Exercise walk-through

Reaction Mechanism and Rate Law ▪ 5.8

eXercise

You must be able to

- write the rate law from the **rate-determining step** when it is first
- confirm the mechanism is consistent with an experimental rate law
- avoid putting intermediates in the final rate law

Method — Slow first step → easy rate law

If the **first** step is the slow (rate-determining) step, its reactants are the original reactants, so the rate law comes straight from its molecularity.

Method — A worked example

Mechanism: Step 1 (slow) $H_2 + ICl \rightarrow HI + HCl$; Step 2 (fast) $HI + ICl \rightarrow I_2 + HCl$. The slow step gives

$$\text{rate} = k[H_2][ICl].$$

Method — Consistency check

A proposed mechanism is **valid** only if its predicted rate law matches the **experimental** one and its steps add to the overall equation.

Method — No intermediates in the rate law

The final rate law may contain only **reactants** (or catalysts), never intermediates. If the slow step contains an intermediate, you must substitute for it (next subtopic).

Practice 2.1 ▪ 1 mark

If the slow step is $A + B \rightarrow X$, write the rate law.

Solution 2.1

Method: A worked example

Worked steps

rate $= k[\mathrm{A}][\mathrm{B}]$ B1.

Practice 2.2 ▪ 1 mark

Can the final rate law contain an intermediate?

Solution 2.2

Method: No intermediates in the rate law

Worked steps

No B1.

Practice 2.3 ▪ 1 mark

A slow first step is $2\mathrm{NO} \rightarrow \mathrm{N_2O_2}$. Write its rate law.

Solution 2.3

Method: A worked example

Worked steps

rate $= k[\mathrm{NO}]^2$ B1.

Exam-style 3.1 ▪ 1 mark

For a mechanism with a slow **first** step, the rate law is written from

A the overall equation

B the slow first step's molecularity

C the fast step

D the products

Solution 3.1

A the overall equation

B the slow first step's molecularity ✓

C the fast step

D the products

Worked steps

B — the slow first step's molecularity.

Exam-style 3.2 ▪ 2 marks

A mechanism for $NO_2 + CO \rightarrow NO + CO_2$ is: Step 1 (slow) $NO_2 + NO_2 \rightarrow NO_3 + NO$; Step 2 (fast) $NO_3 + CO \rightarrow NO_2 + CO_2$.
(a) Write the predicted rate law.
(b) The experimental rate law is rate $= k[NO_2]^2$. Is the mechanism consistent?

Solution 3.2

Method: A worked example

Worked steps

(a) rate $= k[\mathrm{NO_2}]^2$ M1 A1. (b) Yes — it matches the experimental rate law B1.

Exam-style 3.3 ▪ 2 marks

Explain why the concentration of CO does **not** appear in the rate law for the mechanism in 3.2.

Solution 3.3

Worked steps

CO reacts only in the fast **second** step, after the rate-determining step; the slow step (which sets the rate) does not involve CO, so it is absent from the rate law M1 A1.