Topic 16: Kinetics II

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

16.1

Understand the terms: rate of reaction, rate equation, order, overall order, rate constant, half-life, rate-determining step, activation energy, catalysts.

Rate of reaction: change in concentration per unit time (mol dm^{-3} s^{-1}).

Rate equation: rate = $k[A]^m[B]^n$ – determined experimentally only. Cannot be deduced from the balanced equation.

Order with respect to A: the power m to which [A] is raised in the rate equation.

Overall order: sum of all individual orders (m + n + ...).

Rate constant (k): the proportionality constant in the rate equation. Its value depends on temperature (increases with T) and is independent of concentration.

Half-life (t½): the time taken for the concentration of a reactant to halve. For first-order reactions, t½ is constant (independent of starting concentration).

Rate-determining step (rds): the slowest step in a multi-step reaction mechanism. It controls the overall rate.

Activation energy (Ea): minimum energy required for a successful collision.

Heterogeneous catalyst: different phase from reactants (e.g. solid/gas). Homogeneous catalyst: same phase as reactants (e.g. both aqueous).

16.2

Be able to determine and use rate equations of the form rate = $k[A]^m[B]^n$, where m and n are 0, 1 or 2.

Determining order from initial rate data:

- [A] doubles, rate unchanged → zero order in A (m = 0)
- [A] doubles, rate doubles → first order in A (m = 1)
- [A] doubles, rate quadruples → second order in A (m = 2)
- [A] triples, rate ×9 → second order in A

Calculating k: substitute known values of rate and concentrations into the rate equation and rearrange.

Units of k depend on overall order:

- Zero order: mol dm^{-3} s^{-1}
- First order: s^{-1}
- Second order: dm^3 mol^{-1} s^{-1}

Always work out units of k by substituting units into the rate equation and simplifying.

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16.3 Be able to select and justify suitable experimental techniques to obtain rate data: (i) titration, (ii) colorimetry, (iii) mass change, (iv) volume of gas, (v) others.

(i) Titration (titrimetric method): remove fixed-volume aliquots at timed intervals, quench the reaction (e.g. by adding to ice-cold water or excess $NaHCO_3$), then titrate to find the concentration of a reactant or product. Used when a reactant or product can be titrated (e.g. I_2/propanone reaction).

(ii) Colorimetry: measure absorbance/transmission if a coloured species is involved (e.g. I_2 is brown, MnO_4^- is purple). Beer-Lambert Law: absorbance is proportional to concentration.

(iii) Mass change: place the reaction on a balance. If a gas is produced, mass decreases over time. Simple but gas may escape before being measured.

(iv) Gas volume: collect gas evolved in a gas syringe or over water. Record volume at timed intervals.

(v) Other methods: conductivity (if ionic concentration changes), pH measurement (if H^+ produced or consumed), clock reactions (time for a visible change – 1/time ≈ initial rate).

16.4 Understand experiments to investigate rates by: (i) initial-rate method, (ii) continuous monitoring.

(i) Initial-rate method: carry out multiple separate experiments, each with a different initial concentration of one reagent (keeping all others constant). Measure the initial rate for each (e.g. from 1/time for a clock reaction). Compare rates to deduce the order with respect to each reactant. Advantage: simple to set up. Disadvantage: only gives information at t = 0.

(ii) Continuous monitoring: follow the reaction over time in a single experiment (e.g. measuring absorbance, gas volume, or mass at regular intervals). Plot concentration vs time or volume vs time. Can determine order from the shape of the curve and half-life. Advantage: gives full time-course data. Disadvantage: requires equipment that can monitor continuously.

16.5 Be able to calculate rate and half-life of a first-order reaction from a concentration-time or volume-time graph.

Rate at time t: draw a tangent to the concentration-time curve at time t. The gradient of the tangent (taking care with sign and units) = the rate at that instant.

Half-life: read off successive half-lives from the concentration-time graph. For a first-order reaction, each half-life is equal (constant t½). E.g. if [A] goes from 1.0 → 0.5 mol dm^{-3} in 20 s, and from 0.5 → 0.25 mol dm^{-3} in another 20 s → first order ($t_{½}$ = 20 s, constant).

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16.6 Be able to deduce order (0, 1 or 2) from: (i) concentration-time graph, (ii) rate-concentration graph.

