AP CHEMISTRY • EXERCISE SHEET

5.9 When the First Step Is Fast

Name: ____________ Class: ________ Date: __________ **Total: 10 marks**

Objective

Build the skills to answer exam questions on mechanisms with a **fast first step** (a pre-equilibrium).

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

1 Worked examples

Study these first. Each one shows the method for a question type used later —follow the steps and you can do the Practice and Exam-style questions yourself.

■ 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.

■ 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.

■ A worked outline

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

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

■ The result

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

2 Practice

Now apply the methods above.

2.1 Why can't an intermediate stay in the final rate law? [1]

2.2 In a fast equilibrium, the forward rate equals the _____ rate. [1]

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

3 Exam-style questions

3.1 When the slow step contains an intermediate, you replace it using the [1]

- **A** overall equation
- **B** fast pre-equilibrium step
- **C** products
- **D** activation energy

3.2 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. [1]

(b) Substitute for the intermediate to give the overall rate law. [2]

3.3 Explain why a fast reversible first step is called a "pre-equilibrium". [2]

4 Go further

You are now ready for the real exam questions on this subtopic:

- work through the **5.9 When the First Step Is Fast** lesson on the **Learn** page;
- read the **When the First Step Is Fast** section of the AP Chemistry handout on the **Know** page.

Solutions

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

2.2 reverse (backward).

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

3.1 **B** —the fast pre-equilibrium step.

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

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