A-LEVEL CHEMISTRY • EXERCISE SHEET

26.1 Rate equations, orders of reaction and rate constants

Name: _____ Class: _____ Date: _____ **Total: 31 marks**

KEY WORDS rate equation 速率方程 • initial rate 初始速率 • rate constant 速率常数 • order of reaction 反应级数 • half-life 半衰期

Objective

Build the skills to answer exam questions on **rate equations** 速率方程 — **order of reaction** 反应级数, the **rate constant** 速率常数, **half-life** 半衰期, and the **rate-determining step** 决速步.

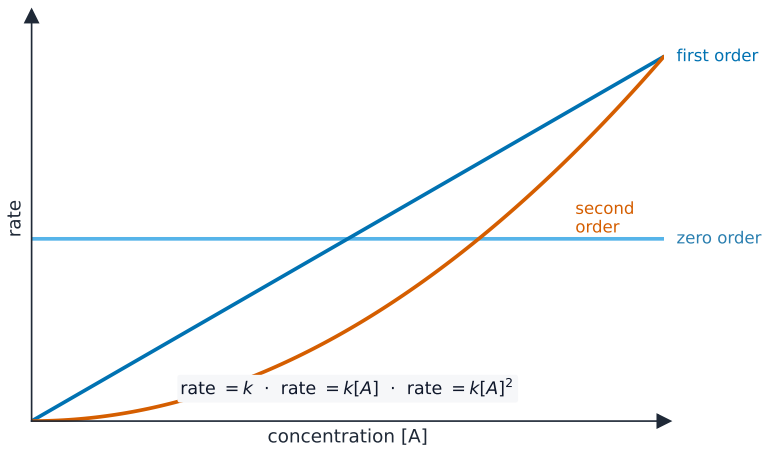
You must be able to:

- deduce orders from initial-rates data or concentration–time graphs and construct a rate equation
- use first-order half-life and calculate the rate constant
- deduce a rate equation from a mechanism and identify the rate-determining step

1 Worked examples

■ Rate equation and order

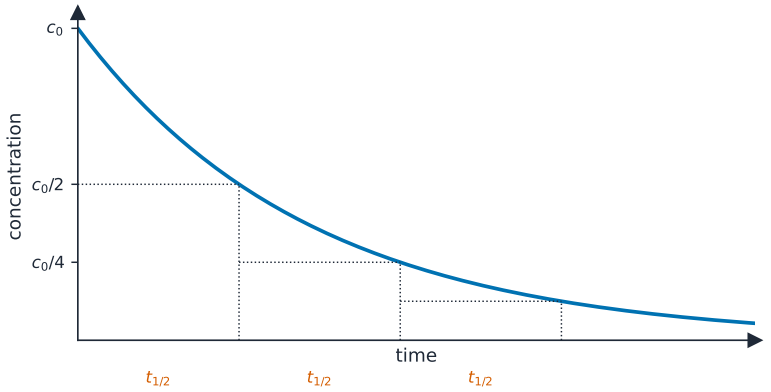
rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$ — found only by **experiment**. Order m/n = 0, 1 or 2; overall order = $m + n$.



Deduce the order from the shape of the graphs, or from initial-rates data

Initial rates: if doubling [A] doubles the rate → 1st order; if it quadruples → 2nd order; no change → 0 order.

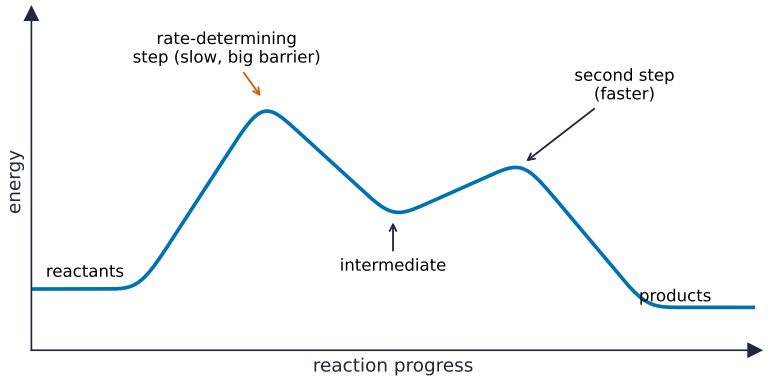
■ Half-life and rate constant



$$t_{1/2} = \frac{\ln 2}{k} \quad \text{(constant for 1st order)}$$

*A first-order reaction has a **constant** half-life (independent of concentration):* $k = 0.693/t_{1/2}$

Mechanism and rate-determining step



rate-determining step = highest E_a barrier (slowest elementary step)

*The rate equation reflects the species in the **rate-determining (slowest) step**; an intermediate is made then used up*

Finding the orders, and what each graph tells you

The rate equation is rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$, where m and n are the **orders** with respect to each reactant. They are found **experimentally** — never from the stoichiometric equation. The **overall order** is $m + n$, and it fixes the units of k:

Overall order	Units of k
0	$\mathrm{mol\ dm^{-3}\ s^{-1}}$
1	$\mathrm{s^{-1}}$
2	$\mathrm{mol^{-1}\ dm^{3}\ s^{-1}}$
3	$\mathrm{mol^{-2}\ dm^{6}\ s^{-1}}$

Derive them rather than memorising: rearrange the rate equation for k and cancel.

From initial-rate data. Compare two experiments in which only ONE concentration changes:

- concentration $\times 2$, rate unchanged $\rightarrow$ **zero order**;
- concentration $\times 2$, rate $\times 2$ $\rightarrow$ **first order**;
- concentration $\times 2$, rate $\times 4$ $\rightarrow$ **second order**.

