MEGA LECTURE

IB DP CHEMISTRY

Reactivity 2: How Much, How Fast and How Far?

Reactivity 2.2 How Fast? The Rate of Chemical Change

Revision Notes · Standard and Higher Level

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Original notes prepared for the IB Diploma Programme Chemistry course (first assessment 2025)

What the syllabus requires

Reactivity 2.2 asks a single question: how fast does a reaction go, and what controls that speed? Use this checklist as a final revision pass. Items marked **(HL)** are Higher Level only.

Understanding	You should be able to...
Rate of reaction	Define rate as the change in concentration (or amount) of reactant or product per unit time, and state its units.
Measuring rate	Select an appropriate experimental method (gas volume, mass loss, colorimetry, pH, turbidity, conductivity) for a given reaction.
Rate from graphs	Find rate from the gradient of a concentration–time graph, using a tangent for instantaneous rate; distinguish average from instantaneous and initial rate.
Collision theory	Explain that a reaction occurs only when particles collide with energy ≈ or greater than E_a and with the correct orientation.
Maxwell–Boltzmann	Interpret the energy distribution and use it to explain the effect of temperature and of a catalyst on rate.
Factors affecting rate	Explain, using collision theory, the effect of concentration, pressure, surface area, temperature and catalysts.
Catalysts	Describe how a catalyst provides an alternative pathway of lower E_a; distinguish homogeneous and heterogeneous catalysis.
(HL) Rate law	Determine orders and the rate constant k from initial–rate data; deduce the units of k.
(HL) Mechanisms	Deduce a rate law from a mechanism and identify the rate-determining step, intermediates and catalysts.
(HL) Arrhenius	Use $k = A\,e^{-E_a/RT}$ and the ln k against 1/T graph to find E_a.

> **Exam note:** Rate of reaction (kinetics) links directly to Structure 1.5 (kinetic theory) and Reactivity 2.3 (equilibrium). Kinetics tells you how fast equilibrium is reached; it says nothing about how far.

1. Rate of reaction: definition and units

The **rate of reaction** is the change in the concentration (or amount) of a reactant or product per unit time. Because reactants are used up and products form, rate is always quoted as a positive quantity:

$$\textbf{rate} = -\,\Delta[\text{reactant}]/\Delta t = +\,\Delta[\text{product}]/\Delta t$$

The minus sign in front of the reactant term makes the rate positive, because [reactant] is falling. When concentration is measured in mol dm^{-3} and time in seconds, the units of rate are **mol dm^{-3} s^{-1}**. If the quantity followed is an amount (mol) or a volume of gas (cm^3), the units change accordingly (for example mol s^{-1} or cm^3 s^{-1}).

Note that rates measured for different species in the same reaction are related by the stoichiometric coefficients. For $2H_2O_2 \rightarrow 2H_2O + O_2$, the hydrogen peroxide disappears twice as fast as oxygen is produced.

Worked example 1 — relating rates of different species

Hydrogen peroxide decomposes: $2H_2O_2 \rightarrow 2H_2O + O_2$. Oxygen is produced at 3.0×10^{-4} mol dm^{-3} s^{-1}. At what rate is H_2O_2 being consumed?

The mole ratio $H_2O_2 : O_2$ is 2 : 1, so H_2O_2 is used up twice as fast as O_2 forms.

rate of loss of $H_2O_2 = 2 \times (3.0 \times 10^{-4}) =$ **6.0×10^{-4} mol dm^{-3} s^{-1}**.

Measuring rate in the laboratory

You follow a rate by measuring some property that changes as the reaction proceeds. The right method depends on what changes: choose a property that is easy to measure continuously and that changes by a measurable amount.

Method	Property measured	Best used when...	Example
Gas collection	Volume of gas (gas syringe / inverted cylinder)	A gas is produced	$Mg + HCl \rightarrow H_2$
Mass loss	Falling mass on a balance	A gas escapes the flask	$CaCO_3 + HCl \rightarrow CO_2$
Colorimetry	Absorbance / light transmitted	A reactant or product is coloured	I_2 fading; MnO_4^- decolourising
pH / pH probe	Hydrogen-ion concentration	H^+ is consumed or produced	acid + carbonate
Turbidity	Time for a mark to disappear	A precipitate clouds the mixture	$S_2O_3^{2-}$ + acid → S(s)
Conductivity	Electrical conductivity	The number or type of ions changes	ester hydrolysis

Choosing a method: A good method changes measurably, can be recorded continuously, and does not itself disturb the reaction. The 'disappearing cross' turbidity method gives only one point per run (time for a fixed amount of precipitate) and so is used to compare initial rates across conditions.

2. Rate from graphs

A **concentration–time graph** is the standard record of a reaction. Its gradient at any point is the rate at that instant. For a reactant the curve falls and levels off; for a product it rises and levels off, both flattening as reactant runs out.

