08 Reaction Kinetics



1 Collision Theory

For a reaction to occur, particles must collide with

1. sufficient kinetic energy, greater than or equal to the _____ (E_a)
2. the correct _____ (orientation)

Such a collision is an **effective collision**. The greater the frequency of effective collisions, the faster the rate. Usually at most **two** particles collide in one step.

DEFINITION **Activation energy**: the minimum amount of energy reacting particles must possess for an effective collision to take place for reaction to occur.

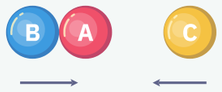
Collision	Energy ≥ E_a?	Right orientation?	Result
effective	✓	✓	bonds break and form: products
ineffective	✗	✓	bounce apart
ineffective	✓	✗	bounce apart

✓ right orientation



C meets the B end: B–C forms

✗ wrong orientation



C meets the A end: they bounce apart

2 Factors Affecting Rate

2.1 Concentration, pressure and surface area

Concentration or pressure ↑

1. No. of reactant particles per _____ ↑
2. → frequency of collisions ↑, and hence frequency of _____ ↑ → rate ↑

Particle size of solid ↓

1. Larger _____ of contact between reactant particles
2. → frequency of effective collisions ↑ → rate ↑

Rate is fastest at the start, when reactant concentrations are highest.

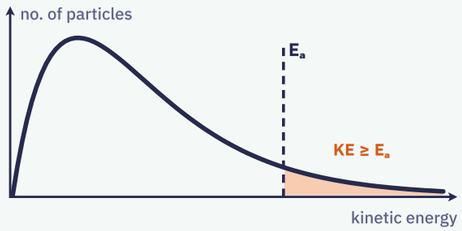
2.2 The Boltzmann distribution curve

Features of the curve

- Starts at the **origin** and never touches the energy axis
- Area under the curve = total no. of particles
- Shaded area = particles with energy **≥ E_a**

How the curve changes when T increases

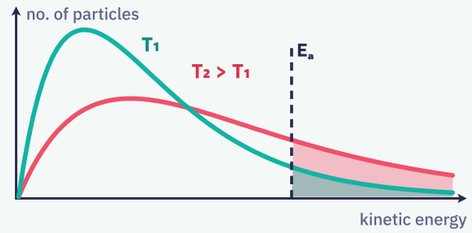
- The peak shifts to the _____, as the most probable energy increases
- The curve _____ out: a larger spread of energies, with more particles at higher energies and fewer at lower energies
- The area under the curve stays _____, as the total number of particles is constant



2 Factors Affecting Rate (continued)

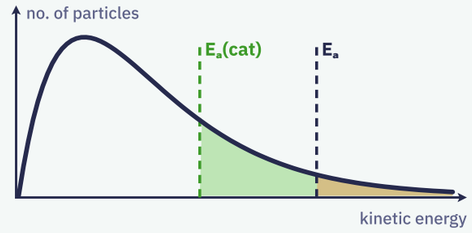
2.3 Effect of temperature on rate

1. As the temperature increases, the average _____ of the particles increases
2. → a larger number of reactant particles have energy _____ (larger shaded area)
3. → frequency of effective collisions ↑ → rate ↑ (k ↑). Rate roughly doubles for every 10 °C rise.



2.4 Effect of a catalyst on rate

1. Provides an _____ with a lower E_a
2. → more reactant particles possess energy ≥ E_a (larger shaded area)
3. → frequency of effective collisions ↑ → rate ↑ (k ↑)



3 Rate of Reaction

DEFINITION **Rate of reaction**: the change in concentration of a reactant or product per _____.

Measuring rate

$$\text{rate} = \frac{\text{change in [reactant] or [product]}}{\text{time taken}}$$

Rate is always positive: [reactant] falls with time and [product] rises. Units: mol dm^{-3} s^{-1}.

Rates of different species are related by the mole ratio

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

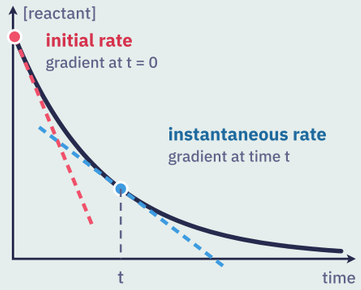
- Br^- is used up _____ as fast as BrO_3^-
- Br_2 is formed _____ as fast as BrO_3^- is used up

So "the rate" must say which species it refers to.

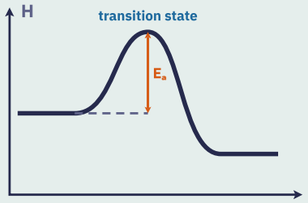
Instantaneous and initial rate

DEFINITION **Instantaneous rate**: gradient of the _____ to the concentration–time graph at time t.

