3.1.9 Rate Equations

★ A-LEVEL ONLY — not examined at AS level

3.1.9.1 *Rate equations: rate = k[A]m[B]n. Orders of reaction. Rate constant k and units. Half-life of first-order reactions.*

Rate equation: rate = k[A]m[B]n where m and n are orders of reaction (found experimentally, NOT from equation).

Order: power of a reactant in the rate equation. Overall order = m + n.

Rate constant k: the constant of proportionality. Increases with temperature (more molecules have E ≥ Ea).

Units of k: derived by substituting (mol dm■³)■ min■¹ — depend on overall order:

Zero order: mol dm■³ s■¹

First order: s■¹

Second order: mol■¹ dm³ s■¹

Half-life (t½): time for concentration of reactant to halve. For first order: t½ = ln2/k — constant (independent of starting concentration). Plot [A] vs time: t½ is constant if first order.

3.1.9.2 *Determination of orders from concentration–time and rate–concentration graphs.*

From [A]–time graphs:

Zero order: straight line (constant rate).

First order: exponential decay — constant half-life.

Second order: steeper than exponential — half-life doubles each time.

From rate–concentration graphs (initial rates method):

Zero order: horizontal line.

First order: straight line through origin.

Second order: parabola (curve).

Initial rates method: vary [A], keep others constant. Measure initial rate from gradient at t=0. Doubling [A]: rate unchanged = 0 order; rate doubles = 1st order; rate quadruples = 2nd order.

3.1.9.3 *Effect of temperature on k: Arrhenius equation k = Ae^(–Ea/RT). Graphical determination of Ea.*

Arrhenius equation: k = Ae^(–Ea/RT)

A = pre-exponential (frequency) factor, Ea = activation energy, R = 8.314 J K■¹ mol■¹, T in K.

Linearised form: ln k = –Ea/R × (1/T) + ln A

Plot ln k (y-axis) vs 1/T (x-axis): straight line with gradient = –Ea/R.

Ea = –gradient × R (in J mol■¹, convert to kJ by ÷1000).

As T increases, k increases — explains why rate increases with temperature.

3.1.9.4	*Rate-determining step: identify from rate equation. Propose mechanisms consistent with the rate equation.*

Rate-determining step (RDS): the slowest step in a multi-step mechanism — determines the overall rate.

The rate equation includes only species involved in the RDS (or steps before it).

If rate = k[A][B]: both A and B appear in the RDS — the mechanism involves A and B colliding in the slowest step.

If rate = k[A]² and B is a reactant: B must be introduced after the RDS. A appears twice — perhaps two A molecules react in the slow step.

Propose mechanisms: must be consistent with the stoichiometry, the rate equation, and the overall equation.