How fast? The rate of chemical change

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 2.2, How fast? The rate of chemical change, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: concentration and moles from Structure 1.4, enthalpy changes and energy profiles from Reactivity 1.1, and drawing tangents to curves. At Higher Level you will also use natural logarithms and the Arrhenius equation from the data booklet.

Measuring the rate of reaction

Why does food last longer in a fridge?

Milk goes sour in two days on a warm table but lasts a week in a fridge. A firework burns in a second, iron rusts over months. Chemists need to know not only what forms but how fast, and how to make a reaction faster or slower.

What rate means

The **rate of reaction** is the change in the amount or concentration of a reactant or product per unit time.

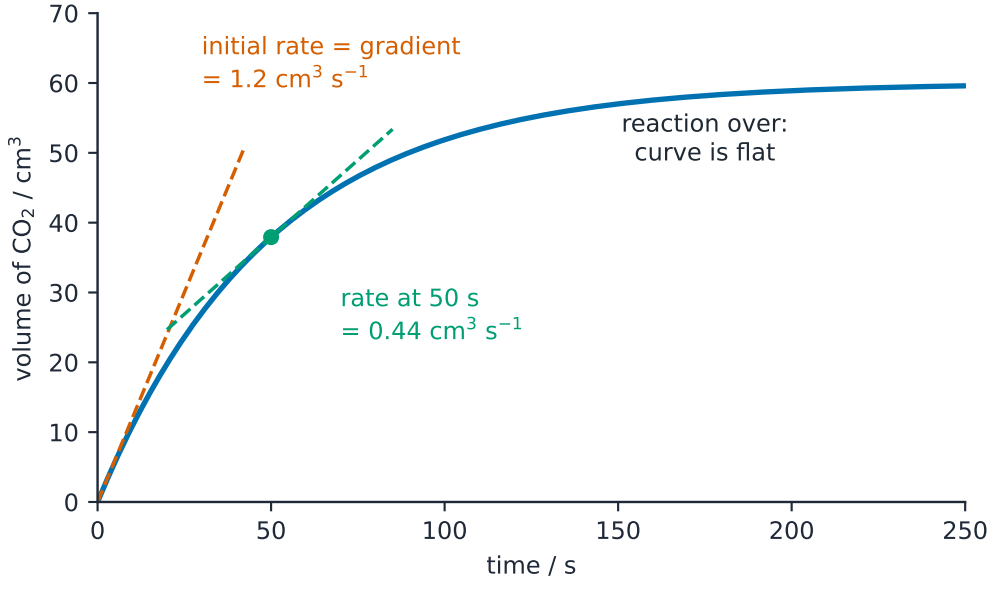
$$\text{rate} = \frac{\Delta[\text{product}]}{\Delta t} \quad \text{or} \quad -\frac{\Delta[\text{reactant}]}{\Delta t}$$

The unit is usually mol dm^{-3} s^{-1}. If you follow something else, such as a gas volume, the unit follows it: cm^3 s^{-1} or g s^{-1}.

Ways to follow a reaction

What changes	Method	Example
gas is given off	collect the gas in a gas syringe; read the volume every 10 s	$CaCO_3$ + HCl
gas escapes	stand the flask on a balance; read the mass loss	$CaCO_3$ + HCl
colour	colorimeter: measure how much light passes through	bromine reacting with methanoic acid
ions form or are used	conductivity or pH meter	ester hydrolysis
a precipitate forms	time until a cross under the flask disappears	sodium thiosulfate + HCl

Reading a rate from a graph



The rate at any moment is the gradient of the tangent to the curve

- The rate at any time is the gradient of the curve at that time. Draw a **tangent** and find its gradient.
- The curve is steepest at the start, where reactant concentrations are highest. The **initial rate** is the gradient of the tangent at $t = 0$.
- The rate falls as reactants are used up. When the curve is flat, the reaction has stopped.