- **Average rate** over an interval = (change in concentration) / (time interval) = the gradient of the *chord* joining two points.
- **Instantaneous rate** at a moment = the gradient of the *tangent* drawn to the curve at that point.
- **Initial rate** = the instantaneous rate at t = 0, found from the tangent at the very start, where the curve is steepest and concentrations are known most precisely.

The rate is greatest at the start (reactant concentration is highest) and falls continuously as reactant is consumed, reaching zero when the reaction is complete and the graph is horizontal.

Worked example 2 — rate from a concentration–time graph

In the decomposition of a reactant A, [A] falls from 0.80 mol dm^{-3} at t = 0 to 0.20 mol dm^{-3} at t = 40 s. A tangent drawn at t = 0 would reach [A] = 0 at t = 25 s. Find (a) the average rate over the first 40 s, (b) the initial rate.

(a) Average rate = $-\Delta[A] / \Delta t = (0.80 - 0.20) / 40 = 0.60 / 40 =$ **0.015 mol dm^{-3} s^{-1}**.

(b) Initial rate = gradient of the tangent at t = 0 = 0.80 / 25 = **0.032 mol dm^{-3} s^{-1}**.

The initial rate is larger than the average rate, because the reaction is fastest at the start and slows down thereafter.

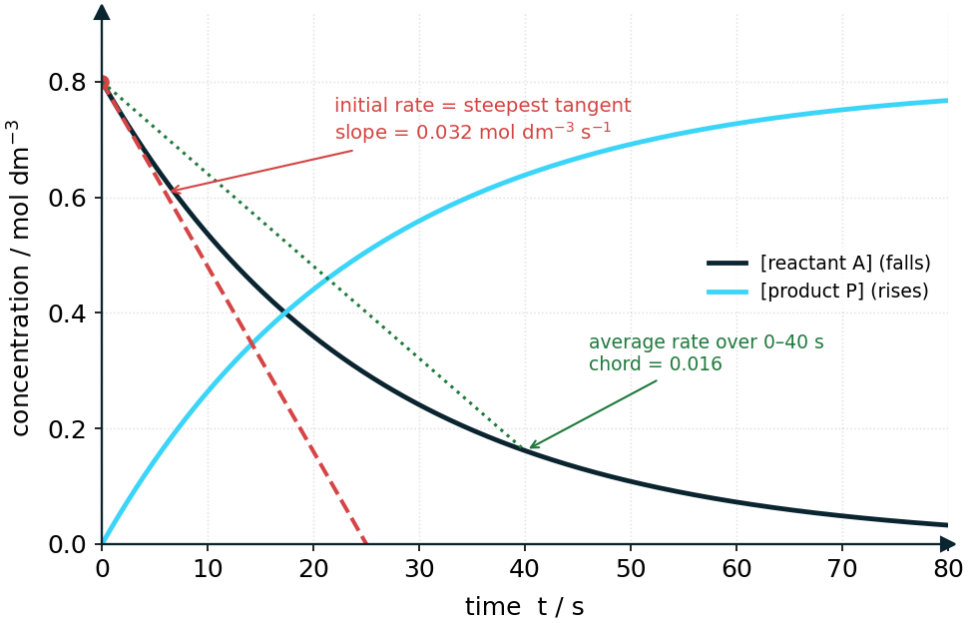

Figure 1. Concentration–time curves for A → P: the reactant falls and the product rises to a plateau. The steepest tangent (at t = 0) gives the initial rate ≈ 0.032 mol dm^{-3} s^{-1}; the chord gives the average rate over the first 40 s ≈ 0.016 mol dm^{-3} s^{-1}.

Worked example 3 — initial rate from gas-volume data

In $Mg + 2HCl \rightarrow MgCl_2 + H_2$, hydrogen is collected in a gas syringe. A tangent drawn to the volume–time curve at t = 0 rises by 40 cm^3 over the first 10 s, while only 24 cm^3 is actually collected in that time. Find the initial rate of gas production.

Initial rate = gradient of the tangent at t = 0 = 40 / 10 = **4.0 cm^3 s^{-1}**.

The average rate over the first 10 s (24 / 10 = 2.4 cm^3 s^{-1}) is smaller, because the reaction has already slowed by 10 s. Always use the tangent, not the chord, for an initial rate.

3. Collision theory

Collision theory explains rate at the particle level. For particles to react they must **collide**; but not every collision leads to reaction. A collision is **successful** (leads to products) only if two conditions are met:

- the colliding particles have a combined kinetic energy at least equal to the **activation energy**, E_a – the minimum energy needed to break bonds and start the reaction; and
- they collide in the **correct orientation**, so that the reactive parts of the molecules meet.

