Lecture 35: Mechanisms

Catalyst, Intermediate, Elementary Reaction, Rate Determining Step

What is a mechanism?

Series of steps that produce the overall reaction

$$\begin{aligned} \mathrm{Cl}^{\bullet} + \mathrm{N_3} &\longrightarrow \mathrm{ClN}^{\bullet} + \mathrm{N_2} \\ \mathrm{ClN}^{\bullet} + \mathrm{N_3} &\longrightarrow 2\,\mathrm{N_2} + \mathrm{Cl}^{\bullet} \end{aligned}$$

$$2\,\mathrm{N_3} \longrightarrow 3\,\mathrm{N_2}$$

- **Catalyst**: goes into the reaction and comes out, lowers activation energy
- **Intermediate**: is formed and consumed during a reaction

Elementary Reactions

Elementary reactions are simple collisions or dissociations

Type	Reaction	Rate
Unimolecular	$A \rightarrow$	$k[A]$
Bimolecular	$A + A \rightarrow$	$k[A]^2$
	$A + B \rightarrow$	$k[A][B]$
Termolecular	$A + A + A \rightarrow$	$k[A]^3$
	$A + A + B \rightarrow$	$k[A]^2[B]$
	$A + B + C \rightarrow$	$k[A][B][C]$

Elementary reactions

For an **elementary reaction**, the order is based on stoichiometric coefficients

$$A + 2B \rightarrow C \implies \text{rate} = k[A][B]^2$$

Mechanism Example

Overall Reaction:

$$2\,\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}$$

Proposed Mechanism
(each step has a different k):

1) $\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k_1}} \mathrm{Q} \qquad v_1(t) = k_1[\mathrm{A}][\mathrm{B}]$

2) $\mathrm{Q} + \mathrm{A} \xrightarrow{\mathrm{k_2}} \mathrm{R} \qquad v_2(t) = k_2[\mathrm{Q}][\mathrm{A}]$

3) $\mathrm{R} + \mathrm{B} \xrightarrow{\mathrm{k_3}} \mathrm{C} \qquad v_3(t) = k_3[\mathrm{R}][\mathrm{B}]$

$$\boxed{2\,\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}}$$

The overall rate law will depend on the relative values of the different rate constants

Rate-Determining Step

Overall Reaction:

$$2\,\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}$$

Proposed Mechanism:

1) $\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{Q}$ $\quad v_1(t) = k_1[\mathrm{A}][\mathrm{B}]$ Slow
2) $\mathrm{Q} + \mathrm{A} \xrightarrow{k_2} \mathrm{R}$ $\quad v_2(t) = k_2[\mathrm{Q}][\mathrm{A}]$ Fast
3) $\mathrm{R} + \mathrm{B} \xrightarrow{k_3} \mathrm{C}$ $\quad v_3(t) = k_3[\mathrm{R}][\mathrm{B}]$ Fast

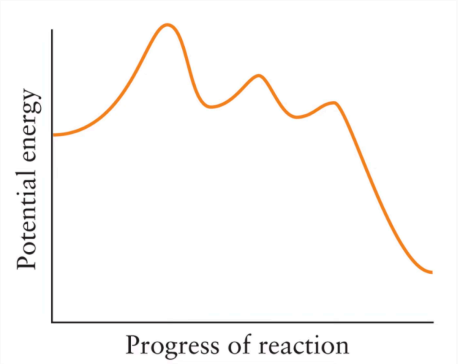
$$\boxed{2\,\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}}$$

Rate–Determining Step

The slowest step determines the overall reaction rate.
Small $k \implies$ slow Large $k \implies$ fast

Example: Energy Diagram

1. How many steps does this reaction have? 3
2. Which is the rate-determining step? 1
3. Which step is fastest? 3
4. How many intermediates form in the reaction? 2
5. Do any intermediates build up in concentration? No
6. A catalyst is added that accelerates the third step only. What effect, if any, will the catalyst have on the overall rate of reaction? None



Rate Law: Slow First Step

Overall Reaction:

$$2\,\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}$$

Proposed Mechanism:

1) $\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{Q}$
2) $\mathrm{Q} + \mathrm{A} \xrightarrow{k_2} \mathrm{R}$
3) $\mathrm{R} + \mathrm{B} \xrightarrow{k_3} \mathrm{C}$

$$\boxed{2\,\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}}$$

Key Idea: Rate law is based off of the bottleneck in slow first step

$\boxed{v_1(t) = k_1[\mathrm{A}][\mathrm{B}]}$ Slow

~~$v_2(t) = k_2[\mathrm{Q}][\mathrm{A}]$~~ Fast

~~$v_3(t) = k_3[\mathrm{R}][\mathrm{B}]$~~ Fast

Rate Law: Fast Equilibrium into Slow Step

Overall Reaction:

$$2\,O_3 \longrightarrow 3\,O_2$$

Proposed Mechanism:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O \qquad \text{Fast (eq)}$$

$$O_3 + O \xrightarrow{k_2} 2\,O_2 \qquad \text{Slow}$$

$$\boxed{2\,O_3 \longrightarrow 3\,O_2}$$

Key Idea: No intermediates, ideally no products in overall rate law. Reactants and catalyst are fine.

Rate from slow step:

$$v(t) = k_2[O_3][O]$$

Rate forward = rate reverse:

$$k_1[O_3] = k_{-1}[O_2][O]$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$v(t) = k_2[O_3] \cdot \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$= \frac{k_1 k_2}{k_{-1}} \cdot \frac{[O_3]^2}{[O_2]} = k\frac{[O_3]^2}{[O_2]}$$