

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.

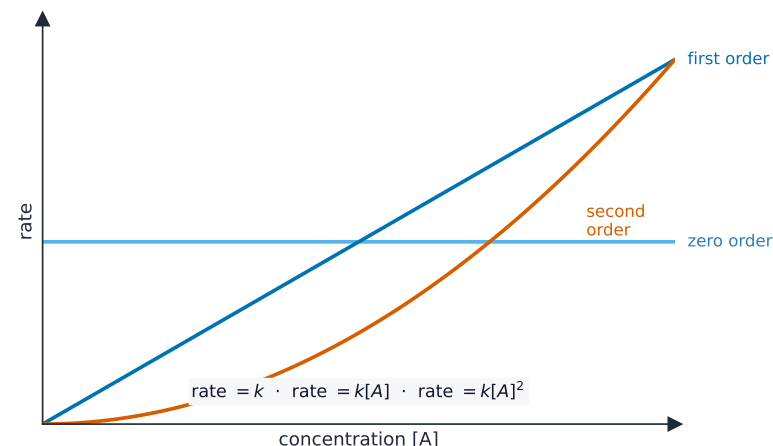
You must be able to:

- 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

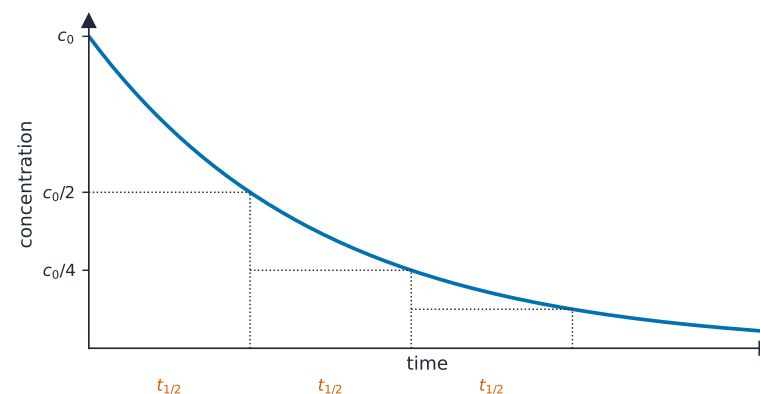
rate = $k[A]^m[B]^n$ — found only by **experiment**. Order $m/n = 0, 1$ or 2 ; overall order = $m + n$.



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.

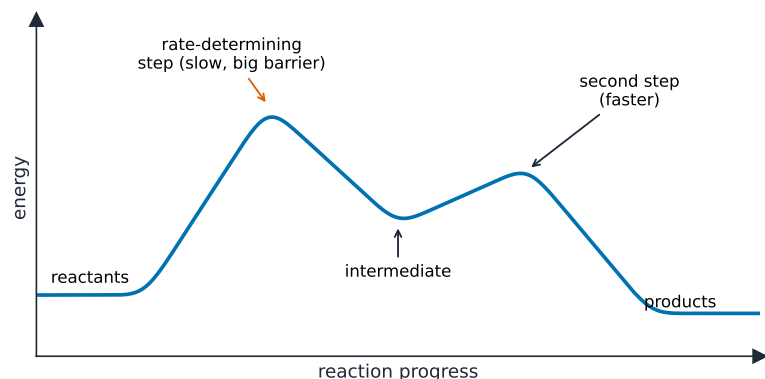
■ Half-life and rate constant



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

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 $\text{rate} = k[\text{A}]^m[\text{B}]^n$, 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	$\text{mol dm}^{-3} \text{s}^{-1}$
1	s^{-1}
2	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
3	$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

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 $[\text{A}]$ doubles the rate; tripling $[\text{B}]$ multiplies the rate by nine. Give the rate equation, the overall order and the units of k .

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

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

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

[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 $\text{rate} = k[X]$. 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 / $\text{mol dm}^{-3} \text{ s}^{-1}$
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]