(i) From concentration-time graphs:

- Zero order: straight line (constant rate of decrease in concentration)
- First order: exponential decay curve (constant half-life)
- Second order: steeper curve that decreases more slowly at lower concentrations

(ii) From rate-concentration graphs:

- Zero order: horizontal line (rate does not change with concentration)
- First order: straight line through the origin (rate [A])
- Second order: upward curve through the origin (rate $[A]^2$)

16.7 Be able to deduce order from initial-rate data.

Compare experiments where only ONE concentration changes at a time (all others constant):

- [A] doubles, rate unchanged → zero order in A
- [A] doubles, rate doubles → first order in A
- [A] doubles, rate quadruples → second order in A
- [A] triples, rate ×9 → second order in A

Repeat the analysis for each reactant separately, then write the full rate equation combining all orders.

16.8 Understand how to: (i) obtain data for the acid-catalysed iodination of propanone, (ii) use data to predict species in the rds, (iii) deduce a mechanism.

Reaction: $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ (catalysed by H^+).

Experimentally determined rate equation: rate = $k[CH_3COCH_3][H^+]$

The rate is zero order in $[I_2]$ – iodine does NOT appear in the rate equation.

This means I_2 is not involved in the rate-determining step. The rds involves only propanone and H^+.

Proposed mechanism:

1. H^+ protonates propanone (slow, rds) – involves propanone and H^+ → consistent with rate equation
2. Enolisation (fast step)
3. Reaction with I_2 (fast step) – since this is after the rds, $[I_2]$ does not affect the overall rate

This explains why the reaction is zero order in I_2.

16.9 Be able to deduce a rate-determining step from a rate equation and vice versa.

The rate-determining step contains the species that appear in the rate equation, in the same stoichiometric quantities as their orders.

E.g. if rate = $k[A][B]$: the rds involves one molecule of A and one molecule of B.

If rate = $k[A]^2$: the rds involves two molecules of A (or A appears in a step prior to the rds as well).

Conversely: given a proposed mechanism with a designated slow step, write the rate equation directly from the species in the rds.

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16.10 Be able to deduce a reaction mechanism from the rate equation and stoichiometric equation.

Method:

1. Write the rate equation from experimental data.
2. Identify which species are in the rds (those appearing in the rate equation).
3. The rds + subsequent fast steps must together give the overall stoichiometric equation.
4. Propose a mechanism: write the rds first (slow), then fast step(s) to account for remaining reactants/products.
5. Check: all species in the mechanism must balance, and the sum of all steps must give the overall equation.

16.11 Understand that rate equations for halogenoalkane hydrolysis provide evidence for SN1 or SN2 mechanisms.

Primary halogenoalkanes: rate = k[halogenoalkane][OH^-] → SN2 mechanism.

Both species are in the rds → one-step, bimolecular. The nucleophile (OH^-) attacks from the opposite side to the leaving group simultaneously (backside attack). Results in inversion of configuration at the carbon centre.

Tertiary halogenoalkanes: rate = k[halogenoalkane] → SN1 mechanism.

Only the halogenoalkane is in the rds → two-step, unimolecular.

Step 1 (slow, rds): C–X bond breaks heterolytically to form a carbocation + X^-.

Step 2 (fast): nucleophile attacks the carbocation from either side.

SN1 produces a racemic mixture because the planar carbocation can be attacked from both sides equally. SN2 produces inversion of configuration.

16.12 Be able to use graphical methods to find activation energy from experimental data.

The Arrhenius equation: $k = Ae^{-\ a}/$

Taking natural logs: ln k = ln A – Ea/RT

This is in the form y = c + mx:

- y = ln k
- x = 1/T (T in Kelvin)
- gradient = –Ea/R
- y-intercept = ln A

Method: measure k at several different temperatures. Calculate ln k and 1/T for each. Plot ln k (y-axis) vs 1/T (x-axis). Draw a line of best fit. Measure the gradient.

Ea = –gradient × R where R = 8.314 J K^{-1} mol^{-1}.

T must be in Kelvin. Ea will be in J mol^{-1} – divide by 1000 for kJ mol^{-1}.

Rates of Reaction – Iodine-Propanone Reaction (Titrimetric Method)

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Investigating a Clock Reaction (Harcourt-Esson / Iodine Clock)

Finding the Activation Energy of a Reaction

ABOUT THESE NOTES

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