Why orientation matters

Even an energetic collision fails if the particles are wrongly aligned. In a reaction between a molecule and an atom, only collisions that strike the reactive end of the molecule can lead to products; a glancing or wrong-end collision simply bounces the particles apart. The proportion of collisions with a suitable geometry is one of the things captured by the Arrhenius factor A (Section 9). Larger, more complex molecules generally have a stricter orientation requirement.

The rate therefore depends on both the **frequency** of collisions and the **fraction** of those collisions that are successful. Anything that raises either factor speeds the reaction up.

Activation energy

E_a is an energy barrier that reacting particles must climb. At the top of the barrier lies the high-energy **transition state**. A large E_a means only a small fraction of collisions are energetic enough, so the reaction is slow at ordinary temperatures.

Reaction profiles

A **reaction profile** (energy-level diagram) plots potential energy against the progress of the reaction. Reactants and products sit at their own energy levels, and between them the curve rises to a peak – the transition state – whose height above the reactants is the activation energy E_a. For an **exothermic** reaction the products lie below the reactants (ΔH negative); for an **endothermic** reaction they lie above (ΔH positive). The forward and reverse reactions climb the same peak from opposite sides, so E_a(reverse) = E_a(forward) – ΔH.

The Maxwell–Boltzmann distribution

In any sample the particles do not all move at the same speed; they have a wide spread of kinetic energies described by the **Maxwell–Boltzmann distribution**. Its key features are: it starts at the origin (no particle has zero energy for long), rises to a peak at the most probable energy, then falls with a long tail towards high energy. The area under the whole curve equals the total number of particles. Only the particles in the **tail beyond E_a** can react on collision, so the shaded area past E_a represents the fraction of particles with enough energy.

> **Why temperature matters so much:** A modest rise in temperature shifts the distribution to higher energies and flattens the peak. The fraction of particles with $E \approx E_a$ or greater grows sharply – which is why rate often roughly doubles for a 10 °C rise, far more than the small increase in collision frequency alone could explain.

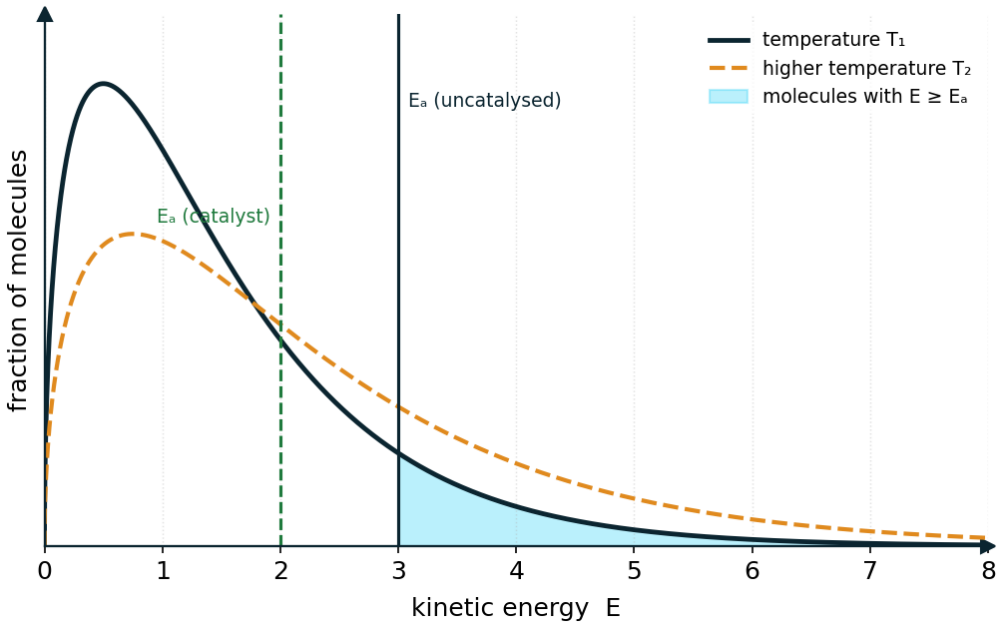

Figure 2. Maxwell–Boltzmann energy distribution. The shaded tail is the fraction of molecules with $E \geq E_a$ (11.1% at T_1). A catalyst lowers E_a (green dashed line), raising that fraction to 26.1%; a higher temperature T_2 shifts the curve to higher energy, raising it to 25.1%.

4. Factors affecting rate

Every factor below is explained the same way: it changes either the collision frequency or the fraction of successful collisions (or both). Learn the explanations, not just the outcomes.

Factor	Effect on rate	Collision-theory explanation
Concentration (increase)	Faster	More particles per unit volume → collisions are more frequent.
Pressure of gases (increase)	Faster	Compressing a gas raises its concentration → more frequent collisions.
Surface area of solid (increase)	Faster	More particles exposed at the surface → more frequent collisions (powder reacts faster than a lump).
Temperature (increase)	Much faster	Particles move faster (slightly more frequent collisions) and, crucially, a much larger fraction have $E \approx E_a$.
Catalyst (add)	Faster	Provides an alternative pathway of lower E_a → a larger fraction of collisions are successful.