Collision theory

Three conditions for a reaction

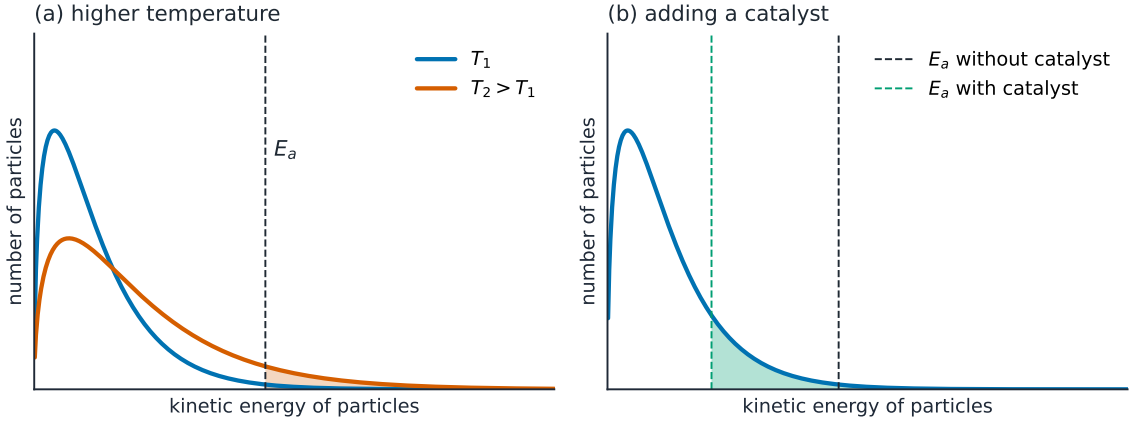
Collision theory says that particles react only when they collide, and only some collisions work. A successful collision needs:

1. A collision: the particles must meet.
2. Enough energy: the collision energy must be at least the **activation energy**, E_a, the minimum energy needed for a reaction.
3. The right orientation: the reacting parts of the particles must meet.

The rate depends on how many successful collisions happen each second.

The Maxwell–Boltzmann distribution

The particles in a gas or solution do not all have the same energy. The **Maxwell–Boltzmann distribution** - shows how many particles have each energy.



The shaded areas are the particles with at least enough energy to react

- The curve starts at the origin: no particle has zero energy.
- It has no maximum energy: the curve never meets the x-axis.
- The area under the curve is the total number of particles. At a higher temperature the area stays the same, so the peak moves right and falls.
- Only particles in the shaded area beyond E_a can react.

Factors that affect the rate

Concentration, pressure and surface area

Change	Effect on collisions	Effect on rate
higher concentration of a solution	more particles per dm^3, so more frequent collisions	faster
higher pressure of a gas	particles closer together, so more frequent collisions	faster
smaller pieces of a solid (larger **surface area**)	more particles exposed, so more frequent collisions	faster

These three change only the **frequency** of collisions. The fraction of collisions with enough energy stays the same.

