

5.8 Finding the Rate Law From a Mechanism

Name: _____ Class: _____ Date: _____ **Total: 9 marks**

KEY WORDS rate-determining step 决速步骤 • rate law 速率方程 • intermediates 中间体
• catalyst 催化剂

Objective

Build the skills to answer exam questions on **finding the rate law from a mechanism** (slow first step).

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

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.

■ 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.

■ A worked example

Mechanism: Step 1 (slow) $\text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl}$; Step 2 (fast) $\text{HI} + \text{ICl} \rightarrow \text{I}_2 + \text{HCl}$.
The slow step gives

$$\text{rate} = k[\text{H}_2][\text{ICl}].$$

■ 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.

■ 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).

2 Practice

Now apply the methods above.

2.1 If the slow step is $\text{A} + \text{B} \rightarrow \text{X}$, write the rate law. [1]

2.2 Can the final rate law contain an intermediate? [1]

2.3 A slow first step is $2\text{NO} \rightarrow \text{N}_2\text{O}_2$. Write its rate law. [1]

3 Exam-style questions

3.1 For a mechanism with a slow **first** step, the rate law is written from [1]

- **A** the overall equation
- **B** the slow first step's molecularity
- **C** the fast step
- **D** the products

3.2 A mechanism for $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ is: Step 1 (slow) $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; Step 2 (fast) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$.

(a) Write the predicted rate law. [2]

(b) The experimental rate law is $\text{rate} = k[\text{NO}_2]^2$. Is the mechanism consistent? [1]

3.3 Explain why the concentration of CO does **not** appear in the rate law for the mechanism in 3.2. [2]

Solutions

2.1 $\text{rate} = k[\text{A}][\text{B}]$.

2.2 No.

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

3.1 B — the slow first step's molecularity.

3.2 (a) $\text{rate} = k[\text{NO}_2]^2$. (b) Yes — it matches the experimental rate law.

3.3 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.