Concentration, pressure and surface area

These three act through collision **frequency** only. They do not change the energy of the particles or the value of E_a, so the fraction of successful collisions is unchanged – there are simply more collisions each second. On a Maxwell–Boltzmann diagram the curve shape is unaffected.

Because these factors act independently, they can be combined: a hot, concentrated solution reacting with a finely powdered solid in the presence of a catalyst reacts far faster than any single change would achieve. In an exam always name the mechanism (collision frequency and/or fraction of successful collisions) rather than simply stating that the rate goes up.

Temperature and the Maxwell–Boltzmann curve

Raising the temperature does two things. It increases the average speed, giving slightly more collisions per second; far more importantly, it broadens the distribution and shifts it to higher energy, so the **area under the curve beyond E_a** increases greatly. A much larger fraction of collisions now clears the barrier, so the rate rises steeply. Note that E_a itself does not move – it is the particles that gain energy.

Catalysts and the Maxwell–Boltzmann curve

A catalyst does not change the temperature or the distribution of energies. Instead it lowers E_a, moving the E_a line to the **left** on the same curve. This puts a larger area of the distribution beyond the barrier, so a greater fraction of collisions are successful and the rate increases.

Worked example 4 – explaining a factor

Marble chips ($CaCO_3$) react with dilute hydrochloric acid. Explain, using collision theory, why the reaction is faster when (a) the acid is more concentrated and (b) the chips are ground to a powder.

(a) A more concentrated acid has more H^+ ions per unit volume, so acid particles collide with the marble surface more frequently. The fraction of successful collisions is unchanged, but there are more collisions per second, so the rate rises.

(b) Grinding increases the surface area, exposing more $CaCO_3$ particles to the acid at once. Again this raises the collision frequency without changing E_a, so the rate increases. (Temperature would raise the rate by a different mechanism – a larger fraction of collisions exceeding E_a.)

Worked example 5 – pressure of a gas-phase reaction

For the gas-phase reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$, state and explain the effect on the rate of halving the volume of the container at constant temperature.

Halving the volume doubles the concentration (and partial pressure) of both H_2 and I_2. There are now twice as many of each per unit volume, so collisions between H_2 and I_2 molecules become much more frequent.

The energy of the particles and E_a are unchanged, so the fraction of successful collisions is the same; the higher collision frequency alone **increases the rate**. Compressing a gas is the gas-phase equivalent of increasing concentration in solution.

5. Catalysts

A **catalyst** increases the rate of a reaction without being consumed overall. It works by providing an **alternative reaction pathway with a lower activation energy**. Because E_a is lower, a greater fraction of colliding particles has enough energy to react, so both the forward and reverse reactions are speeded up equally.

- A catalyst is **regenerated**: it is used in one step and re-formed in a later step, so it does not appear in the overall equation.
- It does **not** change ΔH, the position of equilibrium, or the yield – it only changes how fast equilibrium is reached.

- Only a small amount is needed, because it is continuously regenerated.

Homogeneous vs heterogeneous

Type	Meaning	Examples
Homogeneous	Catalyst is in the **same** phase as the reactants	Aqueous H^+ catalysing ester hydrolysis; Fe^{2+}/Fe^{3+} catalysing $S_2O_8^{2-}/I^-$ in solution
Heterogeneous	Catalyst is in a **different** phase (usually a solid with gaseous or liquid reactants)	Fe in the Haber process; Pt/Pd/Rh in a catalytic converter; Ni in hydrogenation of alkenes

A heterogeneous catalyst typically works by **adsorbing** reactant molecules onto active sites on its surface, weakening bonds and holding molecules in a favourable orientation; the products then **desorb**, freeing the site. This is why surface area (and poisoning of the surface) matters so much for solid catalysts.

Why catalysts matter

Catalysts are central to both industry and life. Heterogeneous catalysts such as iron in the Haber process and vanadium(V) oxide in the Contact process allow large-scale synthesis to run quickly at lower temperatures, saving energy and cost. In living cells, **enzymes** are highly specific protein catalysts that lower E_a for biochemical reactions, letting them proceed rapidly at body temperature. In every case the catalyst speeds the reaction without being consumed and without changing the yield.

Enthalpy profile with and without a catalyst

On an energy profile the reactants and products sit at the same levels with or without the catalyst – so ΔH is **unchanged**. The only difference is the **height of the barrier**: the catalysed pathway has a lower peak (lower E_a). A catalysed route often proceeds through several smaller humps (the elementary steps), but the highest of these is still below the uncatalysed barrier.

