Essential Question

How does the slowest step control the rate?

The Rate-Determining Step

- The slowest step limits the overall rate
- Also called the rate-limiting step



When the First Step Is Slow

Step 1 (slow): $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2 (fast): $NO_3 + CO \rightarrow NO_2 + CO_2$



$$\text{rate} = k[NO_2]^2$$

- Rate law = rate law of the slow step

Matching the Experiment

Mechanism predicts
rate = $k[NO_2]^2$

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Experiment shows
rate = $k[NO_2]^2$

- CO is not in the rate law (zero order)
- A reasonable mechanism must:
  - add up to the overall equation
  - match the experimental rate law

Catalysts Can Appear in the Rate Law

Step 1 (slow): $H_2O_2 + I^- \rightarrow H_2O + IO^-$

Step 2 (fast): $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

$$\text{rate} = k[H_2O_2][I^-]$$

- The catalyst is used in the slow step, so it's in the rate law

Example: Rate Law from a Mechanism

Write the overall reaction and the rate law for this mechanism.

Step 1 (slow): $NO_2Cl \rightarrow NO_2 + Cl$

Step 2 (fast): $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$

Example: Which Mechanism Fits?

For $2NO_2 + F_2 \rightarrow 2NO_2F$, rate = $k[NO_2][F_2]$. Which mechanism is consistent with this rate law?

Mechanism A

Step 1 (slow): $NO_2 + F_2 \rightarrow NO_2F + F$

Step 2 (fast): $NO_2 + F \rightarrow NO_2F$

Mechanism B

One step:

$2NO_2 + F_2 \rightarrow 2NO_2F$

Example: Which Step Is Slow?

For A + 2B → D, experiments show rate = k[A][B]. Which step in this mechanism must be the slow step?

Step 1: A + B → C

Step 2: C + B → D

Big Ideas

- Slowest step = rate-determining step
- Slow first step → its rate law is the rate law
- Mechanism must match the experiment
- Catalysts can appear in the rate law

