Exercise walk-through

Simple rate equations, orders of reaction and rate constants ▪ 26.1

eXercise

You must be able to

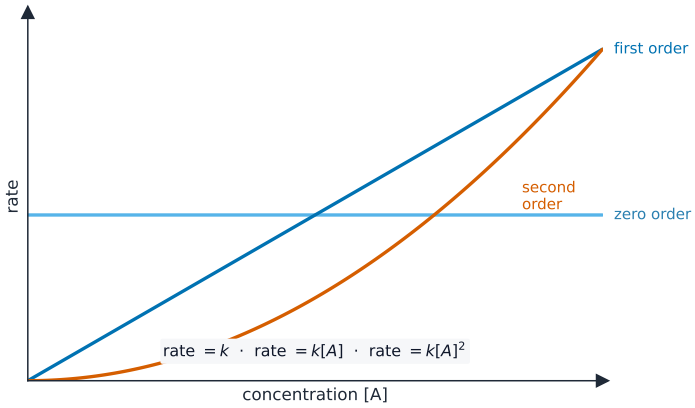
- deduce orders from initial-rates data or concentration–time graphs and construct a rate equation
- use first-order half-life and calculate the rate constant
- deduce a rate equation from a mechanism and identify the rate-determining step

Method — 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 $= m + n$.

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

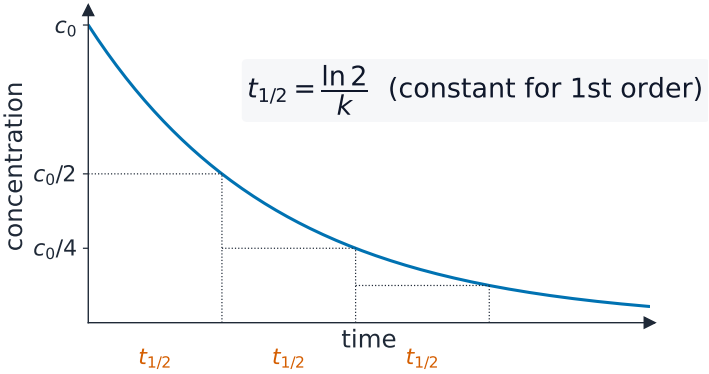
Method — Rate equation and order



Concentration–time and rate–concentration graphs for zero, first and second order

Method — Half-life and rate constant

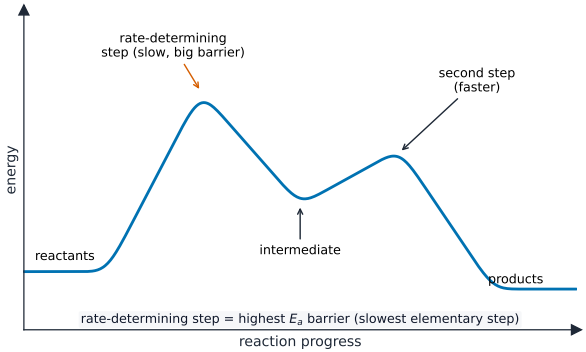
*A first-order reaction has a **constant** half-life (independent of concentration):*
$k = 0.693/t_{1/2}$



A first-order decay with a constant half-life

Method — Mechanism and rate-determining step

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



A reaction profile with the slowest (rate-determining) step the highest barrier

Practice 2.1 ▪ 1 mark

State what is meant by the **overall order** of a reaction.

Solution 2.1

Worked steps

the sum of the orders with respect to each reactant $(m + n)$ B1.

Practice 2.2 ▪ 1 mark

State how the half-life of a first-order reaction changes as the reaction proceeds.

Solution 2.2

Method: Half-life and rate constant

Worked steps

it stays constant (independent of concentration) B1.

Exam-style 3.1 ▪ 1 mark

A reaction is first order in A and second order in B. Its overall order is:

A 1

B 2

C 3

D 0

Solution 3.1

Method: Rate equation and order

A 1

B 2

C 3 ✓

D 0

Worked steps

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

Exam-style 3.2 ▪ 1 mark

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

A 0.014 s^{-1}

B 0.0139 s^{-1}

C 36 s^{-1}

D 50 s^{-1}

Solution 3.2

Method: Half-life and rate constant

A 0.014 s^{1}

B 0.0139 s^{1} ✓

C 36 s^{1}

D 50 s^{1}

Worked steps

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

Exam-style 3.3 ▪ 2 marks

Experiment data for $\mathrm{A} + \mathrm{B} \rightarrow$ 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.
(b) Write the rate equation and calculate the rate constant k (with units).

Solution 3.3

Method: Rate equation and order

Worked steps

(a) A: doubling [A] (rows 1→2) doubles the rate → first order M1; B: doubling [B] (rows 2→3) makes the rate ×4 → second order M1 A1 *implicit*.

(b) rate $= k[\mathrm{A}][\mathrm{B}]^2$ M1; $k = \dfrac{2.0 \times 10^{-3}}{(0.10)(0.10)^2} = 2.0\ \mathrm{mol^{-2}dm^6s^{-1}}$ M1 A1.

Exam-style 3.4 ▪ 2 marks

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

Solution 3.4

Method: Mechanism and rate-determining step

Worked steps

the first step (or whichever contains only X) must be rate-determining **M1**; because only X appears in the rate equation, so the slow step involves X **A1**.