lower** and **further right** (the most probable energy is higher).
- The curve crosses the original **once**, to the right of the original peak.
- The **area stays the same**, because the number of molecules has not changed.
- E_A does **not** move: temperature does not change the activation energy.

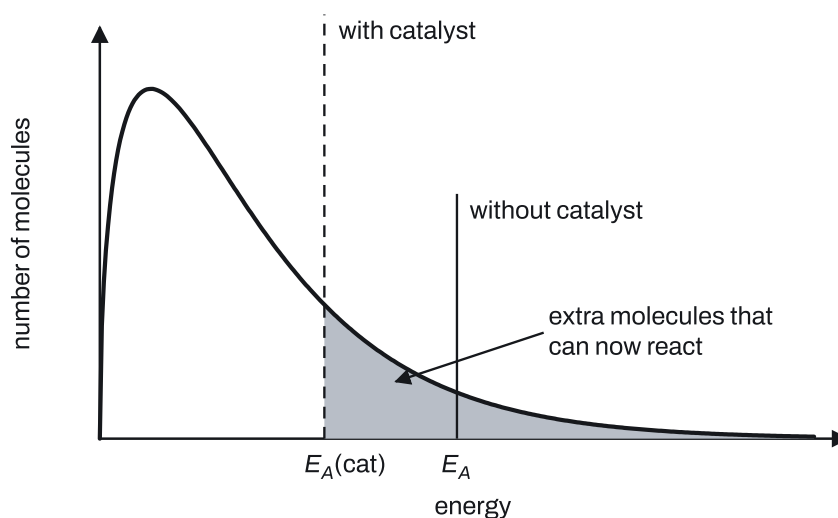
The area beyond E_A is now much bigger: a **greater proportion of molecules have energy $\geq E_A$** . So a greater fraction of collisions are effective, and the **frequency of effective collisions** increases. The molecules also move faster and collide a little more often, but that is a small effect; the extra molecules with enough energy is the main reason. That is why a small rise in temperature makes such a large difference: for many reactions, about 10°C roughly doubles the rate. Cooling does everything in reverse (taller peak further left, smaller area beyond E_A , slower rate).

Temperature is the only one of these changes that alters the average energy of the particles. Concentration, pressure, surface area and catalysts do not.

Catalysts

A **catalyst** speeds up a reaction without being used up: it is chemically unchanged at the end. **Catalysis** is the speeding up of a reaction by a catalyst. A catalyst gives the reaction a **different mechanism** (a different route) with a **lower activation energy**. Often the catalyst takes part in one step and is made again in a later step, so the same catalyst particles are used over and over and only a small amount is needed.

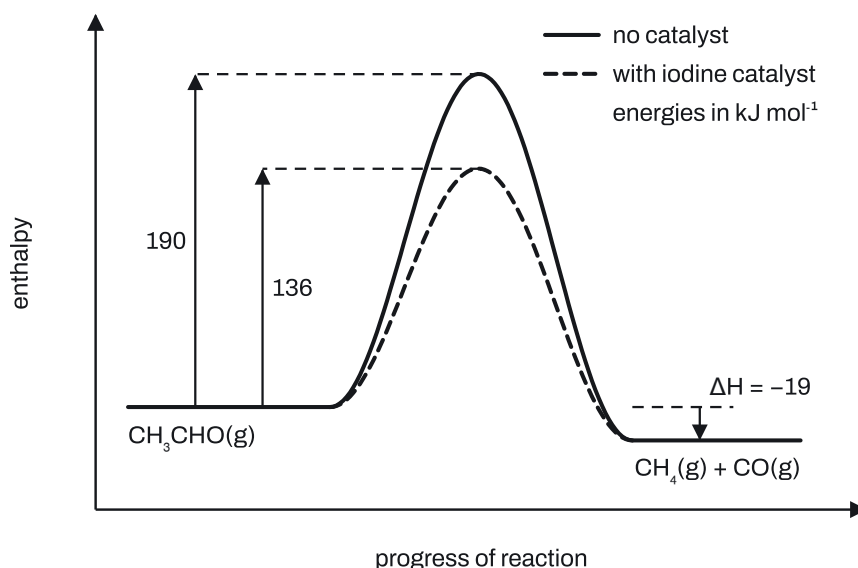
On the Boltzmann distribution the **curve does not change**: the catalyst does not give molecules any extra energy. Only the E_A line moves **left**. The area to the right of the new E_A is larger, so a greater proportion of molecules have enough energy to react, and the frequency of effective collisions increases.



