Reaction kinetics

Rate of reaction and collision theory, the Boltzmann distribution and activation energy, the effect of temperature, and how homogeneous and heterogeneous catalysts lower the activation energy.

8.1 Rate of reaction

The **rate of reaction** is the change in the concentration of a reactant or product per unit time. Its unit is mol dm^{-3} s^{-1}.

Collision theory

A reaction needs particles to **collide**. The **frequency of collisions** is how many occur per second. An **effective collision** is one with at least the activation energy and the correct orientation, so that it leads to reaction; **non-effective** collisions do not.

- **Concentration (or pressure for gases):** more particles per unit volume, so more frequent collisions and a higher frequency of **effective** collisions. The rate increases.
- The fraction of molecules with enough energy does not change when only concentration changes.

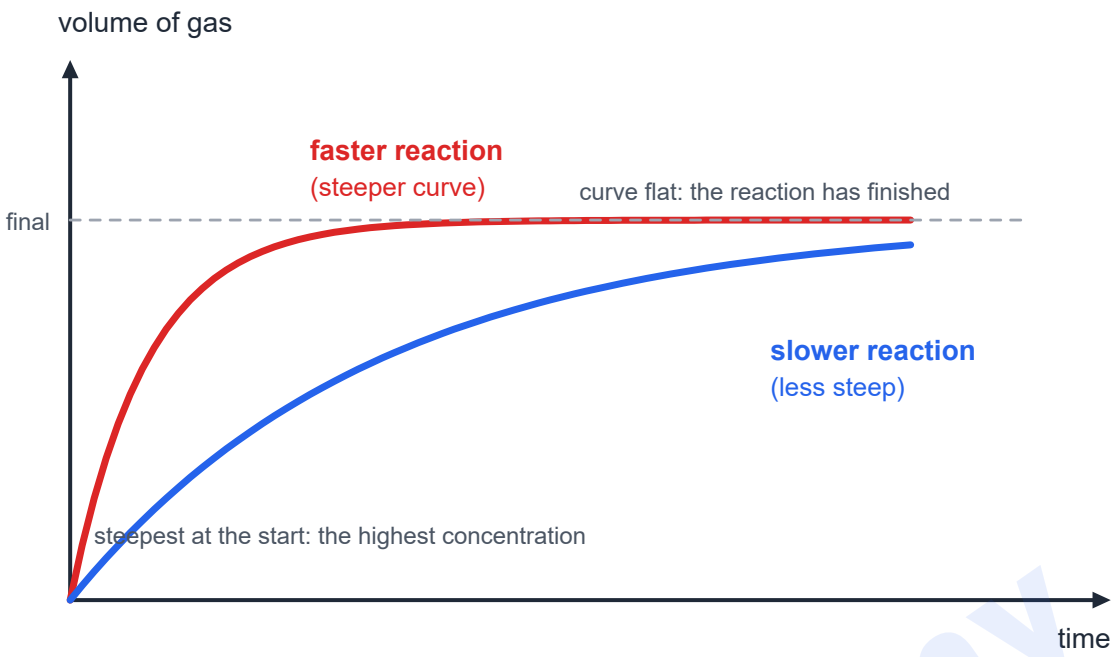
Calculating a rate

Plot concentration against time and take the **gradient of the tangent** at the time of interest. The **initial rate** is the gradient at $t = 0$. For gas evolution, use volume against time.

Measuring rate in a practical investigation

Choose a measurable quantity linked to reaction progress. Gas volume works if a gas is produced and can be collected; mass loss works if a gas escapes from an otherwise stable apparatus. Colorimetry can follow a coloured reactant or product. A disappearing-cross experiment records the time to reach a fixed visual endpoint as sulfur forms. For identical endpoints, $1/t$ can compare initial rates approximately; it is not automatically a concentration rate in mol dm^{-3} s^{-1}.

Note Academy



the same amount of the limiting reactant gives the same final volume; the faster reaction just gets there sooner

Control temperature, reactant amounts, solution volume and mixing when investigating concentration. For solid reactants, particle size affects exposed surface area, so keep it comparable unless surface area is the independent variable. Collect gas promptly and check for leaks. Consistent delay before starting a stopwatch matters particularly for fast reactions.