> **Exam trap:** A catalyst lowers E_a for both the forward and the reverse reaction by the same amount. It therefore speeds up the approach to equilibrium but never shifts the equilibrium position or increases the equilibrium yield.

6. (HL) The rate law

The **rate law** (rate equation) is an experimentally determined relationship between the rate and the concentrations of reactants:

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

Here k is the **rate constant** and the powers m and n are the **orders** of reaction with respect to A and B. The **overall order** is m + n. Crucially, orders are found **from experiment**, not from the stoichiometric coefficients of the balanced equation.

Order (in a reactant)	Meaning	Effect of doubling that concentration
Zero (0)	Rate does not depend on [reactant]	No change in rate
First (1)	Rate ≈ [reactant]	Rate doubles (×2)
Second (2)	Rate ≈ [reactant]^2	Rate quadruples (×4)

Summary: how each order is diagnosed

Observation on doubling one reactant	Order in that reactant
Rate unchanged	Zero (0)
Rate doubles (×2)	First (1)
Rate quadruples (×4)	Second (2)
Rate ×8	Third (3)

In general, if multiplying a concentration by a factor f multiplies the rate by f^x, the order in that reactant is x. Always change just one concentration at a time so the effect can be isolated.

Determining orders from initial-rate data

The standard method: run several experiments in which you change **one** concentration at a time and measure the initial rate. Compare two experiments in which only one reactant changes, and see how the rate responds.

Worked example 6 — finding orders and k

For A + B → products, the following initial rates were measured:

Expt	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	4.0×10^{-3}
3	0.20	0.20	1.6×10^{-2}

Order in A: compare 1 and 2 — [B] fixed, [A] doubles, rate doubles (2.0 to 4.0×10^{-3}). Rate ≈ $[A]^1$, so first order in A.

Order in B: compare 2 and 3 — [A] fixed, [B] doubles, rate ×4 (4.0×10^{-3} to 1.6×10^{-2}). Rate ≈ $[B]^2$, so second order in B.

Rate law: rate = k $[A][B]^2$; overall order = 1 + 2 = **3**.

Rate constant: using Expt 1, k = rate / ($[A][B]^2$) = (2.0×10^{-3}) / (0.10×0.10^2) = (2.0×10^{-3}) / (1.0×10^{-3}) = **2.0**.

Units of the rate constant

The units of k depend on the overall order, because the rate always has units of mol dm^{-3} s^{-1}. Rearranging the rate law and cancelling units gives the general result: units of k = (mol dm^{-3})$^{1-(\text{overall order})}$ s^{-1}.

Overall order	Rate law form	Units of k
0	rate = k	mol dm^{-3} s^{-1}
1	rate = k[A]	s^{-1}

Overall order	Rate law form	Units of k
2	rate = k[A]^2 or k[A][B]	mol^{-1} dm^3 s^{-1}
3	rate = k[A][B]^2	mol^{-2} dm^6 s^{-1}

Worked example 7 — units of k

Deduce the units of k for the third-order rate law found in Worked example 6, rate = k[A][B]^2.

Rearrange: k = rate / ([A][B]^2). Substituting units: (mol dm^{-3} s^{-1}) / (mol dm^{-3} × (mol dm^{-3})^2).

Denominator = (mol dm^{-3})^3 = mol^3 dm^{-9}. So k has units (mol dm^{-3} s^{-1}) × (mol^{-3} dm^9) = **mol^{-2} dm^6 s^{-1}**.

This matches the general rule with overall order 3: (mol dm^{-3})$^{1-3}$ s^{-1} = (mol dm^{-3})$^{-2}$ s^{-1}.

Worked example 8 — a reactant that is zero order

For X + Y → products, the following initial rates were measured:

Expt	[X] / mol dm^{-3}	[Y] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.20	1.0 × 10^{-2}
2	0.40	0.20	2.0 × 10^{-2}
3	0.40	0.40	2.0 × 10^{-2}

Order in X: compare 1 and 2 — [Y] fixed, [X] doubles, rate doubles → first order in X.

Order in Y: compare 2 and 3 — [X] fixed, [Y] doubles, rate unchanged → zero order in Y.

Rate law: rate = k[X]; overall order 1. k = rate / [X] = (1.0 × 10^{-2}) / 0.20 = **5.0 × 10^{-2} s^{-1}** (the units of a first-order k).

7. (HL) Concentration–time behaviour and half-life

The order of a reaction leaves a fingerprint on the shape of its concentration–time and rate–concentration graphs. Recognising these shapes is a common HL exam skill.