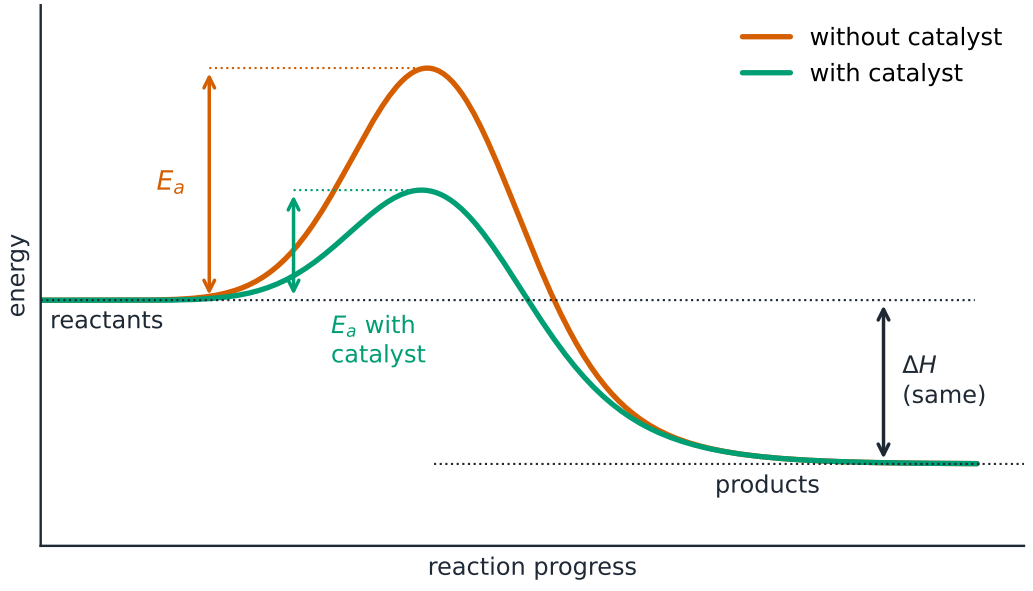
Temperature

A temperature rise of 10 K often roughly doubles the rate. Two effects add together:

1. Particles move faster, so collisions are a little more frequent.
2. Much more important: more particles have energy at least E_a (panel (a) above), so a much larger fraction of collisions succeeds.

Catalysts

A **catalyst** increases the rate of a reaction without being used up. It gives an **alternative reaction pathway** with a lower activation energy.



A catalyst lowers E_a but does not change ΔH

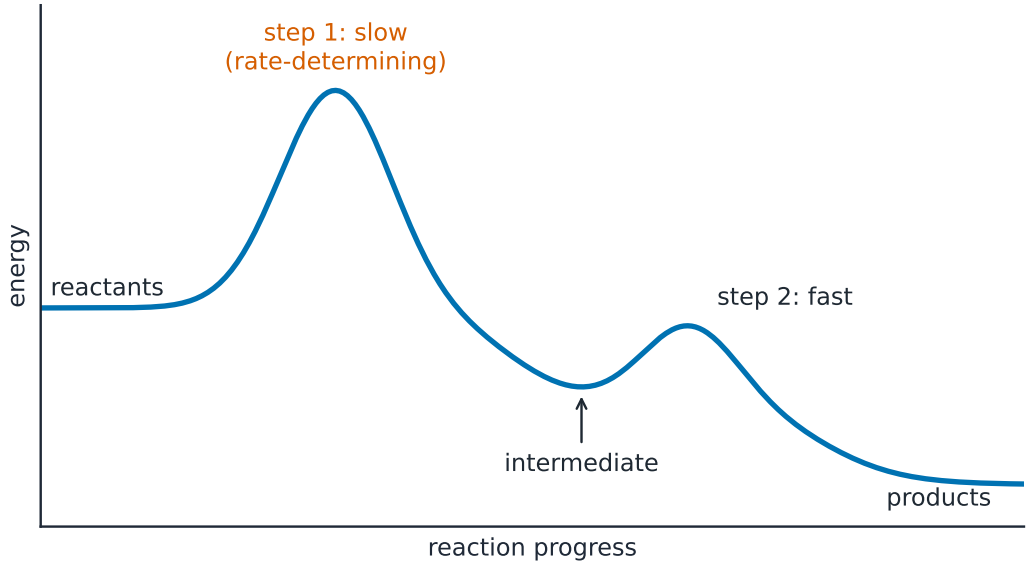
- With a lower E_a, more particles have enough energy (panel (b) above), so more collisions succeed.
- A catalyst does not change ΔH, and it does not change the position of an equilibrium.
- Examples: iron in the Haber process, MnO_2 for the decomposition of hydrogen peroxide, enzymes in living cells.

AHL: Rate equations

Elementary steps and mechanisms

Most reactions happen in a series of simple steps called **elementary steps** . The list of steps is the **reaction mechanism** .

- The **molecularity** of a step is the number of particles that collide in it: unimolecular (1), bimolecular (2) or, rarely, termolecular (3).
- An **intermediate** is made in one step and used up in a later step. It does not appear in the overall equation.
- The slowest step is the **rate-determining step** . The overall reaction cannot go faster than it.