Reaction pathway diagrams

A reaction pathway diagram (energy profile) plots enthalpy against the progress of the reaction. The reactants and products are flat lines; between them the route rises to a peak. The **activation energy** is the height from the **reactants** up to the peak, and ΔH is the drop (or rise) from reactants to products.

With a catalyst, the reactants and products are at the **same** levels, so ΔH **does not change**, but the peak is **lower**. The diagram below uses the decomposition of ethanal gas, $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$, $\Delta H = -19 \text{ kJ mol}^{-1}$, which is catalysed by iodine vapour.



The reverse reaction. Read the same diagram from right to left. The reverse reaction starts at the products, so its activation energy is measured from the products' level up to the same peak:

$$E_A(\text{reverse}) = E_A(\text{forward}) - \Delta H(\text{forward})$$

Here $E_A(\text{reverse}) = 190 - (-19) = 209 \text{ kJ mol}^{-1}$. For an exothermic forward reaction the reverse always has the larger activation energy. A catalyst lowers the peak, so it lowers **both** activation energies **by the same amount** and speeds up the forward and reverse reactions equally. That is why a catalyst makes a reversible reaction reach equilibrium **sooner** but does **not** change the position of equilibrium, the yield or K_c .

At equilibrium the forward and reverse reactions go at the same rate, so the **frequencies of effective collisions** in the two directions are equal. The total collision frequencies usually are not, because the two directions have different activation energies.

Homogeneous and heterogeneous catalysts

- A **homogeneous** catalyst is in the **same phase** as the reactants: for example iodine vapour in the gas-phase decomposition of ethanal above, or concentrated sulfuric acid mixed into liquid reactants.
- A **heterogeneous** catalyst is in a **different phase**, usually a solid catalysing gases or liquids: for example solid nickel in the reaction of an alkene with hydrogen gas, or solid iron in the Haber process.

Iodine shows how a homogeneous catalyst takes part and is reformed. It reacts in the first step and is made again in the second:



Add the two steps and cancel what appears on both sides: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$, with the iodine unchanged overall.

Biological catalysts (enzymes) work in the same way and are usually very specific: each speeds up only one reaction or one kind of reaction.

Following a reaction's rate

To measure a rate you follow something that changes with time: the volume of gas given off (a gas syringe), the loss in mass as a gas escapes, a change in colour, or the concentration of a reactant or product (for example by titrating samples). Pick a property that really tracks the reaction: a gas that dissolves in or reacts with water, such as sulfur dioxide, gives a volume that is too low, so collecting it over water does not follow the rate accurately.

Key facts and formulas

"Given" means it is in the 9701 Data Booklet. "Learn it" means you must remember it.

Formula	Status
Rate = $\frac{\text{change in concentration (or amount)}}{\text{time}}$, units $\text{mol dm}^{-3} \text{ s}^{-1}$ (or mol s^{-1} , $\text{cm}^3 \text{ s}^{-1}$)	Learn it
Rate at a moment = gradient of the tangent to the amount–time graph	Learn it
Activation energy E_A : the minimum energy for a collision to be effective	Learn it
$E_A(\text{reverse}) = E_A(\text{forward}) - \Delta H(\text{forward})$	Learn it
Moles of gas = $\frac{\text{volume in dm}^3}{24.0}$ at room conditions	Given
Concentration = $\frac{\text{moles}}{\text{volume in dm}^3}$	Learn it
Higher concentration or pressure: more collisions per unit time, same proportion effective	Learn it
Higher temperature: greater proportion of molecules with energy $\geq E_A$; E_A unchanged	Learn it
Catalyst: different mechanism, lower E_A ; curve, ΔH , K_c and yield unchanged	Learn it

The molar volume is printed as $24.0 \text{ dm}^3 \text{ mol}^{-1}$ (that is, $24\,000 \text{ cm}^3 \text{ mol}^{-1}$) at room conditions.