From graphs, which the exam asks you to recognise:

Graph	Zero order	First order	Second order
concentration against time	straight line, constant gradient	curve with a **constant half-life**	curve, half-life doubles each time
rate against concentration	horizontal line	straight line through the origin	upward curve

The **constant half-life** is the single most useful signal: measure $t_{1/2}$ from the first half of the decay and again from the next, and if they agree the reaction is first order in that reactant.

Worked example. In three experiments, doubling [A] doubles the rate; tripling [B] multiplies the rate by nine. Give the rate equation, the overall order and the units of k.

1. [A]: rate $\propto [\mathrm{A}]^1$, so first order.
2. [B]: $3^n = 9$, so $n = 2$, second order.
3. rate $= k[\mathrm{A}][\mathrm{B}]^2$; overall order $= 3$.
4. $k = \dfrac{\text{rate}}{[\mathrm{A}][\mathrm{B}]^2} = \dfrac{\mathrm{mol\ dm^{-3}\ s^{-1}}}{(\mathrm{mol\ dm^{-3}})^3} = \mathrm{mol^{-2}\ dm^{6}\ s^{-1}}$.

The rate-determining step. The orders give the composition of the slowest step: an order of 1 in A and 2 in B means the rate-determining step involves one A and two B. A species that appears in the equation but NOT in the rate equation enters after the rate-determining step — a catalyst, or a fast subsequent step.

2 Practice

2.1 State what is meant by the **overall order** of a reaction. [1]

2.2 State how the half-life of a first-order reaction changes as the reaction proceeds. [1]

2.3 State the units of k for a reaction that is first order overall, and show how you obtained them. [2]

2.4 A concentration–time graph is a straight line. State the order and explain how you know. [2]

2.5 Explain why the orders cannot be deduced from the stoichiometric equation. [2]

3 Exam-style questions

3.1 A reaction is first order in A and second order in B. Its overall order is: [1]

- **A** 1
- **B** 2
- **C** 3
- **D** 0

3.2 A first-order reaction has a half-life of 50 s. Its rate constant is ($k = 0.693/t_{1/2}$): [1]

- **A** 0.014 s^{-1}
- **B** 0.0139 s^{-1}
- **C** 36 s^{-1}
- **D** 50 s^{-1}

3.3 Experiment data for $A + B \rightarrow$ products:

[A]	[B]	initial rate
0.10	0.10	2.0×10^{-3}
0.20	0.10	4.0×10^{-3}
0.20	0.20	1.6×10^{-2}

(a) Deduce the order with respect to A and to B. [2]

(b) Write the rate equation and calculate the rate constant k (with units). [3]

3.4 The rate equation for a reaction is rate $= k[X]$. A proposed mechanism has two steps. State which step must be rate-determining and why. [2]

3.5 The reaction $P + 2Q \rightarrow R$ was investigated at constant temperature. The initial rates are shown.

experiment	[P] / mol dm^{-3}	[Q] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	4.0×10^{-4}
3	0.20	0.30	3.6×10^{-3}

(a) Deduce the order with respect to P, showing which experiments you used. [2]

(b) Deduce the order with respect to Q, showing your reasoning. [2]

(c) Write the rate equation and state the overall order. [2]

(d) Calculate the value of k and give its units. [3]

(e) The accepted mechanism has a rate-determining step involving one P and two Q. Explain how your rate equation supports this. [2]

(f) A concentration–time graph for a different reactant, S, shows successive half-lives of 40 s, 40 s and 41 s. Deduce the order with respect to S and explain your reasoning. [3]

Solutions

2.1 the sum of the orders with respect to each reactant ($m + n$).

2.2 it stays constant (independent of concentration).

2.3 Rearranging, $k = \dfrac{\text{rate}}{[\text{A}]}$, so the units are $\dfrac{\text{mol dm}^{-3}\,\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$.

2.4 Zero order; the rate is independent of concentration, so the concentration falls at a constant rate and the graph has a constant gradient.

2.5 The orders depend on the mechanism, specifically on the species in the rate-determining step; the stoichiometric equation only gives the overall ratio of reactants to products, and says nothing about the steps.

3.1 C. Overall order = 1 + 2 = 3.

3.2 B. $k = 0.693/50 = 0.0139\ \text{s}^{-1}$.

3.3 (a) A: doubling [A] (rows 1→2) doubles the rate → first order; B: doubling [B] (rows 2→3) makes the rate ×4 → second order.
(b) rate = $k[\text{A}][\text{B}]^2$; $k = \dfrac{2.0 \times 10^{-3}}{(0.10)(0.10)^2} = 2.0\ \text{mol}^{-2}\text{dm}^6\text{s}^{-1}$.

3.4 the first step (or whichever contains only X) must be rate-determining; because only X appears in the rate equation, so the slow step involves X.

3.5 (a) Experiments 1 and 2: [Q] is constant, [P] doubles and the rate doubles; so the reaction is first order in P.
(b) Experiments 2 and 3: [P] is constant, [Q] trebles and the rate rises by a factor of 9; since $3^2 = 9$, the reaction is second order in Q.
(c) rate = $k[\text{P}][\text{Q}]^2$; overall order 3.
(d) Using experiment 1: $k = \dfrac{2.0 \times 10^{-4}}{(0.10)(0.10)^2} = 2.0$; units $\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$.
(e) The rate equation is first order in P and second order in Q, and the orders give the number of each species in the rate-determining step, so one P and two Q is exactly what the equation predicts.
(f) First order in S; the half-life is constant within experimental error, and a constant half-life is the characteristic of a first-order decay.