Section 15.6
Reaction Mechanisms and Catalysis

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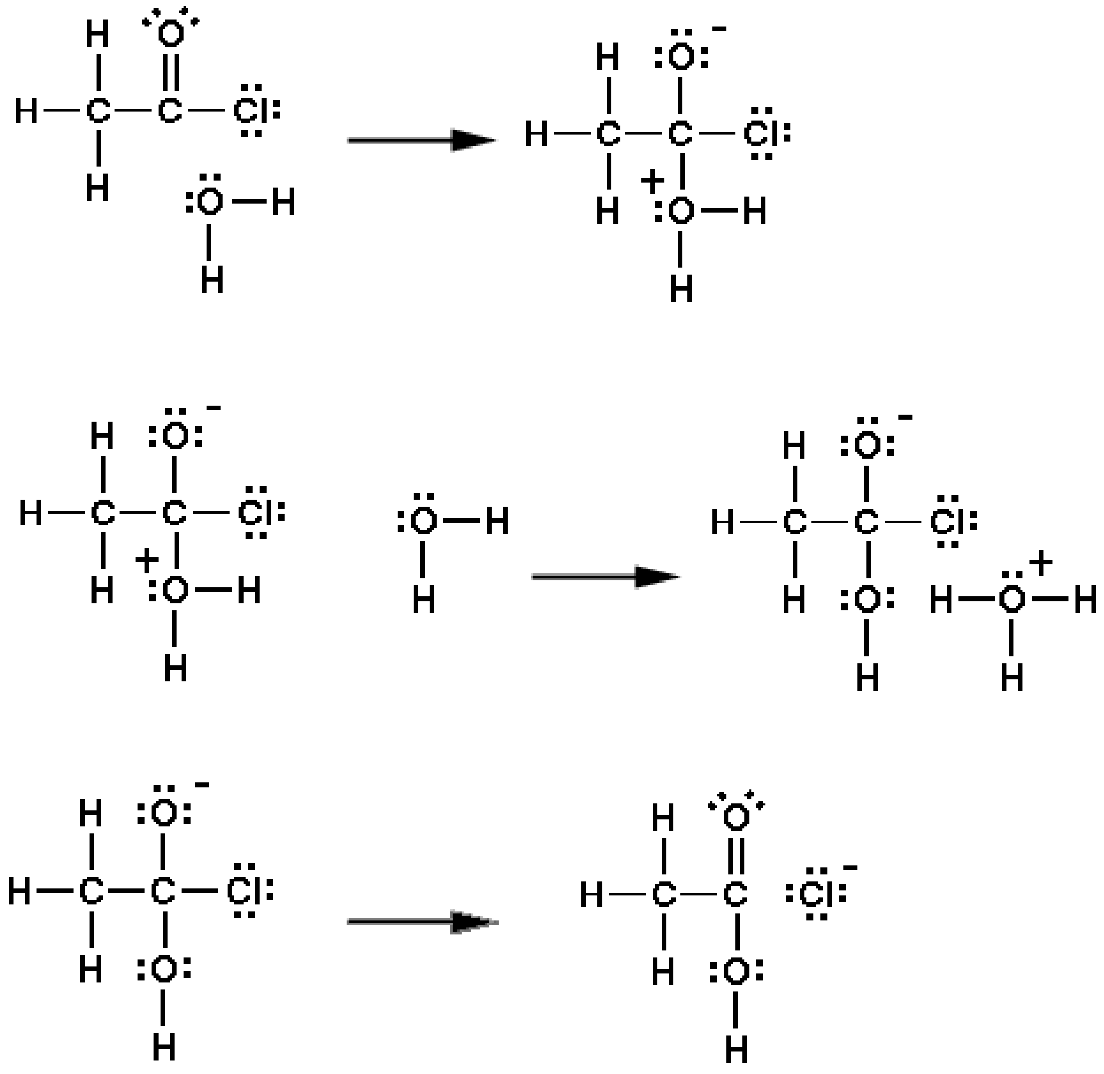
Reaction Mechanisms and Catalysis

In this section…

a. Elementary steps and reaction mechanisms
b. Reaction mechanisms and rate laws
c. More complex mechanisms
d. Catalysis

A reaction mechanism is a series of elementary steps



Reaction Mechanisms: The pathway by which a reaction proceeds from reactants to products.