How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (81 questions, 2021–2025), the types came up this often. 20 of the 81 questions mix more than one type, so the counts add up to 108.

Question type	Questions
Boltzmann distribution: effect of temperature (or amount of gas)	21
Effect of a catalyst	21
Collision theory: concentration, pressure, surface area, bond strength	11
Interpret or sketch rate curves	11
Calculate an average rate	9

Question type	Questions
Explain why raising the temperature increases the rate	9
Reaction pathway diagrams	8
Draw, label or read a Boltzmann distribution	7
Homogeneous and heterogeneous catalysts; catalyst reformed	5
Choose a way to measure a rate	3
Define activation energy or rate of reaction	2
Initial-rates data	1

1. Boltzmann distribution: effect of temperature (or amount of gas) (21 questions)

1. **Sketch the original curve lightly in your head**, then decide which way it moves: hotter means lower peak, further right; cooler means higher peak, further left.
2. **When you draw the new curve**, make sure it: starts at the origin; has its peak **lower and to the right** (hotter); crosses the original curve **once**, to the right of the original peak; and has a tail **above** the original that stays above the axis without touching it.
3. **Keep E_A where it was**. Then compare the areas beyond it.
4. **Link it to rate** if asked: bigger area beyond $E_A \rightarrow$ greater proportion of molecules can react $\rightarrow$ higher frequency of effective collisions $\rightarrow$ faster.

Variations you will meet:

- **Peak height.** Cooling raises the peak and heating lowers it (same amount of gas). Compressing or expanding a fixed sample at constant temperature leaves the whole curve unchanged.
- **Energies well above the peak**, including E_A itself: heating puts more molecules there, so the curve is higher at those energies; cooling puts fewer there.
- **Low energies**, below the original peak: heating leaves fewer molecules there; cooling leaves more.
- **More gas at the same temperature:** the curve is taller everywhere, with the peak at the same energy.
- **Temperature and E_A together:** the rate is greatest when the temperature is high and the activation energy is low, because that gives the largest area beyond E_A .
- **Linking to a rate graph:** a hotter reaction gives a steeper volume–time curve that levels off at the same final volume, sooner.

2. Effect of a catalyst (21 questions)

1. **Say what it does:** it increases the rate by providing a **different route (mechanism) with a lower activation energy**, and it is not used up.
2. **On a Boltzmann diagram:** draw the new E_A **to the left** of the original on the energy axis and label it. **Do not** draw a new curve.

3. **Explain with areas:** the area beyond the new E_A is larger $\rightarrow$ a greater proportion of molecules have energy $\geq E_A \rightarrow$ a higher **frequency** of effective collisions $\rightarrow$ faster rate.

Variations you will meet:

- **Judging statements about catalysts.** Test each against the principles: a catalyst changes only the route (and so E_A), for the forward and reverse reactions alike, and is regenerated. It adds no energy to the particles, so nothing about the Boltzmann curve itself changes, and it cannot move an equilibrium. Its whole effect is that a larger fraction of collisions succeed, so more particles react each second.
- **Equilibrium questions.** A catalyst does not change K_c , the yield or the position of equilibrium; equilibrium is just reached sooner.
- **Name a catalyst** for a familiar reaction, such as nickel (or platinum) for adding hydrogen to an alkene, iron in the Haber process.
- **Catalyst plus temperature** on one diagram: pick the curve with the lower peak (hotter) and the E_A line further left (catalysed).
- **Enzymes** are catalysts that are usually specific to one reaction.

3. Collision theory: concentration, pressure, surface area, bond strength (11 questions)

1. **Say what changes:** particles per unit volume (concentration, pressure) or exposed surface (surface area).
2. **Link it to collisions:** more collisions **per unit time**, so a higher **frequency of effective collisions**.
3. **Say what does not change:** the energy of the particles and the proportion of collisions that are effective (only temperature and catalysts change that).

