

26.1 Rate equations, orders of reaction and rate constants

Name: _____ Class: _____ Date: _____

Total: 11 marks

KEY WORDS rate equation 速率方程 • rate constant 速率常数 • initial rate 初始速率 • 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.

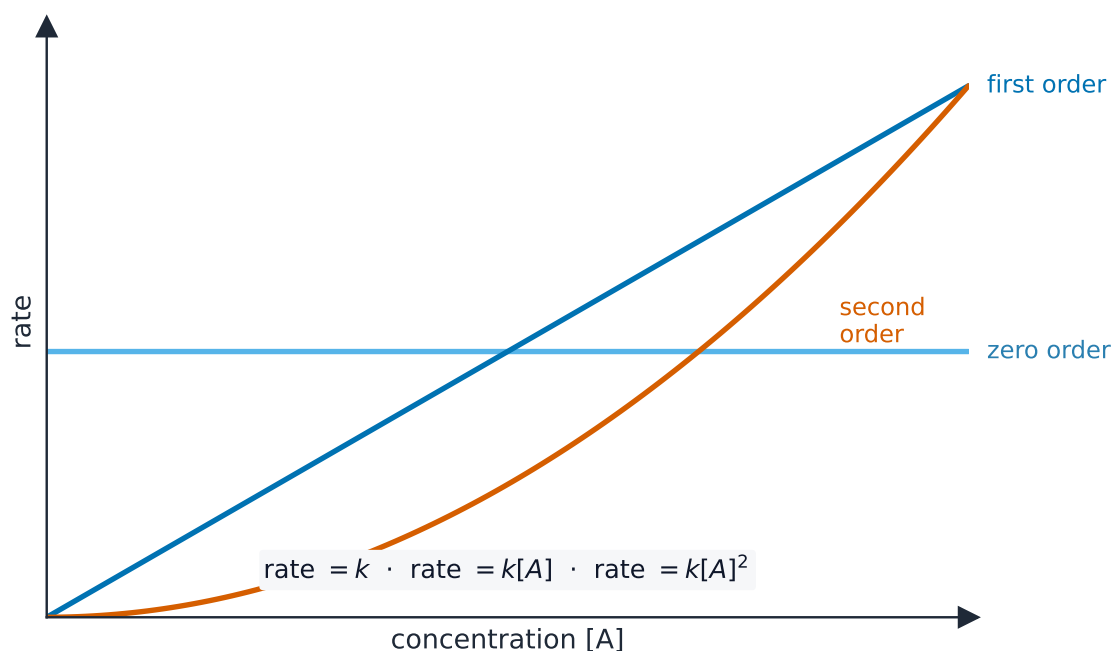
You must be able to:

- 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

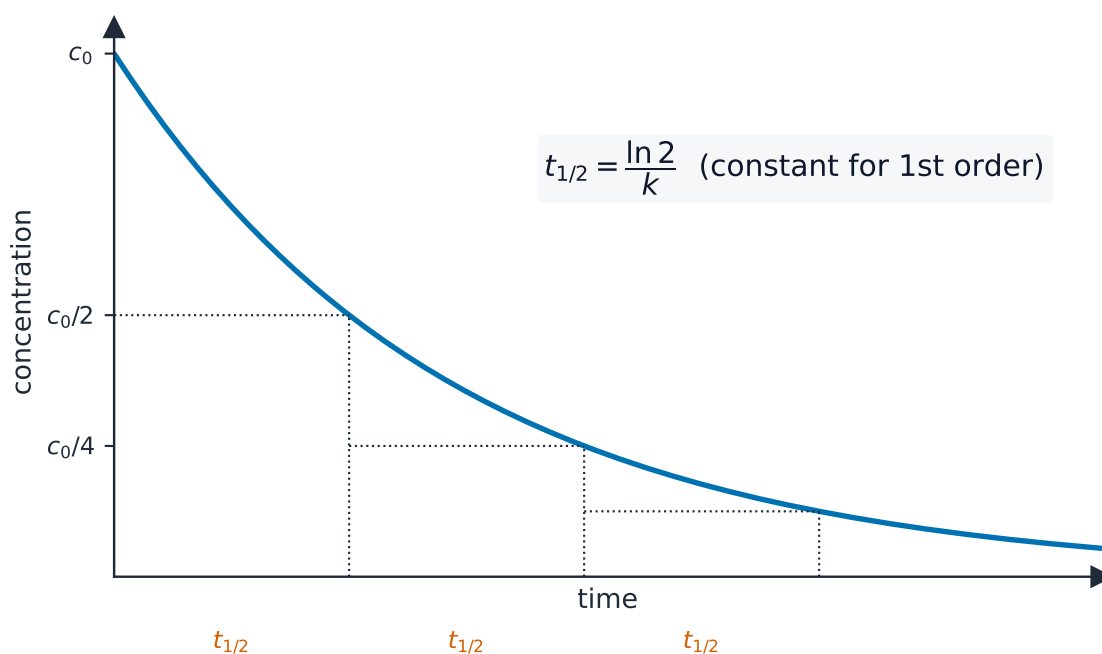
rate = $k[A]^m[B]^n$ — found only by **experiment**. Order $m/n = 0, 1$ or 2 ; overall order = $m + n$.