The step with the highest barrier is the rate-determining step

The rate equation

For a reaction A + B → products, experiments give a **rate equation** of the form:

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

- m and n are the **orders** with respect to A and B. They are usually 0, 1 or 2, and they can only be found by experiment, not from the balanced equation.
- The overall order is $m + n$.
- k is the **rate constant** . It is constant at one temperature, and it increases when the temperature rises.

Units of k

Work out the units from rate = $k\times$ concentrations:

Overall order	**Units of k**
0	mol dm^{-3} s^{-1}
1	s^{-1}
2	dm^3 mol^{-1} s^{-1}
3	dm^6 mol^{-2} s^{-1}

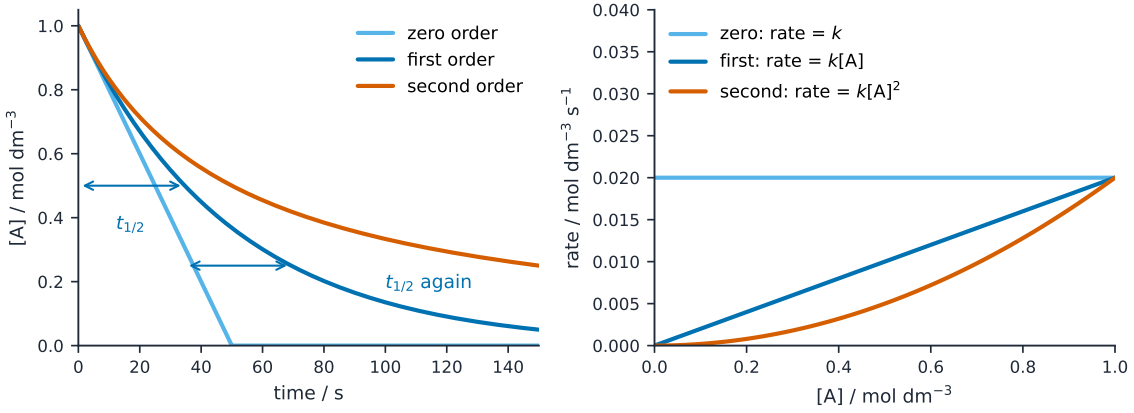
Finding orders from initial rates

Worked example. For $2\text{NO(g)} + \text{Br}_2\text{(g)} \rightarrow 2\text{NOBr(g)}$:

Experiment	**[NO] / mol dm^{-3}**	**[Br_2] / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	0.10	0.10	1.2×10^{-3}
2	0.20	0.10	4.8×10^{-3}
3	0.10	0.20	2.4×10^{-3}

1. Experiments 1 and 2: [NO] doubles, [Br_2] is the same, and the rate goes up 4 times $= 2^2$. Second order in NO.
2. Experiments 1 and 3: [Br_2] doubles and the rate doubles $= 2^1$. First order in Br_2.
3. Rate $= k[\text{NO}]^2[\text{Br}_2]$, third order overall.
4. $k = \dfrac{1.2 \times 10^{-3}}{(0.10)^2 \times 0.10} = 1.2$ dm^6 mol^{-2} s^{-1}.

Graphs of each order



The shape of each graph shows the order

- **Zero order:** [A] falls in a straight line; the rate does not depend on [A].
- **First order:** the rate is proportional to [A]. The **half-life** , the time for [A] to halve, is constant: $t_{1/2} = \dfrac{0.693}{k}$.
- **Second order:** the rate–concentration graph is a curve; doubling [A] makes the rate four times faster.

Linking the rate equation and the mechanism

The rate equation contains only the species in the rate-determining step and the steps before it.

> **Worked example.** Below 500 K, $NO_2 + CO \rightarrow NO + CO_2$ has rate $= k[NO_2]^2$. A mechanism that fits:

$$\text{step 1 (slow): } 2NO_2 \rightarrow NO_3 + NO$$

$$\text{step 2 (fast): } NO_3 + CO \rightarrow NO_2 + CO_2$$

- The slow step involves two NO_2, so the rate is second order in NO_2.
- CO only appears in the fast step after it, so it is zero order and is not in the rate equation.
- NO_3 is an intermediate. The steps add up to the overall equation.