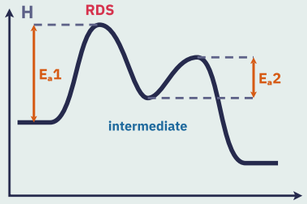
Initial rate: gradient of the tangent at _____, the highest rate, as [reactant] is at its maximum.



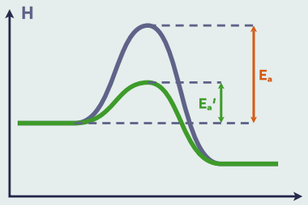
4 Energy Profile Diagrams



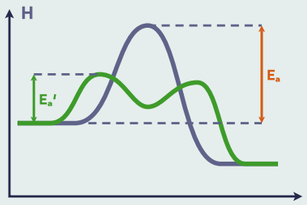
One step
one transition state



Two steps
intermediate in the dip, step 1 is the RDS



Heterogeneous catalyst
one lower hump



Homogeneous catalyst
two lower humps

- **Transition state**: the unstable arrangement at the energy maximum, equally likely to form reactants or products
- **Intermediate**: short-lived species formed in one step and used up in a later step
- The **rate-determining step** (slow step) has the _____
- Higher E_a → slower reaction. Very high E_a:
  reactant is _____

5 Catalysis

DEFINITION **Catalyst**: a substance that increases the rate of a chemical reaction by providing an _____ _____ with lower activation energy but remains _____ at the end of the reaction.

1. It is _____
2. It is regenerated at the end of the reaction
3. It does not affect the overall stoichiometry
4. It does not affect the position of equilibrium or ____

DEFINITION **Homogeneous** catalysis: catalyst and reactants in the _____.

DEFINITION **Heterogeneous** catalysis: catalyst and reactants in _____.

5.1 Heterogeneous: adsorption theory

1. **Adsorption**: reactant particles form weak bonds to _____ on the catalyst surface, weakening the bonds within them
2. **Reaction**: reactants are held close together in the _____
3. **Desorption**: weak bonds to the products break, products diffuse away and the active sites are freed



Process	Catalyst
Haber: $N_2 + 3H_2 \rightleftharpoons 2NH_3$	_____
Contact: $2SO_2 + O_2 \rightleftharpoons 2SO_3$	_____
Hydrogenation of alkenes	Ni
Catalytic converter: $2CO + 2NO \rightarrow 2CO_2 + N_2$	Pt, Pd, Rh

5 Catalysis (continued)

5.2 Homogeneous: Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction

Iodide ions are oxidised by peroxodisulfate ions. Without a catalyst this is very slow, adding a little Fe^{2+} speeds it up. $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

Why is the reaction slow, and how does Fe^{2+} help?

1. Without a catalyst, the reaction is slow: it has a high E_a, as a large amount of energy is needed to overcome the _____ between the two negatively charged reactant ions
2. Step 1: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$
3. Step 2: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ (Fe^{2+} regenerated)
4. Each step is between _____ ions → lower E_a for each step

Oxides of nitrogen in the oxidation of atmospheric SO_2

- $NO_2 + SO_2 \rightarrow SO_3 + NO$
- $NO + ½O_2 \rightarrow NO_2$ (NO_2 regenerated)
- $SO_3 + H_2O \rightarrow H_2SO_4$, forming _____

5.3 Autocatalysis

DEFINITION **Autocatalysis**: catalysis in which one of the _____ of the reaction catalyses the reaction.

1. Slow at first: very little catalyst (product) present
2. Fast as more product, the catalyst, forms
3. Slow again as the reactants are used up

Example: MnO_4^- with ethanedioate ions

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

The product **Mn^{2+}** catalyses the reaction, so the purple colour fades slowly at first, then quickly.

5.4 Enzymes

- Protein catalysts, highly _____ (lock-and-key)
- Low [S]: first order. High [S]: zero order, as all _____ are saturated
- [S] in excess: rate ∝ [E]
- pH or T beyond optimum changes the 3D structure and active site → _____

rate vs [S]
levels off: sites saturated

rate vs T
optimum 20–50 °C

rate vs pH
optimum pH 5–8

6 The Rate Equation

DEFINITION **Rate equation**: the _____ determined relationship between rate and the concentrations of reactants.

$$\text{rate} = k[A]^x[B]^y$$

Overall order = _____

DEFINITION **Order of reaction** w.r.t. a reactant: the _____ of its concentration term in the experimentally determined rate equation.

DEFINITION **Rate constant, k**: the proportionality constant in the rate equation.

