ANSWER KEY.

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5.8 Reaction Mechanism and Rate Law

AP Chemistry | ANSWER KEY

Write each rate law from the slow step. Show how the steps add up to the overall reaction.

1. A mechanism has three steps: step 1 is fast, step 2 is slow, and step 3 is fast.

(a) Which step is the rate-determining step?

(b) Explain why the overall reaction cannot go faster than this step.

(a) Step 2, the slow step.

(b) Everything must pass through the slow step, like a highway narrowing to one lane. The bottleneck sets the rate.

2. Consider this mechanism. (L is a molecule that bonds to the metal.)

Step 1 (slow): $Mo(CO)_6 \rightarrow Mo(CO)_5 + CO$

Step 2 (fast): $Mo(CO)_5 + L \rightarrow Mo(CO)_5L$

(a) Write the overall reaction and identify the intermediate.

(b) Write the rate law.

(c) What is the order with respect to L? Explain why.

(a) Cancel $Mo(CO)_5$: $Mo(CO)_6 + L \rightarrow Mo(CO)_5L + CO$. Intermediate: $Mo(CO)_5$.

(b) rate = $k[Mo(CO)_6]$

(c) Zero order in L. L is a reactant overall, but it is used only in the fast step, so it is not in the slow step's rate law.

3. Consider this mechanism for the reaction of nitrogen monoxide with hydrogen.

Step 1 (slow): $2NO + H_2 \rightarrow N_2O + H_2O$

Step 2 (fast): $N_2O + H_2 \rightarrow N_2 + H_2O$

(a) Write the overall reaction.

(b) Write the rate law predicted by this mechanism and give the overall order.

(a) Cancel N_2O: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

(b) The slow step has two NO and one H_2: rate = $k[NO]^2[H_2]$. Overall order 2 + 1 = 3 (third order).

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4. Consider this mechanism.

Step 1 (slow): $A + X \rightarrow AX$

Step 2 (fast): $AX + B \rightarrow AB + X$

(a) Write the overall reaction. Identify the catalyst and the intermediate.

(b) Write the rate law.

(c) What happens to the rate if [X] is doubled? Explain, even though X is not in the overall equation.

(a) A + B → AB. Catalyst: X (used in step 1, made again in step 2). Intermediate: AX.

(b) rate = k[A][X]

(c) The rate doubles. X is used in the slow step, so it is in the rate law (first order in X), even though it is not used up overall.

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5. For $H_2 + 2ICl \rightarrow I_2 + 2HCl$, experiments show rate = $k[H_2][ICl]$. Which mechanism is consistent with this rate law? Justify your answer for each mechanism.

Mechanism A: Step 1 (slow): $H_2 + ICl \rightarrow HI + HCl$; Step 2 (fast): $HI + ICl \rightarrow I_2 + HCl$

Mechanism B: one step: $H_2 + 2ICl \rightarrow I_2 + 2HCl$

Mechanism A. Its steps add up to the overall equation (HI cancels), and its slow step gives rate = $k[H_2][ICl]$, which matches.

Mechanism B is one elementary step, so it predicts rate = $k[H_2][ICl]^2$, second order in ICl. That does not match, and it needs three molecules to collide at once.

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6. For $2A + B \rightarrow C$, experiments show rate = $k[A]^2$. Which step in this mechanism must be the slow step? Explain.

Step 1: $A + A \rightarrow A_2$

Step 2: $A_2 + B \rightarrow C$

Step 1. If step 1 is slow, rate = $k[A]^2$, which matches. B is zero order because it is used only in the fast step. If step 2 were slow, the rate law would contain the intermediate A_2 and B, which does not match.

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7. For $2NO_2Cl \rightarrow 2NO_2 + Cl_2$, a student writes rate = $k[NO_2Cl]^2$ "because the coefficient of NO_2Cl is 2." Experiments show the reaction is first order in NO_2Cl. Explain the student's error and propose a slow first step that fits the data.

A rate law cannot be read from the overall equation, because the overall reaction is not one elementary step. It comes from experiments or from the slow step of the mechanism.

A slow first step that fits: $NO_2Cl \rightarrow NO_2 + Cl$ (one molecule falling apart), giving rate = $k[NO_2Cl]$. A fast second step, $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$, completes it.

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