A mechanism must agree with the rate equation and add up to the overall equation. Agreement makes it possible, not proven.

AHL: The Arrhenius equation

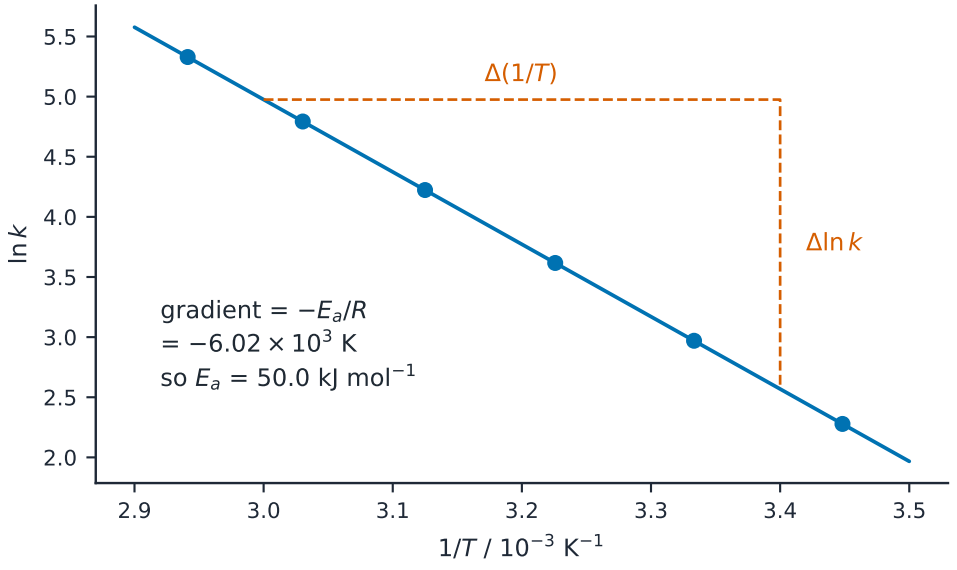
How k depends on temperature

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

- A is the **frequency factor** (also called the pre-exponential factor). It takes account of how often particles collide and with the right orientation. It has the same units as k.
- $e^{-E_a/RT}$ is the fraction of collisions with at least E_a. It rises steeply with T.
- $R = 8.31$ J K^{-1} mol^{-1} and T is in kelvin, so E_a must be in J mol^{-1}.

Finding E_a from a graph

A graph of $\ln k$ against $1/T$ is a straight line. The gradient is $-E_a/R$ and the y-intercept is $\ln A$.



$$Gradient = -E_a/R$$

Here the gradient is -6.02×10^3 K, so $E_a = 6.02 \times 10^3 \times 8.31 = 5.00 \times 10^4$ J mol^{-1} $= 50.0$ kJ mol^{-1}.

Two temperatures

With rate constants at two temperatures, use the data booklet form:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Worked example. The rate constant doubles from 298 K to 308 K. Find E_a.

1. $k_2 = 2k_1$, so $\ln \dfrac{k_2}{k_1} = \ln 2 = 0.693$.
2. $\dfrac{1}{298} - \dfrac{1}{308} = 1.0895 \times 10^{-4}$ K^{-1} (keep all the digits).
3. $E_a = \dfrac{8.31 \times 0.693}{1.0895 \times 10^{-4}} = 5.29 \times 10^{4}$ J mol^{-1} $= 52.9$ kJ mol^{-1}.

This is where the rule "a 10 K rise doubles the rate" comes from: it holds for E_a near 50 kJ mol^{-1} at room temperature.