6.1 Meaning of order

Order	Rate	[A] × 2: rate
0	independent of [A]	_____
1	rate ∝ [A]	_____
2	rate ∝ $[A]^2$	_____

6.2 What changes k?

Change	Rate	k
[reactant] ↑	↑ (if order ≠ 0)	_____
temperature ↑	↑	_____
add a catalyst	↑	_____

6.3 Units of k units of rate ÷ $(\text{mol dm}^{-3})^{\text{overall order}}$

Overall order	0	1	2	3
Rate equation	rate = k	rate = k[A]	rate = $k[A]^2$	rate = $k[A]^2[B]$
Units of k	_____	_____	_____	_____

7 Mechanisms and the Rate Equation

Rules for a reaction mechanism

- Each elementary step involves at most _____ reacting particles
- Steps add up to the overall equation
- The rate equation contains the reactants in the _____ (slow step), with orders = their coefficients in that step
- **Intermediates** do not appear in the overall equation or the rate equation

7.1 Proposing a mechanism

WORKED EXAMPLE $2NO(g) + F_2(g) \rightarrow 2ONF(g)$ has rate = $k[NO][F_2]$. It takes place in two steps, and one step forms ONF and the radical F• in equimolar amounts. Suggest a mechanism.

1. Slow step contains _____, from the rate equation
2. Rate equation ≠ overall equation → not a single step, one more NO still to react

Step 1 (slow) _____ **Step 2 (fast)** _____

7 Mechanisms and the Rate Equation (continued)

7.2 Testing a mechanism

WORKED EXAMPLE For $2A + B \rightarrow A_2B$, the rate equation is found to be rate = $k[A]^2$. Which mechanism is consistent with it?

Mechanism 1	Mechanism 2
$A + A \rightarrow A_2$ (slow)	$A + B \rightarrow AB$ (slow)
$A_2 + B \rightarrow A_2B$ (fast)	$AB + A \rightarrow A_2B$ (fast)

1. Mechanism 1: the slow step involves _____ → predicted rate = $k[A]^2$, which matches the experimental rate equation
2. Mechanism 2: the slow step involves one A and _____ → predicted rate = k[A][B], which does not match
3. ∴ only _____ is consistent

8 Collecting Rate Data

	Continuous method	Initial rate method
Experiments	_____: [reactant] followed over time	_____: one concentration changed at a time
Data	concentration at intervals	time taken for a fixed change
Analysis	concentration–time graph, half-life	rate–concentration graph or the ratio method

8.1 Physical measurements: a property that changes as the reaction goes

gas volume
Mg + 2HCl, H_2 given off

mass loss
$CaCO_3$ + 2HCl, CO_2 escapes

pH
$CH_3Br + OH^-$, pH falls

conductivity
no. of ions changes

colorimetry
brown I_2 used up

pressure at fixed V
$N_2O_4 \rightarrow 2NO_2$

8.2 Titrimetric method

Withdraw portions at intervals, **quench**, then titrate. Quenching slows the reaction abruptly so the concentration at that time can be found:

- rapid cooling in _____
- removing the _____ (e.g. neutralising H^+ with $NaHCO_3$)
- adding a large volume of cold water to _____

8.3 Clock reactions

Time taken, t, for a sudden visible change.

- **Sulfur**: $S_2O_3^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O$, time for the X to be hidden
- **Iodine clock**: fixed, small amount of $S_2O_3^{2-}$ removes I_2 as it forms, blue-black with starch appears once all $S_2O_3^{2-}$ is used up

A **fixed amount** of product forms in every run → rate $\propto \frac{1}{t}$

Disappearance of colour: the amount of coloured reactant varies between runs, so rate = $\frac{[\text{coloured reactant}]}{t}$, it _____ be simplified to 1/t.

9 Initial Rates Method

9.1 Initial rates

WORKED EXAMPLE The initial rates of $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ were measured at different concentrations. Find the rate equation and the rate constant.

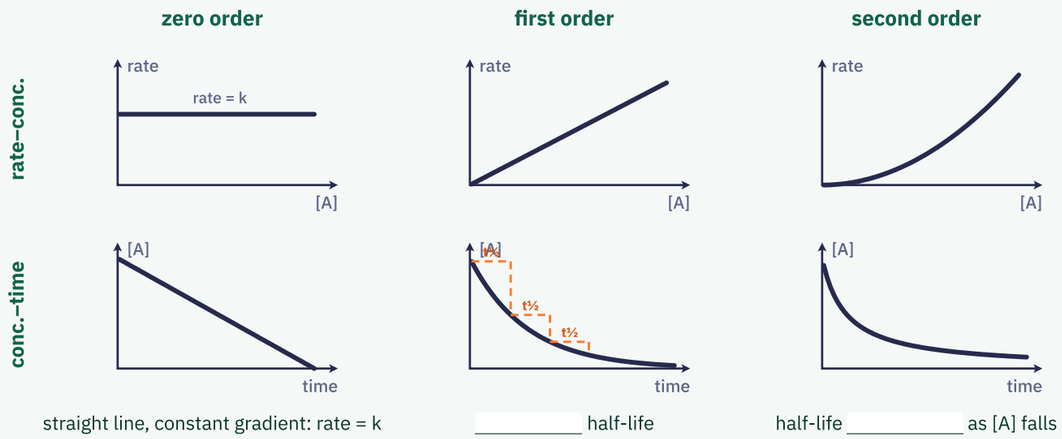
Expt	[NO] / mol dm⁻³	[O₂] / mol dm⁻³	rate / mol dm⁻³ h⁻¹
1	0.001	0.001	7×10^{-6}
2	0.001	0.002	14×10^{-6}
3	0.001	0.003	21×10^{-6}
4	0.002	0.003	84×10^{-6}

