

Reaction kinetics

A-Level Chemistry 9701 · Topic 8 revision notes

Everything from the 3 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Rate of reaction

2. The Boltzmann distribution and activation energy.

3. Homogeneous and heterogeneous catalysis

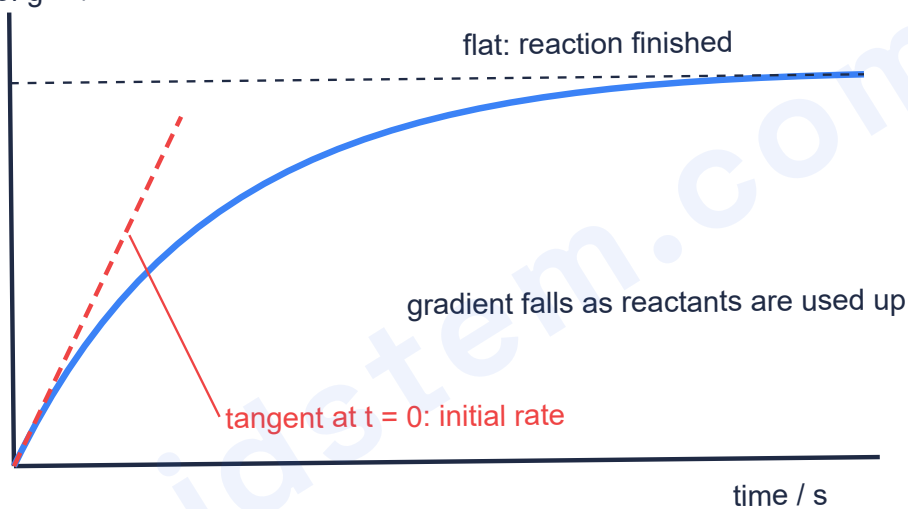
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1 Rate of reaction

Syllabus 8.1

The **rate of reaction** is the change in amount or concentration of a reactant or product per unit time, often in $\text{mol dm}^{-3} \text{ s}^{-1}$. It is found from the **gradient** of a concentration-time (or volume-time) graph; the gradient of the tangent at $t = 0$ is the **initial rate**. By **collision theory**, particles react only if they collide with at least the **activation energy**, E_a , and in the right orientation. Raising the concentration, the pressure of a gas or the surface area of a solid makes collisions **more frequent**, so successful collisions happen more often.

volume of gas / cm^3



rate at any time = gradient of the tangent at that time

Fig. 1: gas volume against time, with the tangent that gives the initial rate

Rate is a gradient.

- ✓ **Rate** = change in concentration $\div$ time.
- ✓ **Initial rate:** tangent at $t = 0$.
- ✓ **Collision theory:** energy $\geq E_a$ and correct orientation.
- ✓ **Concentration, pressure, surface area:** more frequent collisions.

Watch out!

Increasing the concentration does **not** give the particles more energy; it only increases the **frequency** of collisions, so the number of successful collisions per second rises. Say “more frequent successful collisions”, not just “more collisions”. Temperature is the factor that changes the energy of the particles, covered in the next lesson.

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2 The Boltzmann distribution and activation energy

Syllabus 8.2

The **Boltzmann distribution** shows the number of molecules with each energy. It starts at the origin (no molecule has zero energy), rises to a peak (the most probable energy) and then falls, approaching but never touching the energy axis, because there is no maximum energy. The **area under the curve** equals the total number of molecules. Only molecules to the right of E_a can react. At a higher temperature the curve is **lower and broader**, with its peak moved to the right and the **same area**; the area beyond E_a increases greatly, so a much larger proportion of collisions succeed.

number of molecules

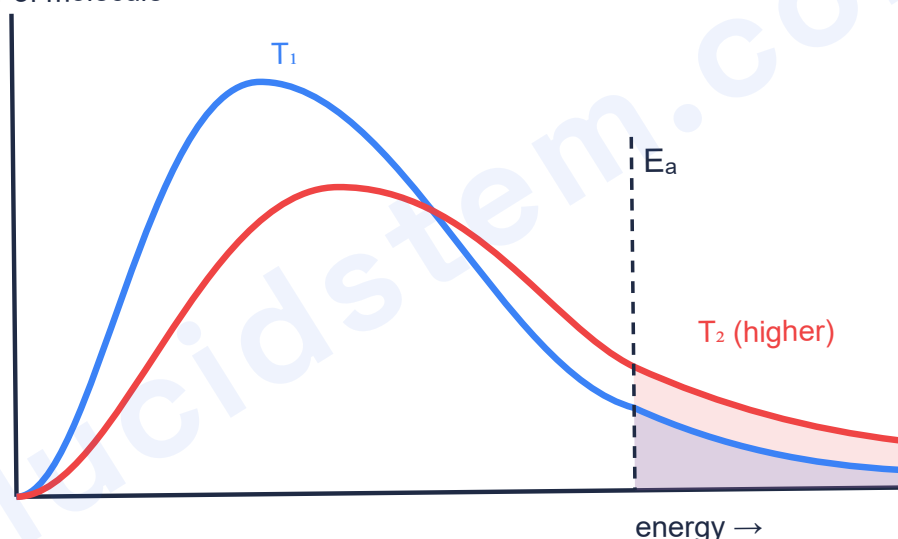


Fig. 1: the Boltzmann distribution at two temperatures, with the activation energy marked

Same area, lower peak, more beyond E_a .