- Each discrete chemical event is an "elementary step."
- The reaction is a series of elementary steps.
- Steps are usually unimolecular or bimolecular.
- The overall reaction is the *sum* of the steps.
- Each elementary step goes at its own rate.
- The rate of the overall reaction is the rate of the slowest (rate determining) step.

Overall Reactions, Intermediates and Catalysts

Overall reaction: sum of all the elementary steps

Intermediate: Formed in one step, and then used in a later step

Catalyst: Used in one step, and then reproduced in a later step

Overall Reactions:

Step 1.	Unimolecular	$O_3(g) \rightarrow O_2(g) + O(g)$
Step 2.	Bimolecular	$O_3(g) + O(g) \rightarrow 2\ O_2(g)$
Overall Reaction:		

Intermediates and Catalysts

$$2\ NO(g) \rightarrow N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

$$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$$

Overall Reaction:

Intermediates:

Catalysts:

Intermediates and Catalysts

Step 1. $H_2O_2(aq) + I^-(aq) \longrightarrow IO^-(aq) + H_2O(l)$

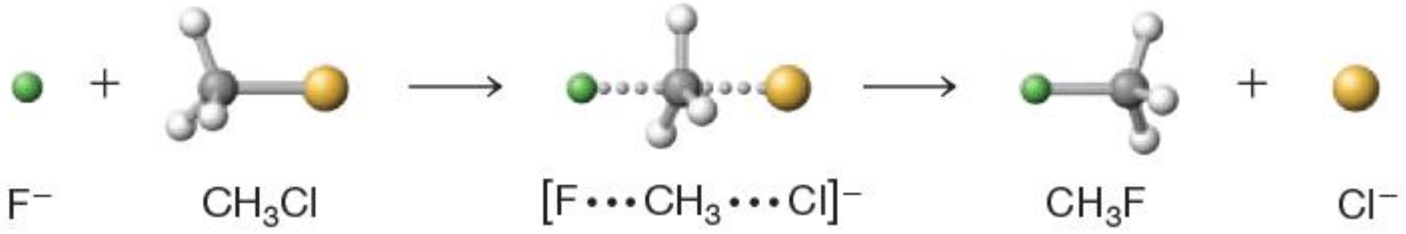
Step 2. $H_2O_2(aq) + IO^-(aq) \longrightarrow I^-(aq) + H_2O(l) + O_2(g)$

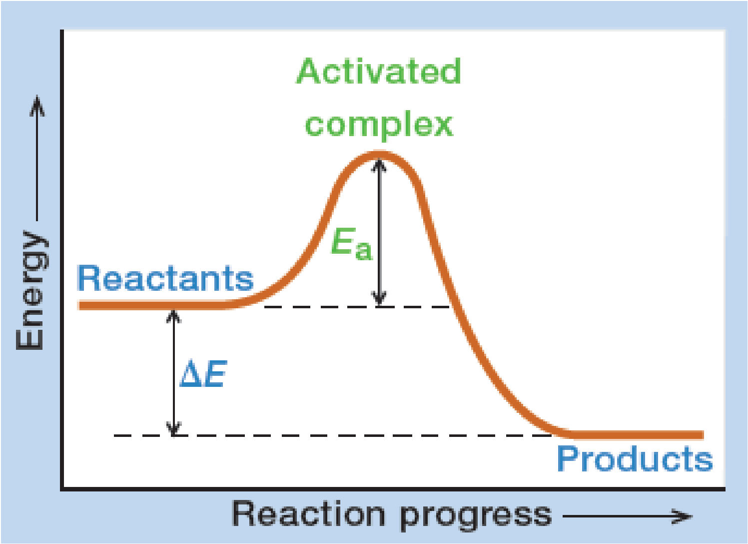
Overall Reaction:

Intermediates:

Catalysts:

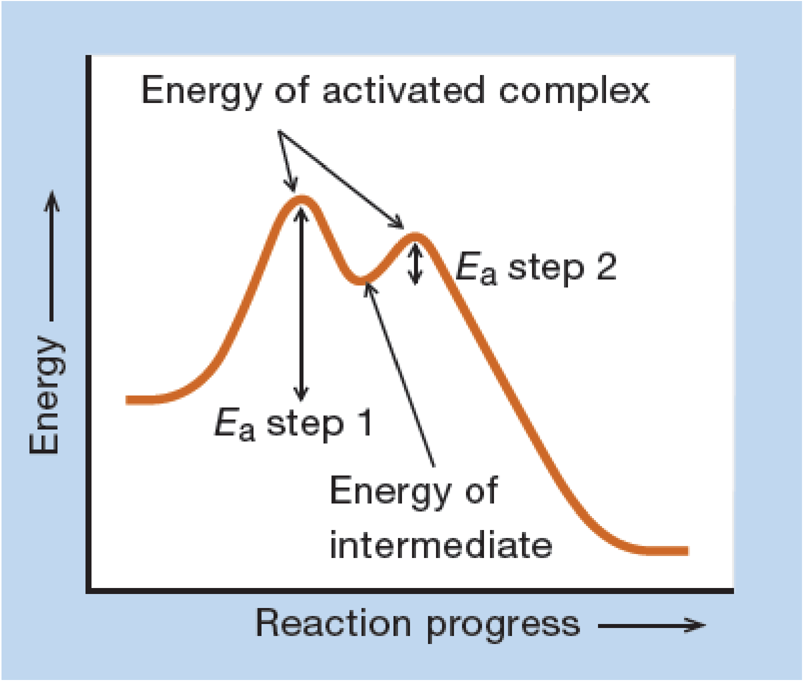
Intermediates vs. Transition States/Activated Complex





Step 1. $H_2O_2(aq) + I^-(aq) \longrightarrow IO^-(aq) + H_2O(l)$

Step 2. $H_2O_2(aq) + IO^-(aq) \longrightarrow I^-(aq) + H_2O(l) + O_2(g)$



Mechanisms and Rate Laws: Rate Laws for Elementary Steps

Unlike an overall reaction, the rate law for a single elementary step can be discerned from the reaction equation:

Example	Rate Law	Molecularity	Order of Elementary Step
$A \rightarrow$ products	rate = $k[A]$	Unimolecular	First order
$A + B \rightarrow$ products	rate = $k[A][B]$	Bimolecular	Second order
$2\ A \rightarrow$ products	rate = $k[A]^2$		
$A + B + C \rightarrow$ products	rate = $k[A][B][C]$	Termolecular	Third order
$2\ A + B \rightarrow$ products	rate = $k[A]^2[B]$		
$3\ A \rightarrow$ products	rate = $k[A]^3$		

Overall rate = Rate of the slowest step (rate determining step: RDS)

Mechanisms and Rate Laws: Predicting Rate Law from Mechanisms

Overall rate = Rate of the slowest step (rate determining step: RDS)

Step 1. $H_2O_2(aq) + I^-(aq) \longrightarrow IO^-(aq) + H_2O(l)$ (slow)

Step 2. $H_2O_2(aq) + IO^-(aq) \longrightarrow I^-(aq) + H_2O(l) + O_2(g)$ (fast)

Mechanisms and Rate Laws: Testing Mechanisms

Predict the rate law for a mechanism and see if it matches the experimental rate law.

- If the two disagree, the mechanism is incorrect.
- If the two agree, the mechanism might be correct, but you never really know for sure

Mechanisms and Rate Laws: Testing Mechanisms Example

Overall reaction and experimental rate law:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ $\quad$ Rate = $k[NO_2]^2$

Two proposed mechanisms:

- Mechanism A

  Step 1. $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ *Rate-determining slow step*

- Mechanism B

  Step 1. $2\ NO_2(g) \rightarrow NO_3(g) + NO(g)$ *Rate-determining slow step*

  Step 2. $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ *Fast second step*

Catalysts and Rate Laws

Step 1. $Cl(g) + O_3(g) \longrightarrow ClO(g) + O_2(g)$

Step 2. $ClO(g) + O_3(g) \longrightarrow Cl(g) + O_2(g)$

Overall Reaction:

Rate Law:

Rate Laws for Complex Mechanisms:

Experimental rate law can't use intermediates

$$\textbf{Step 1.}\ Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Br(g) \qquad \text{Fast in both directions}$$

$$\textbf{Step 2.}\ Br(g) + H_2(g) \xrightarrow{k_2} HBr(g) + H(g) \qquad \text{Slow}$$

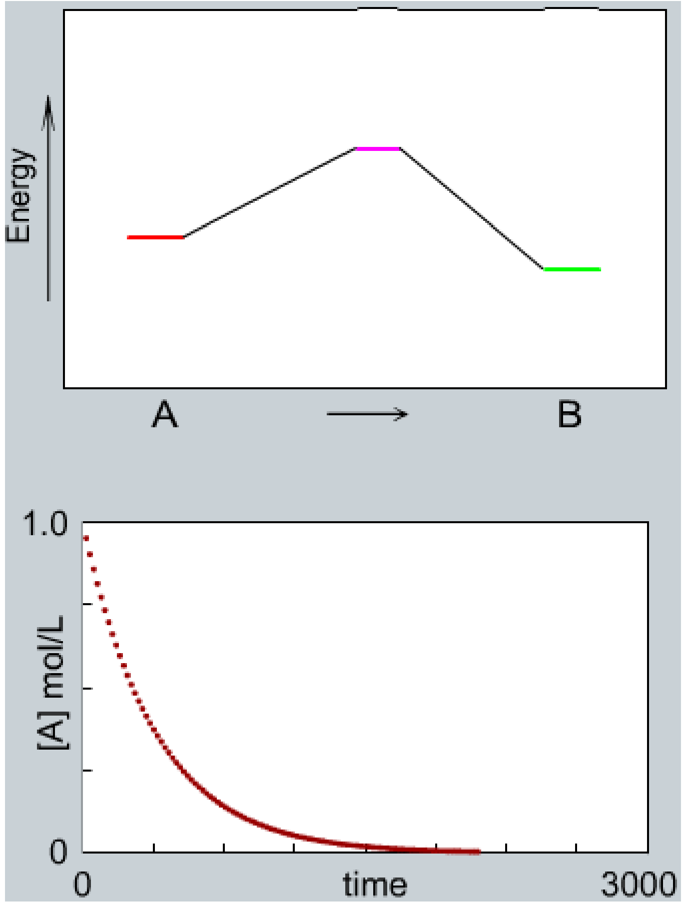
$$\textbf{Step 3.}\ H(g) + Br_2(g) \xrightarrow{k_3} HBr(g) + Br(g) \qquad \text{Fast}$$

Key: In step 1, the forward and reverse rates are equal (they are in equilibrium)