1. Let rate = $k[NO]^x[O_2]^y$. Choose two experiments where only one concentration changes.
2. Expts 1 and 2: $\frac{\text{rate 2}}{\text{rate 1}} = \frac{k(0.001)^x(0.002)^y}{k(0.001)^x(0.001)^y} \rightarrow \frac{14}{7} = 2^y \rightarrow y =$ ____
3. Expts 3 and 4: $\frac{\text{rate 4}}{\text{rate 3}} = \frac{k(0.002)^x(0.003)^y}{k(0.001)^x(0.003)^y} \rightarrow \frac{84}{21} = 2^x \rightarrow x =$ ____
4. rate = _____
5. Expt 1: $7 \times 10^{-6} = k(0.001)^2(0.001) \rightarrow k =$ _____

EXAM TIP Always deduce orders with the **ratio method** above, choosing two experiments where only one concentration changes. Describing it in words ("when $[O_2]$ doubles, rate doubles") is easy to phrase wrongly, and fails when more than one concentration changes.

Volumes instead of concentrations: water is added to keep the _____, so [reactant] in the mixture ∝ volume of reactant used. Relative rate = 1/t.

10 Graphical Methods



straight line, constant gradient: rate = k | _____ half-life | half-life _____ as [A] falls

- From a concentration–time graph: **linear** → zero order, **curve** → check the half-lives
- Rate–conc. for second order: plot rate against $[A]^2$ to get a straight line through the origin

10 Graphical Methods (continued)

10.1 Half-life

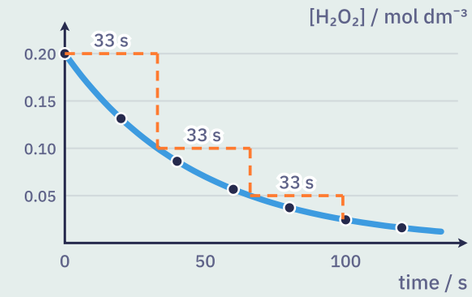
DEFINITION **Half-life, t½**: the time taken for the concentration of a reactant to fall to _____ of its initial value.

$$\text{First order: } t_{½} = \frac{\ln 2}{k}$$

- Any point may be taken as the "initial" concentration, half-lives need not be consecutive
- Half-lives must be read from a _____, not from the data table

time	[reactant]	[product]
0	100%	0%
1 t½	50%	_____
2 t½	25%	_____
3 t½	12.5%	_____

WORKED EXAMPLE The decomposition of hydrogen peroxide, $2H_2O_2 \rightarrow 2H_2O + O_2$, was followed over time. Use the graph to find the order with respect to H_2O_2 and the rate constant.



Rate decreases with a _____ _____ ∴ first order w.r.t. H_2O_2

rate = $k[H_2O_2]$, $k = \frac{\ln 2}{33} =$ _____

11 Pseudo Order

B in large excess (≥ 10 × [A]): why is rate independent of [B]?

1. B is in large excess
2. → only a _____ of B is used up
3. → [B] remains approximately _____
4. → rate appears independent of [B]

rate = $k'[A]^m$, where $k' =$ _____

Also applies to a solvent (e.g. H_2O in hydrolysis) or a catalyst: its order cannot be found.

WORKED EXAMPLE $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$ is run with CH_3Br in large excess (1.5 mol dm⁻³) and $[OH^-] = 0.01$ mol dm⁻³. The initial rate is 8.33×10^{-5} mol dm⁻³ min⁻¹. The $[OH^-]$–time graph has a constant half-life, and repeating with $[CH_3Br] \times 1.5$ makes the initial rate 1.5 times faster. Find the rate equation and k.

1. **Continuous**: $[OH^-]$–time graph has a constant t½ → _____ order w.r.t. OH^-
2. **Initial rates**: $\frac{\text{rate 2}}{\text{rate 1}} = \frac{k(1.5 \times 1.5)^m}{k(1.5)^m} \rightarrow 1.5 = 1.5^m \rightarrow m = 1$: first order w.r.t. CH_3Br
3. rate = $k[CH_3Br][OH^-]$, so $8.33 \times 10^{-5} = k(1.5)(0.01)$
4. k = _____