- ✓ **Axes:** number of molecules against energy.
- ✓ **Origin start**, tail never touches the axis.
- ✓ **Higher T:** peak lower and right, same area.
- ✓ **E_a** unchanged by temperature.

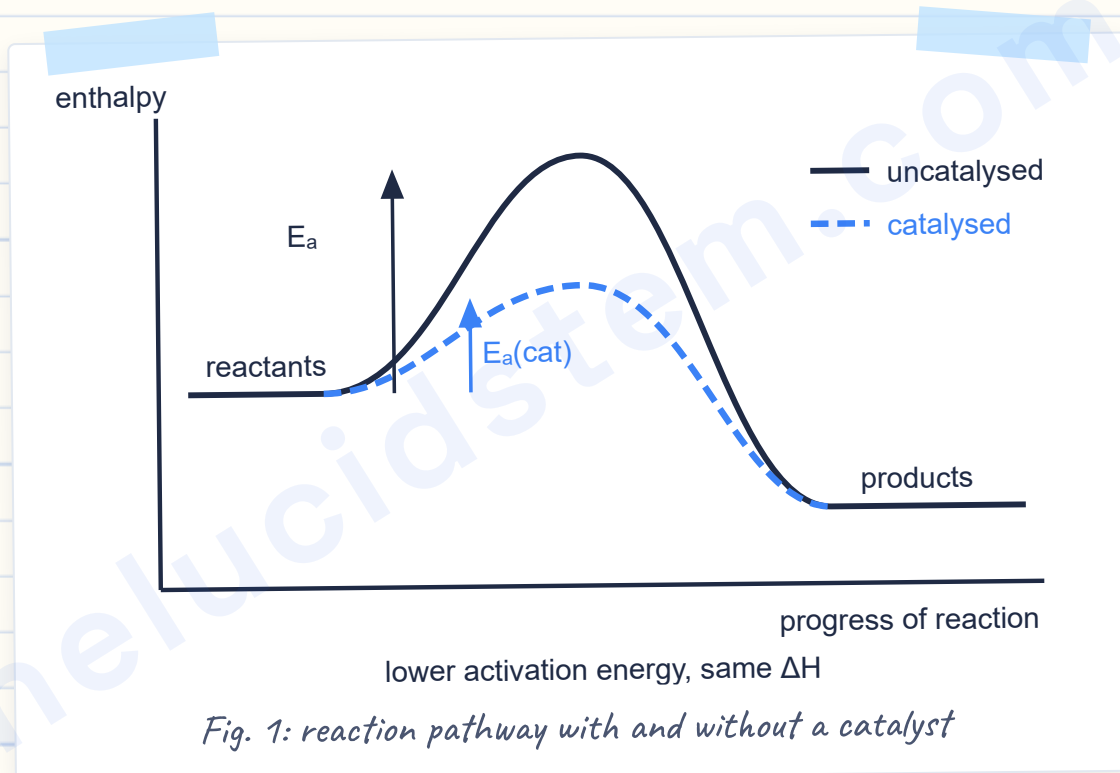
Watch out!

On the higher-temperature curve the peak is **lower** and further right, and the area is the **same**, because the number of molecules has not changed. And temperature does not change E_a ; it changes how many molecules have enough energy to overcome it. The main reason for the faster rate is the larger proportion of molecules with $E \geq E_a$, not the increase in collision frequency.

3 Homogeneous and heterogeneous catalysis

Syllabus 8.3

A **catalyst** increases the rate of a reaction by providing an **alternative route with a lower activation energy**; it is chemically unchanged at the end. On the Boltzmann distribution, E_a moves left, so a larger proportion of molecules can react. ΔH is **unchanged**, and because forward and reverse rates rise equally, a catalyst does not move the position of equilibrium. A **homogeneous** catalyst is in the **same phase** as the reactants and usually forms an intermediate; a **heterogeneous** catalyst is in a **different phase** and works by **adsorbing** reactants onto its surface.



Lower E_a , same ΔH .

- ✓ **Catalyst:** alternative route, lower E_a , not used up.
- ✓ **Homogeneous:** same phase, forms an intermediate.
- ✓ **Heterogeneous:** different phase; adsorb, react, desorb.
- ✓ **No change** to ΔH or equilibrium position.

Watch out!

A catalyst lowers the activation energy of the forward **and** reverse reactions, so it does not change ΔH , the position of equilibrium or the yield. On a Boltzmann diagram for a catalysed reaction, do **not** redraw the curve; just move the E_a line to the left.