Practice

1. In an experiment, 0.050 mol dm^{-3} of a reactant is used up in 25 s. Calculate the mean rate in mol dm^{-3} s^{-1}.
2. Describe how to follow the rate of the reaction between magnesium ribbon and hydrochloric acid.
3. State the three conditions for a successful collision.
4. Use collision theory to explain why powdered calcium carbonate reacts faster with acid than the same mass of lumps.
5. Sketch Maxwell–Boltzmann curves at two temperatures and use them to explain why a small rise in temperature gives a large rise in rate.
6. Explain how a catalyst increases the rate, with reference to an energy profile and a Maxwell–Boltzmann curve.
7. From the gas–time graph in this handout, explain why the rate at 50 s is lower than the initial rate.
8. **AHL.** For A + 2B → C, rate $= k[\mathrm{A}][\mathrm{B}]^2$. State the overall order and the units of k, and the factor by which the rate changes when [B] is tripled.
9. **AHL.** Initial-rate data for X + Y → Z: [X] 0.10, [Y] 0.10, rate 2.0×10^{-4}; [X] 0.30, [Y] 0.10, rate 6.0×10^{-4}; [X] 0.10, [Y] 0.20, rate 2.0×10^{-4}. Deduce the rate equation and calculate k.
10. **AHL.** The hydrolysis of 2-bromo-2-methylpropane has rate $= k[(\mathrm{CH_3})_3\mathrm{CBr}]$. Suggest a two-step mechanism and identify the rate-determining step and the intermediate.
11. **AHL.** A first-order reaction has $k = 0.0231$ s^{-1}. Calculate its half-life.
12. **AHL.** k is 3.0×10^{-4} s^{-1} at 300 K and 1.2×10^{-3} s^{-1} at 320 K. Calculate E_a.
13. **AHL.** State what the gradient and the intercept of a $\ln k$ against $1/T$ graph represent.

Answers.

1. $0.050/25 = 2.0 \times 10^{-3}$ mol dm^{-3} s^{-1}.
2. Collect the hydrogen in a gas syringe and read the volume every 10 s (or measure the mass loss on a balance); keep the temperature, acid concentration and volume the same.

3. The particles collide, with energy at least equal to E_a, and with the correct orientation.
4. Powder has a larger surface area, so more particles are exposed and collisions with acid particles are more frequent.
5. At the higher temperature the curve is lower and broader with the same area; the area beyond E_a is much larger, so a much larger fraction of collisions has enough energy.
6. It gives an alternative pathway with a lower E_a (a lower peak on the profile, the same ΔH). On the Maxwell–Boltzmann curve the lower E_a line has more particles beyond it, so more collisions succeed.
7. Reactants have been used up, so their concentration is lower and collisions are less frequent; the tangent is less steep.
8. **AHL.** Third order; $\text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$; $3^2 = 9$ times faster.
9. **AHL.** Tripling [X] triples the rate: first order in X. Doubling [Y] has no effect: zero order in Y. Rate $= k[\text{X}]$; $k = 2.0 \times 10^{-4}/0.10 = 2.0 \times 10^{-3}\ \text{s}^{-1}$.
10. **AHL.** Step 1 (slow, rate-determining): $(\text{CH}_3)_3\text{CBr} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$. Step 2 (fast): $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH}$. The intermediate is the carbocation $(\text{CH}_3)_3\text{C}^+$.
11. **AHL.** $t_{1/2} = 0.693/0.0231 = 30.0$ s.
12. **AHL.** $\ln(1.2 \times 10^{-3}/3.0 \times 10^{-4}) = \ln 4 = 1.386$. $1/300 - 1/320 = 2.08 \times 10^{-4}\ \text{K}^{-1}$. $E_a = 8.31 \times 1.386/2.08 \times 10^{-4} = 5.53 \times 10^4\ \text{J mol}^{-1} = 55.3\ \text{kJ mol}^{-1}$.
13. **AHL.** Gradient $= -E_a/R$; intercept $= \ln A$.

Exam tips

- Rate is measured from the gradient of a tangent; draw the tangent long and read two far-apart points.
- Concentration, pressure and surface area change the collision frequency; temperature and catalysts change the fraction of collisions with enough energy.
- On a Maxwell–Boltzmann curve: start at the origin, never touch the x-axis, keep the same area at the higher temperature.
- A catalyst does not change ΔH or the equilibrium position.
- **AHL.** Orders come from experiments, never from the balanced equation.
- **AHL.** In the Arrhenius equation, use T in K and E_a in J mol^{-1}; divide by 1000 at the end.