Average rate versus instantaneous rate

An average rate uses a change over a finite interval. An instantaneous rate is the tangent gradient at a stated time; the initial rate uses the tangent at zero. For a consumed reactant, the concentration gradient is negative, so its disappearance rate is normally reported as a positive magnitude. State which reactant or product is being followed: their numerical rates can differ according to stoichiometry.

Worked example: a reactant falls from 0.0800 to 0.0500 mol dm^{-3} in 60.0 s. Its average disappearance rate is $(0.0800 - 0.0500)/60.0 = 5.00 \times 10^{-4}$ mol dm^{-3} s^{-1}. If a tangent at 20 s passes through (0 s, 0.0800) and (40 s, 0.0520), its instantaneous disappearance rate is $0.0280/40 = 7.00 \times 10^{-4}$ mol dm^{-3} s^{-1}. Use well-separated points on the **tangent**, not arbitrary points on the curve.

> **TRY IT**
>
> A gas-volume tangent increases by 18.0 cm^3 over a 30.0 s horizontal interval. Give the rate and explain its units.

Answer: The rate is 0.600 cm^3 s^{-1} because the measured quantity is gas volume. To express it as a molar rate, first convert volume into moles using the gas conditions.

Note Academy

Why surface area and concentration matter

For a solid reacting at its surface, breaking the same mass into smaller pieces exposes more reactant particles to the solution or gas. More collisions can occur at accessible sites per second, increasing rate without changing the total amount of solid. More concentrated solution increases collision frequency per unit volume; it does not necessarily increase the energy of each particle at unchanged temperature.

Worked comparison: equal masses of calcium carbonate powder and large chips react with equal excess acid at the same temperature. The powder gives a steeper gas-volume curve but the same final gas volume if both react completely. The rate differs because of surface area; final yield is fixed by the equal limiting amounts of carbonate.

8.2 Effect of temperature on reaction rates and the concept of activation energy

The **activation energy**, E_a, is the minimum energy required for a collision to be effective.

The Boltzmann distribution

The Boltzmann distribution shows the number of molecules with a given energy. The curve starts at the origin, has a peak, and never touches the axis at high energy. The area under the curve is the total number of molecules. The area to the right of E_a is the number of molecules with enough energy to react.

When the **temperature rises**:

- the peak is lower and moves to the right, and the curve is flatter;
- many more molecules have energy of at least E_a (the area beyond E_a is larger);
- molecules also collide **more frequently**, but the main cause of the large increase in rate is the greater proportion of **effective** collisions.

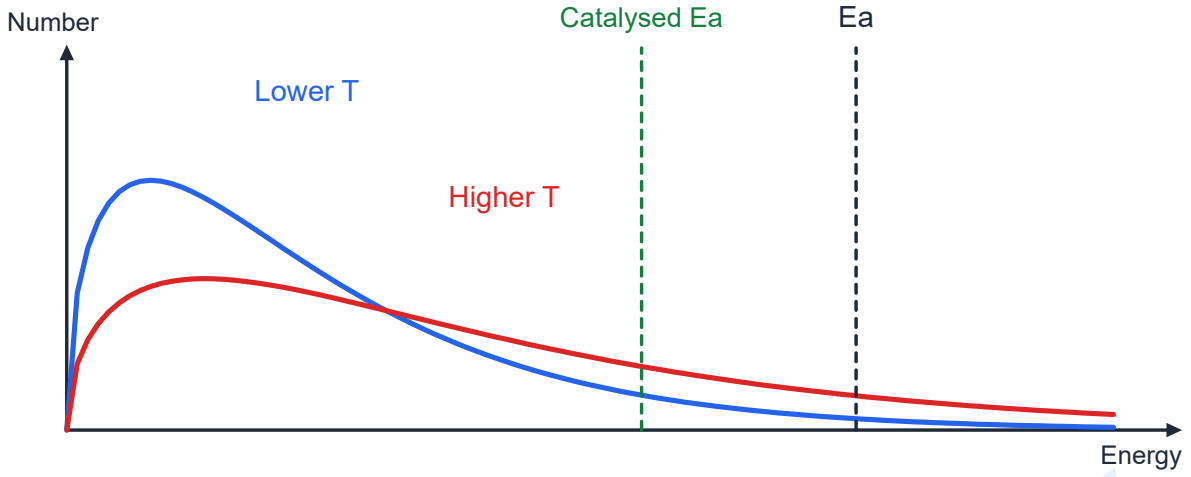
A rise of about 10 °C roughly doubles the rate for many reactions.