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

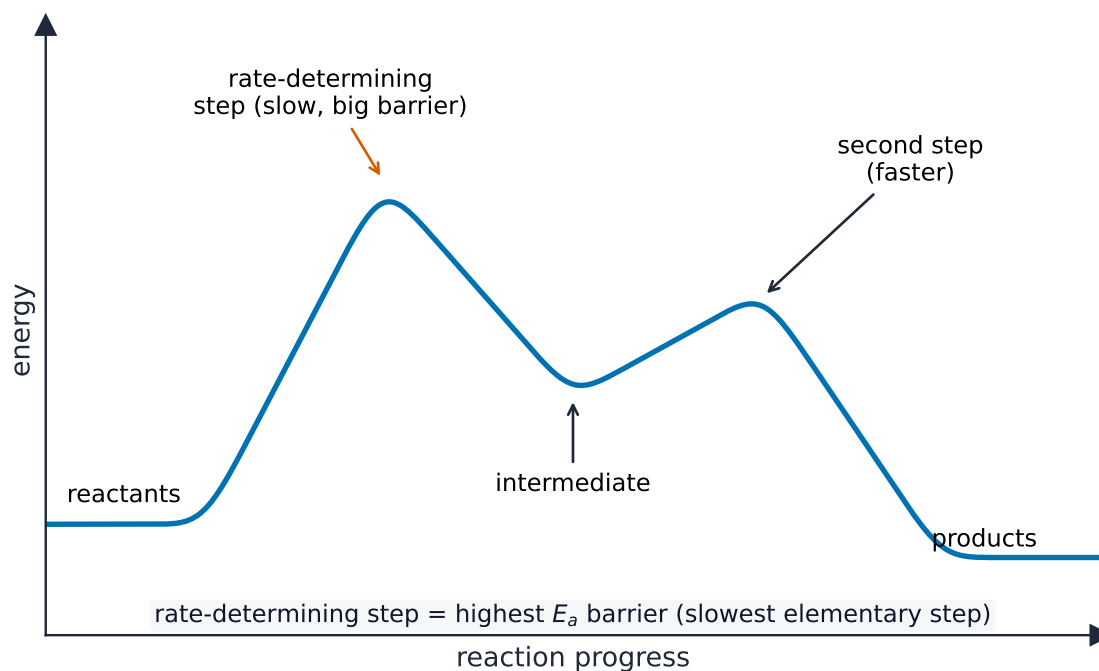
Initial rates: if doubling [A] doubles the rate $\rightarrow$ 1st order; if it quadruples $\rightarrow$ 2nd order; no change $\rightarrow$ 0 order.

■ Half-life and rate constant



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

■ Mechanism and rate-determining step



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

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]

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 $A + B \rightarrow \text{products}$:

[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]

Solutions

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

2.2 it stays constant (independent of concentration).

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 $\times 4$ → second order.

(b) rate = $k[A][B]^2$; $k = \frac{2.0 \times 10^{-3}}{(0.10)(0.10)^2} = 2.0 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$.

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.