Variations you will meet:

- **Rate falls during a reaction** because reactants are used up: lower concentration $\rightarrow$ lower frequency of effective collisions.
- **Rank experiments** by rate or time: powder is faster than lumps; more concentrated is faster; hotter is faster. When two changes pull in opposite directions (say, cooler but more concentrated), compare each with a reference experiment one change at a time.
- **Rate versus amount of product.** A faster rate does not mean more product: the final amount depends only on the limiting reactant. Adding more of a reactant that is already in excess can make the reaction faster without giving more product.
- **Similar reactions at different rates.** The one with the weaker bond to break has a lower E_A and is faster.

4. Interpret or sketch rate curves (11 questions)

1. **Gradient = rate.** Steeper means faster; flat (gradient zero) means the reaction has stopped.
2. **Describe the gradient over time:** it is steepest at the start and decreases, so the rate decreases, until it reaches zero when a reactant runs out.

3. **Find the limiting reactant** from a concentration–time graph: the reactant whose concentration **does not fall to zero** was in excess, so the **other** one was limiting (the reaction stopped before this one was used up).
4. **Sketching a second curve** on the same axes, decide two things separately:
 - **Final height:** set by the amount of the limiting reactant. Same amount → same final volume. Less (for example half the amount) → lower final volume.
 - **Initial steepness:** set by the rate. Hotter, more concentrated, powdered or catalysed → steeper; cooler, diluted or lumps → less steep.

Variations you will meet:

- **Matching a new curve to a change.** Check the final volume first (it tells you whether the amount of limiting reactant changed), then the initial slope. Changes to concentration and to amount are separate: a solution can be less concentrated yet contain more moles in total, giving a gentler start but a higher final volume, or the other way round.
- **An exothermic reaction** can speed up at first as it warms itself, then slow down as the reactants run out.
- **A straight line** means a constant rate (for example a reaction limited by a catalyst's surface).

5. Calculate an average rate (9 questions)

1. **Change in the measured quantity** between the two times (read from the table or graph).
2. **Convert it to what the question wants.** Gas volume at room conditions → moles: $\div 24\,000$ for cm^3 ($\div 24.0$ for dm^3). Then use the equation's ratio to get moles of the substance asked about. Per dm^3 of solution → divide by the volume in dm^3 .
3. **Divide by the time** in the units asked for (seconds or minutes).
4. **Give units**, for example $\text{mol dm}^{-3} \text{s}^{-1}$ or $\text{cm}^3 \text{s}^{-1}$.

Variations you will meet:

- **Rate of a reactant from a gas product.** If 2 mol of reactant give 1 mol of gas, the reactant is used up twice as fast in moles as the gas is made.
- **Two average rates** from a table (first interval and last interval) and their difference.
- **From a graph**, read two points on the line: $\text{rate} = \frac{\Delta(\text{concentration})}{\Delta t}$. A concentration that falls gives a negative change; quote the rate of reaction as a positive number.
- **Measured by another property** (such as colour intensity): convert it to concentration first using the calibration graph given.

6. Explain why raising the temperature increases the rate (9 questions)

1. **Energy:** a greater **proportion** of molecules have energy **greater than or equal to** E_A (say it with the Boltzmann curve if one is given).
2. **Collisions:** so there is a higher **frequency of effective (successful) collisions**.

Variations you will meet:

- **"Why does a 10 °C rise roughly double the rate?"** Mostly because many more molecules now have energy $\geq E_A$; the increase in collision frequency is much smaller.
- **Effect on E_A :** none. Answer the question asked; don't explain the rate change instead.
- **Reversible reactions:** raising the temperature increases the rates of **both** the forward and the reverse reactions.
- **Average kinetic energy** of the particles changes only with temperature, not with concentration, pressure or a catalyst.