Order	Concentration–time graph	Rate–concentration graph	Diagnostic feature
Zero	Straight line with constant negative gradient	Horizontal line (rate independent of [A])	Rate constant until reactant runs out
First	Exponential-style decay curve	Straight line through the origin	**Constant half-life**
Second	Steeper decay that tails off more slowly	Upward curve (rate ≈ [A]^2)	Half-life doubles as reaction proceeds

Half-life of a first-order reaction

The **half-life**, $t_{1/2}$, is the time for the concentration of a reactant to fall to half its value. The defining property of a **first-order** reaction is that its half-life is **constant** – it takes the same time to halve, whatever the starting concentration. This makes a constant half-life a quick test for first-order kinetics.

Worked example 9 – using a constant half-life

A first-order reaction has a half-life of 30 s. If the initial concentration of the reactant is 0.80 mol dm^{-3}, what concentration remains after 90 s?

90 s = 3 half-lives (90 / 30 = 3). Each half-life halves the concentration:

0.80 → 0.40 (30 s) → 0.20 (60 s) → 0.10 (90 s).

Concentration remaining = $0.80 \times (1/2)^3 = 0.80 / 8 =$ **0.10 mol dm^{-3}**.

Qualitative use: You are not asked to derive integrated rate equations, but you should be able to read graph shapes, use a constant half-life to identify first order, and reason about how concentration falls over successive half-lives.

8. (HL) Reaction mechanisms

Most reactions do not happen in a single step. The **mechanism** is the sequence of **elementary steps** by which reactants become products. Each elementary step involves a small number of particles colliding, and the steps must add up to the overall balanced equation.

- **Molecularity** is the number of particles that react in an elementary step: unimolecular (1), bimolecular (2), or termolecular (3, rare).
- An **intermediate** is a species produced in one step and used up in a later step; it does not appear in the overall equation.
- A **catalyst** is used up in an early step and regenerated later – the reverse pattern of an intermediate.

The rate-determining step

The overall rate can be no faster than its **slowest step**, called the **rate-determining step (RDS)**. The rate law of the whole reaction is set by the molecularity of the RDS: only species that take part **up to and including** the RDS appear in the rate law, each raised to a power equal to the number of its particles in that step. A proposed mechanism is only valid if the rate law it predicts matches the experimental rate law.

Worked example 10 — deducing a rate law from a mechanism

The reaction $NO_2 + CO \rightarrow NO + CO_2$ is proposed to proceed by:

Step 1 (slow): $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2 (fast): $NO_3 + CO \rightarrow NO_2 + CO_2$

The slow step is rate-determining and is bimolecular in NO_2 (two NO_2 particles). So **rate = $k[NO_2]^2$**.

CO appears only in the fast step, *after* the RDS, so it does not appear in the rate law — the reaction is zero order in CO. This agrees with experiment, which finds the rate independent of [CO]. NO_3 is an intermediate (made in step 1, used in step 2).

Key idea: The stoichiometry of the overall equation tells you nothing about the orders. NO_2 and CO are 1:1 in the equation, yet the reaction is second order in NO_2 and zero order in CO because of the mechanism.

9. (HL) The Arrhenius equation

The rate constant k depends only on temperature (and the presence of a catalyst) — never on concentration. The **Arrhenius equation** makes this dependence quantitative:

$$k = A\, e^{-E_a/RT}$$

Here A is the **Arrhenius factor** (or pre-exponential / frequency factor), which reflects the frequency of collisions and the fraction with correct orientation; R is the gas constant (8.31 J K^{-1} mol^{-1}); T is the absolute temperature in K. The exponential term $e^{-E_a/RT}$ is the fraction of collisions with energy at least E_a. As T rises this fraction grows rapidly, so k — and the rate — increase steeply.

The ln k against 1/T graph

Taking natural logs of the Arrhenius equation gives a straight-line form:

$$\ln k = \ln A - (E_a / R)(1 / T)$$

A plot of **ln k (y) against 1/T (x)** is a straight line of gradient $-E_a/R$ and intercept **ln A**. So E_a = − (gradient) × R, and A = $e^{(\text{intercept})}$. This graph is the standard way to obtain an activation energy from experimental data.

