9701 CHEMISTRY · TOPIC 8 · AS LEVEL

Reaction Kinetics — AS

01 · COLLISION THEORY

A reaction occurs only when particles collide with **energy ≥ E_a** and in the **correct orientation**. Rate depends on the frequency of successful collisions.

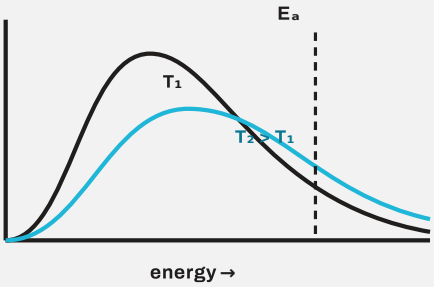
Activation energy — the minimum energy colliding particles need for a reaction to occur.

02 · FACTORS AFFECTING RATE

Factor	Why rate rises
concentration ↑	more particles per volume → more frequent collisions
pressure ↑ (gas)	same effect as concentration
surface area ↑	more particles exposed
temperature ↑	more particles exceed E_a; collisions also more frequent
catalyst	alternative route of lower E_a

Temperature matters most: the fraction of particles with $E \geq E_a$ rises sharply, which outweighs the small rise in collision frequency.

03 · BOLTZMANN DISTRIBUTION



Starts at the origin (no particle has zero energy) and never touches the axis. Raising T flattens and shifts the peak right; the **area under the curve is constant** — it is the total number of particles — but the shaded area beyond E_a grows.

04 · CATALYSIS

A catalyst increases rate by providing an alternative route of **lower E_a**. It is unchanged in mass and chemical composition at the end and does **not** change ΔH or the position of equilibrium — it speeds both directions equally.

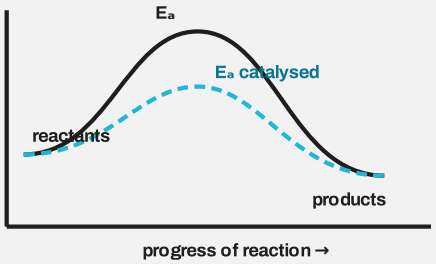
Homogeneous — same phase as the reactants (Cl• radicals in ozone depletion, H^+ in esterification). **Heterogeneous** — different phase, works by adsorption onto active sites (Fe in Haber, V_2O_5 in Contact, Pt/Rh in catalytic converters).

05 · FOLLOWING A REACTION

Choose a property that changes measurably: gas volume in a syringe, mass loss on a balance, colour by colorimetry, pH, or titrating quenched samples at intervals.

Rate at any instant = **gradient of the tangent** to a concentration–time graph. Initial rate is the gradient at t = 0.

06 · REACTION PATHWAY DIAGRAMS



ΔH is the gap between reactant and product levels and is **unchanged** by a catalyst — only the barrier height falls. Label both axes and mark E_a from the reactants to the peak.

07 · WORKED EXAMPLE — INITIAL RATE

$Mg + 2HCl \rightarrow MgCl_2 + H_2$. 48 cm^3 of H_2 collects in the first 20 s.

rate = 48 ÷ 20 = **2.4 $cm^3\ s^{-1}$**

In moles: 48 ÷ 24 000 = 2.0×10^{-3} mol
rate = 1.0×10^{-4} mol s^{-1}

The curve flattens as HCl is used up and its concentration falls; the reaction ends when the limiting reactant is gone.

08 · READING A RATE GRAPH

The curve is **steepest at the start**, where the concentration is highest, and flattens as reactants are used up.

A more concentrated solution, a higher temperature or a powdered solid all give a **steeper initial gradient**. If the same amount of limiting reactant is used, the curves level off at the **same final volume or mass**.

A catalysed reaction reaches that same plateau sooner — the yield is unchanged.

09 · CATALYSIS IN THE ATMOSPHERE

Chlorine radicals from CFCs catalyse ozone breakdown:
$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ then $ClO\bullet + O \rightarrow Cl\bullet + O_2$.
The radical is regenerated, so one atom destroys many ozone molecules.

NO from engines catalyses the same reaction. In a catalytic converter Pt/Rh instead promotes $2CO + 2NO \rightarrow 2CO_2 + N_2$ on its surface.

10 · INDUSTRIAL CATALYSTS

Process	Catalyst
Haber (NH_3)	Fe
Contact (SO_3)	V_2O_5
Ostwald (HNO_3)	Pt/Rh
hydrogenation	Ni
cracking	zeolite

A catalyst lets a plant run at a lower temperature for the same rate, saving energy and — for an exothermic reaction — improving the yield as well.

MARKS LOST HERE

— Saying a catalyst "lowers the activation energy" of the reaction rather than providing a route with a lower E_a.

— Drawing a Boltzmann curve that starts above the origin or touches the x-axis.

— Claiming higher temperature works mainly by more frequent collisions.