7. Reaction pathway diagrams (8 questions)

1. **Draw** the axes (enthalpy up, progress of reaction across), the reactants' level, the products' level (lower for exothermic, higher for endothermic) and a single hump between them.
2. **Label E_A** with an arrow from the **reactants' level up to the peak**, and ΔH with an arrow **from reactants to products** (pointing down for exothermic, up for endothermic).
3. **Catalysed route:** a lower hump between the **same** start and end levels, labelled.
4. **Reverse reaction:** $E_A(\text{reverse}) = E_A(\text{forward}) - \Delta H$.

Variations you will meet:

- **Pick the letter** that shows a given quantity, such as the E_A of the catalysed reverse reaction (from the products up to the lower peak). Read carefully which direction the question describes.
- **Ratio questions:** " E_A is twice as big as ΔH " means the peak is twice as far above the reactants as the products are from the reactants.
- **Equilibrium:** at equilibrium the frequencies of **effective** collisions in each direction are equal; the total collision frequencies are not.

8. Draw, label or read a Boltzmann distribution (7 questions)

1. **Label the axes:** "number of molecules" (or "proportion of molecules") up, "energy" across.
2. **Draw the curve** from the origin, rising to a peak, then a long tail that approaches but never touches the energy axis.
3. **Mark E_A** to the right of the peak and **shade** the area beyond it: the molecules that can react.

Know what each feature means: the peak height is the number of molecules with the most probable energy; the total area is the number of molecules; a point on the vertical axis is a number of molecules, not an energy.

9. Homogeneous and heterogeneous catalysts; catalyst reformed (5 questions)

1. **Homogeneous or heterogeneous:** compare the catalyst's phase with the reactants' (sulfuric acid mixed into liquid reactants is homogeneous; a solid metal with gases is heterogeneous).

2. **Show a catalyst is reformed** from a given mechanism: point to the step where it is used up and the later step where it is made again, so it is unchanged overall. "It doesn't change" is too vague: say it is **regenerated**.
3. **Write the missing step** if asked: the step that turns the intermediate back into the catalyst and gives the overall equation when the steps are added.

In a mechanism, a catalyst appears as a **reactant in an early step** and a **product in a later one**. An intermediate is the reverse: made first, used up later. If you are asked whether a catalyst ion is oxidised or reduced in a step, compare its oxidation numbers on the two sides.

10. Choose a way to measure a rate (3 questions)

Rate can be followed by the **decrease in concentration of a reactant** per unit time, the **increase in concentration of a product** per unit time, or the **volume of gas** given off per unit time (at constant pressure and temperature). Reject a method that doesn't track the reaction, such as collecting a gas that dissolves in or reacts with water over water.

11. Define activation energy or rate of reaction (2 questions)

- **Activation energy**: the **minimum** energy needed for a collision to be **effective** (to lead to a reaction).
- **Rate of reaction**: the change in concentration of a reactant or product **per unit time**.

12. Initial-rates data (1 question)

Compare two experiments in which only one concentration changes. If doubling it leaves the initial rate the same, the rate does not depend on that reactant; if the rate doubles or quadruples, it does. (Working out orders from such data is A Level.)

Worked examples

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

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

Example 1

A student adds an excess of solid sodium hydrogencarbonate to 40.0 cm³ of aqueous ethanoic acid and collects the carbon dioxide in a gas syringe at room conditions.



time / s	0	20	40	60	80	100
volume of CO_2 / cm^3	0	96	168	216	240	240

(a) Calculate the average rate of production of CO_2 , in $\text{cm}^3 \text{s}^{-1}$, between 0 and 20 s and between 60 and 80 s. [2]

(b) Explain, in terms of collisions, why the rate decreases. [2]

(c) Calculate the average rate at which the concentration of ethanoic acid falls during the first 60 s. Give units. [3]

(d) Calculate the initial concentration of the ethanoic acid. [2]

(a) 0–20 s: $\frac{96}{20} = 4.8 \text{ cm}^3 \text{s}^{-1}$. 60–80 s: $\frac{240 - 216}{20} = 1.2 \text{ cm}^3 \text{s}^{-1}$. **B1 B1**

(b) The ethanoic acid is used up, so its concentration falls. **M1** There are fewer collisions per unit time, so a lower frequency of effective collisions. **A1**

(c) Moles of CO_2 in 60 s = $\frac{216}{24\,000} = 0.00900 \text{ mol}$. **M1** The equation is 1 : 1, so 0.00900 mol of ethanoic acid is used, in 0.0400 dm^3 :

$$\Delta c = \frac{0.00900}{0.0400} = 0.225 \text{ mol dm}^{-3} \quad \text{rate} = \frac{0.225}{60} = 3.75 \times 10^{-3}$$

M1 for dividing by the volume and the time, **A1** for $3.75 \times 10^{-3} \text{ mol dm}^{-3} \text{s}^{-1}$ with units.