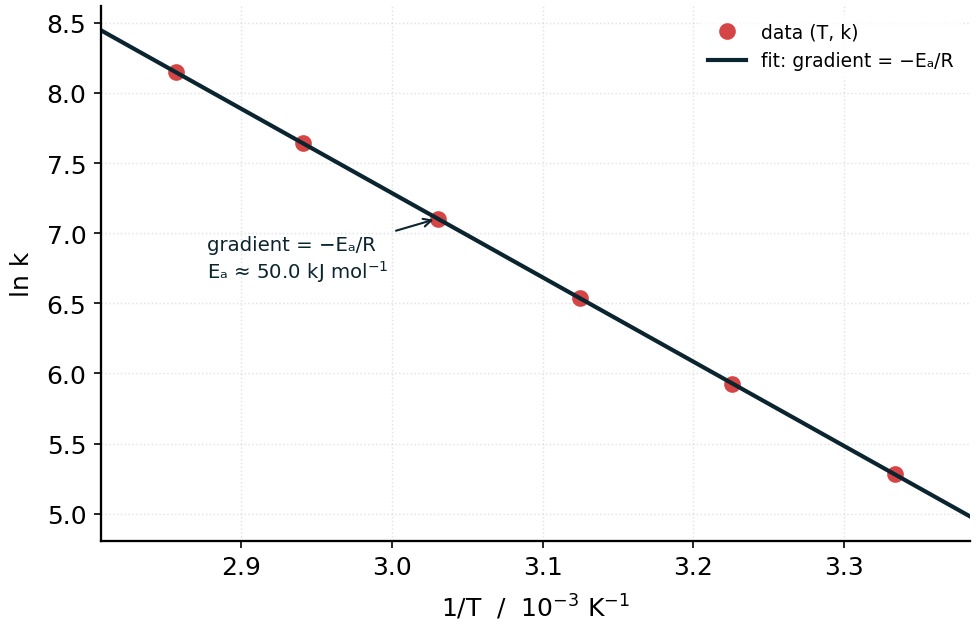

Figure 3. Arrhenius plot: ln k against 1/T is a straight line of gradient $-E_a/R$. A least−squares fit of the worked (T, k) pairs gives $E_a \approx 50.0$ kJ mol^{-1}.

Worked example 11 − E_a from two temperatures

The rate constant of a reaction doubles when the temperature rises from 300 K to 310 K. Estimate the activation energy. (Use the two-temperature form $\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$.)

$k_2/k_1 = 2$, so $\ln 2 = 0.693$.

$1/T_1 - 1/T_2 = 1/300 - 1/310 = 0.0033333 - 0.0032258 = 1.075 \times 10^{-4}$ K^{-1}.

$E_a = R \times \ln 2 / (1/T_1 - 1/T_2) = 8.31 \times 0.693 / (1.075 \times 10^{-4}) = 5.76 / (1.075 \times 10^{-4}) \approx 5.36 \times 10^4$ J mol^{-1} = ≈ **54 kJ mol^{-1}**.

Worked example 12 − E_a from a graph gradient

A plot of ln k against 1/T for a reaction is a straight line of gradient -6.5×10^3 K. Find the activation energy.

Gradient = $-E_a/R$, so $E_a = -$ (gradient) × R.

$E_a = -(-6.5 \times 10^3) \times 8.31 = 6.5 \times 10^3 \times 8.31 = 5.40 \times 10^4$ J mol^{-1} = ≈ **54 kJ mol^{-1}**.

Always convert to kJ mol^{-1} for the final answer, and remember the gradient is negative so the two minus signs cancel to give a positive E_a.

Worked example 13 — using a rate law to predict a rate

A reaction has the rate law rate = k[A][B]^2 with k = 2.0 mol^{-2} dm^6 s^{-1}. Calculate the rate when [A] = 0.30 mol dm^{-3} and [B] = 0.20 mol dm^{-3}, and predict the factor by which the rate changes if both concentrations are then doubled.

rate = 2.0 × 0.30 × 0.20^2 = 2.0 × 0.30 × 0.040 = **0.024 mol dm^{-3} s^{-1}**.

Doubling [A] multiplies the rate by 2^1 = 2; doubling [B] multiplies it by 2^2 = 4. Overall the rate increases by 2 × 4 = **8 times** (consistent with third-order kinetics).

Worked example 14 — identifying order from half-life data

The concentration of a reactant falls from 0.80 mol dm^{-3} to 0.40 mol dm^{-3} in 20 s, and then from 0.40 mol dm^{-3} to 0.20 mol dm^{-3} in the following 20 s. What is the order of the reaction with respect to this reactant?

First half-life (0.80 → 0.40) = 20 s. Second half-life (0.40 → 0.20) = 20 s. The half-life is **constant**.

A constant half-life is the signature of **first-order** kinetics, so the reaction is first order in this reactant. (If the successive half-lives had grown, it would be second order.)

10. Common pitfalls

- Reading orders off the balanced equation. Orders come from experiment (or a mechanism), not from stoichiometric coefficients.
- Thinking a catalyst changes ΔH, yield or equilibrium position. It changes only the rate (via a lower E_a).
- Saying temperature works mainly by making collisions more frequent. The dominant effect is the larger fraction of collisions with $E \approx E_a$ or more.
- Believing k changes with concentration. k depends only on temperature and catalyst; concentration changes the rate, not k.
- Using a chord instead of a tangent for instantaneous or initial rate.
- Forgetting to add the units of k, or getting them wrong for the overall order.
- Confusing an intermediate (made then used) with a catalyst (used then regenerated).
- On a Maxwell–Boltzmann diagram, moving the E_a line for a temperature change. Temperature moves the curve; a catalyst moves E_a.