— Saying a catalyst increases yield; it only shortens the time to reach the same equilibrium.

9701 CHEMISTRY · TOPIC 26 · A LEVEL

Rate Equations — A2

11 · RATE EQUATION

rate = k[A]^m[B]^n

m and n are the **orders** — found only by experiment, never from the stoichiometric equation. Overall order = m + n.

Units of k: 1st order s^{-1}, 2nd order $mol^{-1}\ dm^3\ s^{-1}$, zero order $mol\ dm^{-3}\ s^{-1}$. Work them out by rearranging, don't memorise.

12 · RECOGNISING THE ORDER

Order	conc–time	rate–conc
zero	straight line, constant gradient	horizontal
first	curve, constant half-life	straight through origin
second	steeper curve, half-life doubles	upward curve

Constant half-life is the signature of first order — check two successive half-lives from the graph.

13 · HALF-LIFE AND K

first order: k = ln 2 ÷ t½ = 0.693 ÷ t½

t½ is the time for the concentration to fall to half its value. For first order it is independent of the starting concentration.

14 · WORKED EXAMPLE — INITIAL RATES

Exp	[A]	[B]	rate
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	8.0×10^{-4}
3	0.20	0.20	8.0×10^{-4}

1 → 2: [A] ×2, rate ×4 → **second order in A**
2 → 3: [B] ×2, rate unchanged → **zero order in B**

rate = k[A]²
k = $2.0 \times 10^{-4} \div (0.10)^2$ = **0.020 $mol^{-1}\ dm^3\ s^{-1}$**

15 · MECHANISM AND RATE-DETERMINING STEP

The **rate-determining step** is the slowest step. Only species involved **in or before** it appear in the rate equation, and their coefficients there are the orders.

A species that is zero order takes part only after the rate-determining step. A catalyst can appear in the rate equation even though it is not in the overall equation.

rate = k[CH_3Br][OH^-] → both in the slow step → **S_N2**, one-step, primary halogenoalkane.

rate = k[$(CH_3)_3CBr$] → OH^- absent → **S_N1**, slow step forms a carbocation, tertiary halogenoalkane.

16 · WORKED EXAMPLE — HALF-LIFE

[A] falls 0.80 → 0.40 in 50 s, and 0.40 → 0.20 in a further 50 s.

Half-life constant → **first order**
k = 0.693 ÷ 50 = **0.0139 s^{-1}**
rate = k[A]

At [A] = 0.30: rate = $0.0139 \times 0.30 = 4.2 \times 10^{-3}$ $mol\ dm^{-3}\ s^{-1}$

17 · CATALYSIS BY TRANSITION METALS

Variable oxidation states let a transition metal accept and donate electrons, providing a lower-energy route.

Fe^{3+} catalysing $S_2O_8^{2-} + 2I^-$: Fe^{3+} oxidises I^- to I_2 and is reduced to Fe^{2+}, then $S_2O_8^{2-}$ re-oxidises Fe^{2+}. Both steps involve oppositely charged ions, unlike the uncatalysed reaction between two anions.

18 · FINDING AN ORDER EXPERIMENTALLY

Initial rates — repeat the run changing one concentration at a time and compare the starting gradients.

Continuous monitoring — follow one run to completion, plot concentration against time, then read successive half-lives or take tangents and plot rate against concentration.

Clock reaction — time a fixed small change, such as the appearance of the blue starch–iodine colour. Then 1 ÷ t is proportional to the initial rate.

19 · WORKED EXAMPLE — CHECKING A MECHANISM

Proposed for $NO_2 + CO \rightarrow NO + CO_2$:
step 1 (slow) $2NO_2 \rightarrow NO_3 + NO$
step 2 (fast) $NO_3 + CO \rightarrow NO_2 + CO_2$

Only step 1 is rate-determining, and it involves two NO_2:
rate = k[NO_2]²

CO does not appear, so the mechanism predicts zero order in CO. If experiment shows first order in CO, the mechanism is wrong.

20 · TEMPERATURE AND K

Only **k** changes with temperature; the orders do not. A rise of about 10 K roughly doubles k for many reactions near room temperature.

The reason is the Boltzmann distribution: a small rise in T sharply increases the fraction of molecules with energy ≥ E_a. A reaction with a large E_a is the more sensitive to temperature.

21 · AUTOCATALYSIS

A product catalyses the reaction that makes it, so the rate **rises** after the start instead of falling, then drops away as the reactants run out.

MnO_4^- oxidising ethanedioate is the standard case: the Mn^{2+} formed catalyses the next round, which is why the titration starts slowly and then speeds up. On a concentration–time graph the curve is S-shaped.

MARKS LOST HERE

— Reading orders off the balanced equation instead of the data.

— Changing two concentrations at once when comparing experiments.

— Omitting the units of k, or quoting them from memory for the wrong order.

— Forgetting that a zero-order species still takes part in the reaction, just not in the slow step.