(d) The reaction stops at 240 cm^3 with NaHCO_3 in excess, so the acid was the limiting reactant: $\frac{240}{24\,000} = 0.0100 \text{ mol}$ of acid. **M1** Concentration = $\frac{0.0100}{0.0400} = 0.250 \text{ mol dm}^{-3}$. **A1**

Example 2

Hydrogen iodide gas decomposes slowly when heated: $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$.

(a) Define activation energy. [1]

(b) Sketch the Boltzmann distribution for a sample of $\text{HI}(\text{g})$ at temperature T . Label the axes, and mark the activation energy E_A . [3]

(c) On the same axes, sketch the distribution for the same sample at a higher temperature. Use your sketch to explain why the rate increases. [4]

(d) Hot platinum wire speeds up the decomposition. State whether platinum is a homogeneous or heterogeneous catalyst here, and explain, with reference to your sketch, how it increases the rate. [3]

(a) The minimum energy needed for a collision to be effective. **B1**

(b) As in the first diagram in "Understand it": axes "number of molecules" and "energy" **B1**; a curve starting at the origin, with one peak and a tail that approaches but does not touch the energy axis **B1**; E_A marked to the right of the peak **B1**.

(c) As in the second diagram: a new curve from the origin with a **lower peak to the right** of the original **B1**, crossing the original once and staying above it at high energy **B1**. The area beyond E_A is larger, so a greater proportion of molecules have energy $\geq E_A$ **M1**, so there is a higher frequency of effective collisions **A1**.

(d) Heterogeneous: the platinum is solid and the reactant is a gas. **B1** It provides a different route with a lower activation energy; mark the new E_A to the left of the original on the energy axis, with the curve unchanged. **B1** The area beyond the new E_A is larger, so a greater proportion of molecules can react and effective collisions happen more often. **B1**

Example 3

Ethanal decomposes in the gas phase: $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$, $\Delta H = -19 \text{ kJ mol}^{-1}$. Without a catalyst $E_A = +190 \text{ kJ mol}^{-1}$; with iodine vapour $E_A = +136 \text{ kJ mol}^{-1}$.

(a) Draw a labelled reaction pathway diagram for the reaction with and without iodine. **[3]**

(b) Calculate the activation energy of the reverse reaction, with and without iodine. **[2]**

(c) Iodine reacts in step 1: $\text{CH}_3\text{CHO} + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{HI} + \text{CO}$. Write an equation for step 2, and explain why iodine is a catalyst and not a reactant. **[2]**

(d) State, with a reason, whether iodine is a homogeneous or heterogeneous catalyst here. **[1]**

(a) As in the fourth diagram in "Understand it": products below reactants, with ΔH labelled as a downward arrow from reactants to products **B1**; a hump with E_A labelled from the reactants up to its peak **B1**; a lower hump for the iodine route between the same two levels, labelled **B1**.

(b) $E_A(\text{reverse}) = E_A(\text{forward}) - \Delta H$. **M1**

Without iodine: $190 - (-19) = +209 \text{ kJ mol}^{-1}$. With iodine: $136 - (-19) = +155 \text{ kJ mol}^{-1}$. **A1** Both are 54 kJ mol^{-1} lower with the catalyst, so the reverse reaction is sped up too.