11. Quick reference

Item	Statement
Rate	rate = − Δ[reactant]/Δt = + Δ[product]/Δt; units mol dm^{-3} s^{-1}
Successful collision	energy ≈ E_a or greater **and** correct orientation
Temperature effect	shifts Maxwell–Boltzmann curve right → larger fraction past E_a
Catalyst	alternative pathway, lower E_a; ΔH and equilibrium unchanged

Item	Statement
(HL) Rate law	rate = $k[A]^m[B]^n$; overall order = m + n; orders are experimental
(HL) Units of k	$(\text{mol dm}^{-3})^{1-(\text{overall order})}\ \text{s}^{-1}$
(HL) First order	constant half-life; ln k against t straight-line behaviour
(HL) RDS	slowest step sets the rate law; only species up to and including the RDS appear
(HL) Arrhenius	$k = A\,e^{-E_a/RT}$; ln k vs 1/T gradient = $-E_a/R$

12. Test yourself

Attempt all ten without notes, then check against the worked answers. Questions marked (HL) are Higher Level.

1. Define the rate of reaction and give its units when concentration is in mol dm^{-3} and time in seconds.

2. A reaction between a metal carbonate and acid releases CO_2. Suggest two experimental methods to follow its rate, and state what each measures.

3. Using collision theory and the Maxwell–Boltzmann distribution, explain why a 10 °C rise in temperature can roughly double the rate.

4. Explain, in terms of activation energy, how a catalyst speeds up a reaction, and state one quantity a catalyst does *not* change.

5. Distinguish homogeneous and heterogeneous catalysis, giving one example of each.

6. (HL) For 2A + B → products: doubling [A] (with [B] fixed) quadruples the rate; doubling [B] (with [A] fixed) doubles the rate. Write the rate law and give the overall order.

7. (HL) Given [A] = 0.10 mol dm^{-3}, [B] = 0.10 mol dm^{-3} gives an initial rate of 4.0×10^{-3} mol dm^{-3} s^{-1} for the rate law in Q6, find k and its units.

8. (HL) A first-order reaction has a half-life of 25 s and an initial concentration of 0.40 mol dm^{-3}. Find the concentration after 75 s.

9. (HL) The reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ has the mechanism: step 1 (slow) $NO_2 + F_2 \rightarrow NO_2F + F$; step 2 (fast) $NO_2 + F \rightarrow NO_2F$. Deduce the rate law and identify the intermediate.

10. (HL) A plot of ln k against 1/T has gradient -5.0×10^3 K. Calculate E_a in kJ mol^{-1}.

Answers

1. Rate = the change in concentration of a reactant or product per unit time (rate = $-\Delta[\text{reactant}]/\Delta t$). Units: **mol dm^{-3} s^{-1}**.

2. (a) **Gas collection** – measure the volume of CO_2 with a gas syringe against time. (b) **Mass loss** – place the flask on a balance and record the falling mass as CO_2 escapes. (pH change is also acceptable.)

3. Raising the temperature slightly increases collision frequency, but the dominant effect is on energy: the Maxwell–Boltzmann curve shifts to higher energy, so the fraction of particles (and hence collisions) with $E \approx E_a$ or more increases sharply. Many more collisions are now successful, so the rate roughly doubles.

4. A catalyst provides an alternative pathway with a **lower E_a**, so a larger fraction of collisions has enough energy to react and the rate rises. It does **not** change ΔH (or the equilibrium position / yield).

5. **Homogeneous**: catalyst in the same phase as reactants, e.g. aqueous H^+ catalysing ester hydrolysis. **Heterogeneous**: catalyst in a different phase, e.g. solid iron in the gas-phase Haber process.

6. (HL) Doubling [A] gives ×4 → second order in A; doubling [B] gives ×2 → first order in B. **rate = k[A]^2[B]**; overall order = 2 + 1 = **3**.

7. (HL) k = rate / ([A]^2[B]) = $(4.0 \times 10^{-3}) / (0.10^2 \times 0.10) = (4.0 \times 10^{-3}) / (1.0 \times 10^{-3})$ = **4.0 mol^{-2} dm^6 s^{-1}** (overall order 3).

8. (HL) 75 s = 3 half-lives (75/25). 0.40 → 0.20 → 0.10 → 0.05. Concentration = $0.40 / 2^3$ = **0.05 mol dm^{-3}**.

9. (HL) The slow step is rate-determining: NO_2 + F_2, one of each. **rate = k[NO_2][F_2]** (overall second order). The **intermediate is F** (an F atom), produced in step 1 and consumed in step 2.

10. (HL) gradient = $-E_a/R$, so $E_a = -(-5.0 \times 10^3) \times 8.31 = 4.16 \times 10^4$ J mol^{-1} = ≈ **42 kJ mol^{-1}**.