Exercise walk-through

Pre-Equilibrium Approximation ▪ 5.9

eXercise

You must be able to

- recognise when the slow step contains an **intermediate** 中间体
- substitute for the intermediate using the fast pre-equilibrium
- write a rate law with only reactants

Method — The problem

If the **first** step is fast and reversible and the **second** (slow) step uses an **intermediate**, the raw rate law would contain that intermediate — which is not allowed.

Method — Pre-equilibrium substitution

The fast first step reaches equilibrium: forward rate = reverse rate. Solve that equality for the intermediate's concentration, then substitute it into the slow step's rate law.

Method — A worked outline

Step 1 (fast) $2\mathrm{NO} \rightleftharpoons \mathrm{N_2O_2}$; Step 2 (slow) $\mathrm{N_2O_2} + \mathrm{O_2} \rightarrow 2\mathrm{NO_2}$. Slow-step rate $= k[\mathrm{N_2O_2}][\mathrm{O_2}]$. From step 1's equilibrium, $[\mathrm{N_2O_2}] \propto [\mathrm{NO}]^2$, so

$$\text{rate} = k'[\mathrm{NO}]^2[\mathrm{O_2}].$$

Method — The result

The final rate law has only reactants (NO and O_2) — the intermediate has been replaced.

Practice 2.1 ▪ 1 mark

Why can't an intermediate stay in the final rate law?

Solution 2.1

Method: The result

Worked steps

It is not a measurable starting reactant; the rate law must be in terms of reactants B1.

Practice 2.2 ▪ 1 mark

In a fast equilibrium, the forward rate equals the ____ rate.

Solution 2.2

Method: Pre-equilibrium substitution

Worked steps

reverse (backward) B1.

Practice 2.3 ▪ 2 marks

If $[N_2O_2] \propto [NO]^2$, and rate $= k[N_2O_2][O_2]$, write the rate in terms of reactants.

Solution 2.3

Worked steps

rate $= k[\mathrm{NO}]^2[\mathrm{O_2}]$ M1 A1.

Exam-style 3.1 ▪ 1 mark

When the slow step contains an intermediate, you replace it using the

A overall equation

B fast pre-equilibrium step

C products

D activation energy

Solution 3.1

A overall equation

B fast pre-equilibrium step ✓

C products

D activation energy

Worked steps

B — the fast pre-equilibrium step.

Exam-style 3.2 ▪ 1 mark

Mechanism: Step 1 (fast) $A \rightleftharpoons B$ with $[B] \propto [A]$; Step 2 (slow) $B + C \rightarrow D$.
(a) Write the slow-step rate law.
(b) Substitute for the intermediate to give the overall rate law.

Solution 3.2

Method: A worked outline

Worked steps

(a) rate $= k[\mathrm{B}][\mathrm{C}]$ **B1**. (b) since $[\mathrm{B}] \propto [\mathrm{A}]$, rate $= k'[\mathrm{A}][\mathrm{C}]$ **M1** **A1**.

Exam-style 3.3 ▪ 2 marks

Explain why a fast reversible first step is called a “pre-equilibrium”.

Solution 3.3

Worked steps

The fast reversible step reaches equilibrium **before** the slow step consumes its product, so an equilibrium is established ahead of the rate-determining step M1 A1.