(c) $\text{CH}_3\text{I} + \text{HI} \rightarrow \text{CH}_4 + \text{I}_2$ **B1**. Iodine is used in step 1 and regenerated in step 2, so it is unchanged overall and does not appear in the overall equation. **B1**

(d) Homogeneous: iodine vapour is in the same (gas) phase as the ethanal. **B1**

Example 4

Aqueous sodium chlorate(I), NaClO , decomposes slowly in the presence of a solid catalyst:



In experiment 1, 50.0 cm^3 of $0.400 \text{ mol dm}^{-3}$ $\text{NaClO}(\text{aq})$ reacts completely at 30°C . After 60 s, 168 cm^3 of oxygen has been collected at room conditions.

(a) Calculate the final volume of oxygen at room conditions. **[2]**

(b) Calculate the average rate of production of oxygen over the first 60 s, in mol s^{-1} . **[2]**

(c) Experiment 2 uses 25.0 cm^3 of the same $\text{NaClO}(\text{aq})$ and 25.0 cm^3 of water. Experiment 3 is the same as experiment 1 but at 40°C . Everything else is unchanged. For each, state the final volume of oxygen and how the initial rate compares with experiment 1, and explain the rate in terms of collisions. **[5]**

(d) The gradient of the volume–time graph for experiment 1 decreases with time. State and explain what this shows. **[2]**

(a) $n(\text{NaClO}) = 0.400 \times 0.0500 = 0.0200 \text{ mol}$, so $n(\text{O}_2) = 0.0100 \text{ mol}$ (the ratio is 2 : 1). **M1** Volume = $0.0100 \times 24\,000 = 240 \text{ cm}^3$. **A1**

(b) $\frac{168}{24\,000} = 0.00700 \text{ mol s}^{-1}$ **M1**; rate = $\frac{0.00700}{60} = 1.17 \times 10^{-4} \text{ mol s}^{-1}$ **A1**.

(c) Experiment 2: 0.0100 mol of NaClO , so the final volume is 120 cm^3 . **B1** The same amount of water halves the concentration, so the initial rate is lower: fewer NaClO particles per unit volume, fewer collisions per unit time, a lower frequency of effective collisions. **B1**

Experiment 3: the amount is unchanged, so the final volume is still 240 cm^3 . **B1** The initial rate is higher. **B1** At 40°C a greater proportion of particles have energy $\geq E_A$, so there is a higher frequency of effective collisions. **B1**

The fifth diagram in "Understand it" shows all three curves.

(d) The gradient is the rate, so the rate decreases **B1**, because NaClO is used up and its concentration falls, giving a lower frequency of effective collisions; the gradient reaches zero when all the NaClO has reacted **B1**.

Common mistakes

- **"More collisions" without "per unit time".** The mark is for the **frequency** of effective (successful) collisions. "More successful collisions" on its own is not enough; examiners report this every year.
- **Saying temperature or pressure changes the activation energy.** Neither does. Only a catalyst gives a route with a different E_A , and even then the original reaction's E_A is not "lowered": a new route is provided.
- **Saying a catalyst increases the number of collisions** or gives particles more energy. It does neither: it lowers E_A , so a greater proportion of collisions are effective.
- **Drawing a new curve for a catalyst.** On a Boltzmann diagram a catalyst only moves E_A to the left. The curve stays exactly as it was.
- **Poor sketches of a hotter Boltzmann curve:** the peak higher than the original, the curve not starting at the origin, or the tail merging with the original or touching the energy axis. The hotter peak is lower and further right, and its tail stays above the original.
- **Answering a different question.** Asked for the effect of temperature on E_A (none), many explain why the rate goes up instead.

- **Mixing up rate and amount.** A faster reaction does not give more product; the final amount depends on the limiting reactant.
- **Arrows on pathway diagrams** starting at the wrong level or pointing the wrong way. E_A goes up from the reactants to the peak; ΔH goes from reactants to products.
- **Forgetting to convert.** cm^3 to dm^3 (divide by 1000), minutes to seconds, and the mole ratio from the equation before dividing by time.
- **Being vague about a catalyst being reformed.** "The catalyst doesn't change" is not enough; say it is used in one step and **regenerated** in a later step.