> **When explaining the effect of temperature: say that the proportion of molecules with energy ≥ E_a increases, so the frequency of effective collisions increases. Do not say that "collisions have more energy" alone.**

Note Academy

Drawing and interpreting the distribution

Temperature changes the distribution; a catalyst changes the barrier



Same total area for the same number of molecules. Curves are illustrative.

Label the horizontal axis energy and the vertical axis number or fraction of molecules with that energy. The area, rather than the peak height, represents the total population. At a higher temperature, the peak shifts towards higher energy and falls, while the high-energy tail becomes more substantial. For the same amount of gas, total area remains unchanged.

Draw E_a as a fixed vertical line when comparing temperature effects for the same uncatalysed reaction. Raising temperature changes the distribution, not the barrier itself. Only a proportion of molecules have enough energy at any instant, and effective collisions also require suitable orientation. This explains why increasing average kinetic energy modestly can increase rate much more strongly: the tail beyond the threshold changes substantially.

The statement that a 10 °C rise doubles rate is an approximate observation for some reactions, not a universal law. If numerical data are provided, use them rather than assuming a fixed multiplier. At A Level, rate constants provide a more quantitative description.

> **TRY IT**
>
> On a Boltzmann diagram, what must remain unchanged when temperature rises for a fixed sample, and what area increases?

Answer: The total area remains the same because the number of molecules is unchanged. The area to the right of the same activation-energy line increases, showing a greater fraction capable of effective collisions.

Note Academy

8.3 Homogeneous and heterogeneous catalysts

A **catalyst** increases the rate of reaction without being used up. It provides **an alternative reaction pathway (a different mechanism) with a lower activation energy**.

- In the Boltzmann distribution, the lower E_a is drawn to the left, so a **larger proportion** of molecules have enough energy to react. The distribution curve itself does not change.
- On a **reaction pathway diagram**, the uncatalysed route has one high peak and the catalysed route a lower peak (or two lower peaks, one for each step). The reactants and products are at the same levels, so ΔH **is unchanged**.

A catalyst does not change the position of equilibrium or the value of K.

A **homogeneous** catalyst is in the same phase as the reactants; a **heterogeneous** catalyst is in a different phase. Their modes of action are covered in the A Level chapter on reaction kinetics.

Catalysts and temperature are different interventions

At fixed temperature a catalyst introduces another reaction mechanism with a lower activation barrier. On a Boltzmann diagram, keep the distribution curve unchanged and add a lower threshold to the left. More molecules already have enough energy for that route. On an energy profile, draw lower transition-state barriers but unchanged reactant and product levels. The catalyst does not supply extra energy to particles.

The catalyst can participate in individual steps, but is regenerated overall. A solid catalyst works at its surface and can become less effective if active sites are blocked. A dissolved catalyst may change oxidation state and then return to its starting state. These observations are compatible with the catalyst being unchanged in the **overall** reaction; they do not require it to remain chemically untouched at every instant.

Worked comparison: warming an equilibrium mixture may change both its rate and its final composition because equilibrium position can depend on temperature. Adding a catalyst speeds attainment of the same equilibrium at unchanged temperature. It does not increase K or selectively accelerate only the forward direction.

> **TRY IT**
>
> A student says a catalyst increases yield because it creates more energetic molecules. Correct both parts.

Answer: At fixed temperature it changes the reaction pathway, not the molecular-energy distribution. It accelerates both directions of a reversible reaction and does not change equilibrium yield. It may allow a useful yield to be reached sooner in an industrial process.

Note Academy

Chapter check: explain an increased rate through the **frequency of effective collisions**, choose the right graph gradient and separate a faster reaction from a larger final amount of product. Continue with experimental orders and mechanisms in **A Level kinetics**.

References and further reading

Scope follows section 8 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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