How to get the marks

- **Explaining a rate change** is usually two marks: one for the cause (more particles per unit volume, or a greater proportion with energy $\geq E_A$) and one for "a higher **frequency** of effective (successful) collisions".
- **Temperature and catalysts** need the Boltzmann idea: "a greater proportion of molecules have energy greater than or equal to the activation energy". Say "proportion" (or "more molecules"), and "greater than or equal to E_A ".
- **Catalyst definition:** "increases the rate by providing an alternative route (mechanism) with a lower activation energy". Both parts earn the mark.
- **Sketches** are marked on specific features: starts at the origin, peak lower and to the right (hotter), crosses the original once to the right of its peak, tail above the original and not touching the axis. Draw in pencil, clearly, and label each curve and each E_A .
- **Annotating a catalyst** on a given Boltzmann diagram: mark and label the new E_A on the energy axis, to the left of the original.
- **Calculations** need units ($\text{mol dm}^{-3} \text{s}^{-1}$, $\text{cm}^3 \text{s}^{-1}$), usually for a separate mark. Keep 3 significant figures unless the data show otherwise, and use the time unit the question asks for.
- **"State"** needs only the answer; **"explain"** needs the reason too; **"define"** needs the precise wording (minimum energy, effective collision).
- **Limiting reactant from a graph:** name it and give the reason from the graph ("the other reactant's concentration does not reach zero").

Quick check

1. Define rate of reaction, and explain the difference between an effective and a non-effective collision.
2. Acidified potassium manganate(VII) reacts with ethanedioic acid: $2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$. The concentration of MnO_4^- falls from 0.0200 to $0.0080 \text{ mol dm}^{-3}$ in 150 s . Calculate the average rate of the fall in $[\text{MnO}_4^-]$, and the average rate at which $[\text{H}_2\text{C}_2\text{O}_4]$ falls over the same time.
3. The pressure of a gas mixture is doubled at constant temperature. Explain the effect on the rate and state what happens to the proportion of molecules with energy $\geq E_A$.

4. A reversible reaction has $\Delta H = +40 \text{ kJ mol}^{-1}$ for the forward reaction and $E_A(\text{forward}) = +85 \text{ kJ mol}^{-1}$. A catalyst lowers $E_A(\text{forward})$ to $+60 \text{ kJ mol}^{-1}$. Find $E_A(\text{reverse})$ with and without the catalyst, and state the effect of the catalyst on the equilibrium yield.
5. A sealed sample of gas is cooled. State what happens to (a) the height and position of the peak of its Boltzmann distribution, (b) the number of molecules with energy $\geq E_A$, (c) E_A .

Answers

1. Rate of reaction is the change in concentration of a reactant or product per unit time. An effective collision has at least the activation energy and leads to reaction; a non-effective collision has less than E_A and the particles bounce apart unchanged.
2. $\frac{0.0200 - 0.0080}{150} = \frac{0.0120}{150} = 8.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. The ratio is 5 : 2, so ethanedioic acid falls $\frac{5}{2}$ times as fast: $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.
3. Doubling the pressure doubles the number of molecules per unit volume, so they collide more often and the frequency of effective collisions increases: the rate increases. The proportion with energy $\geq E_A$ is unchanged, because the temperature is unchanged.
4. Without catalyst: $85 - 40 = +45 \text{ kJ mol}^{-1}$. With catalyst: $60 - 40 = +20 \text{ kJ mol}^{-1}$. Both activation energies fall by 25 kJ mol^{-1} , so both directions speed up equally: the equilibrium yield is unchanged (it is just reached sooner).
5. (a) The peak is higher and moves to the left (lower most probable energy); the area is unchanged. (b) It decreases (smaller area beyond E_A). (c) It does not change.

Past questions to try

- **9701/21/M/J/25 Q3**: part (a) sketches a hotter Boltzmann curve, explains the faster rate and marks a catalyst's E_A .
- **9701/23/M/J/25 Q4**: part (a) average rates from a concentration–time graph, the limiting reactant and why the rate falls.
- **9701/12/M/J/25 Q9**: an average rate in $\text{mol dm}^{-3} \text{ s}^{-1}$ from a volume of gas.
- **9701/13/O/N/23 Q15**: activation energies of the forward and reverse reactions.