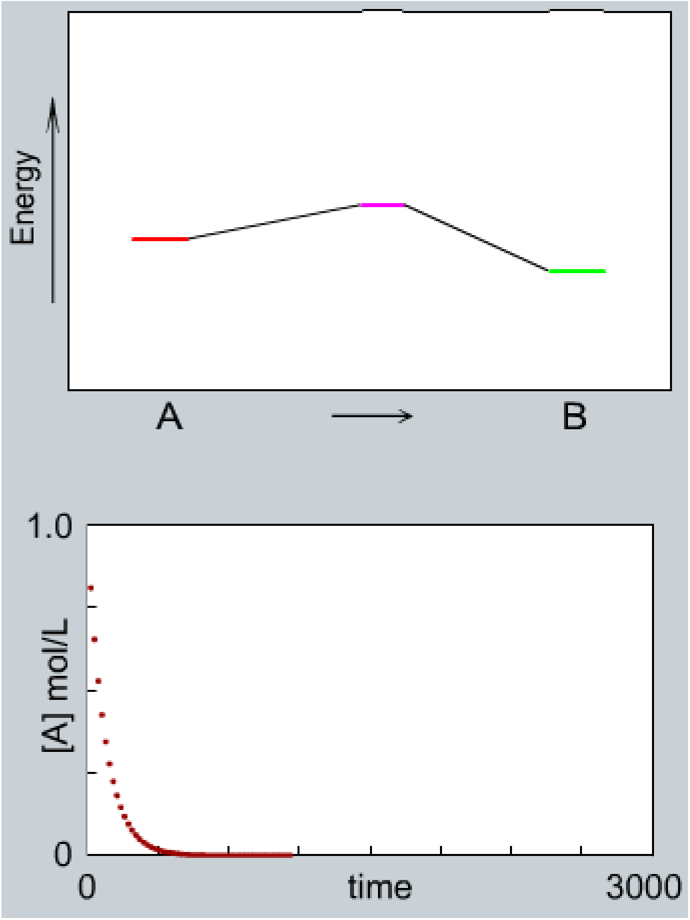
Catalysis for Increasing Reaction Rate

Alternative mechanism is provided with a lower activation energy.

uncatalyzed reactions

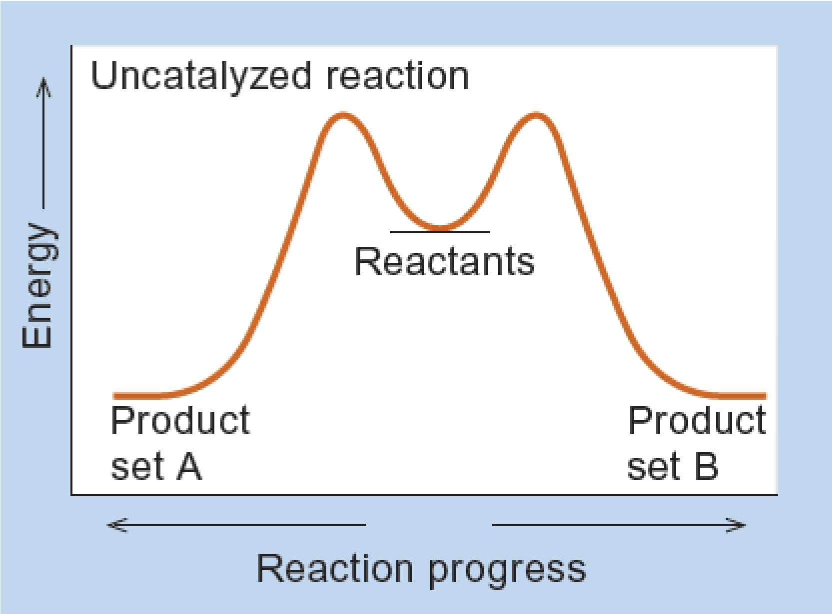


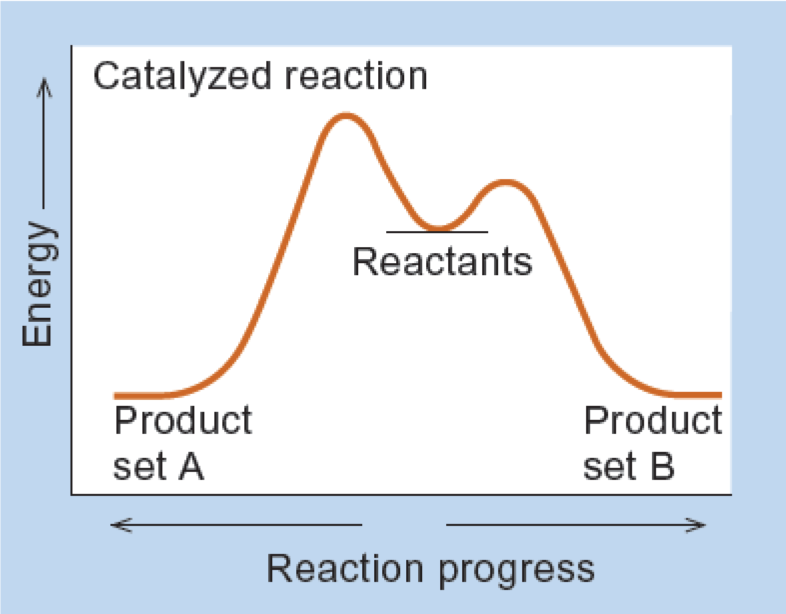
catalyzed reactions



Catalysis for Increasing Selectivity

Favor one pathway (and therefore one product) over another:





Homogeneous vs. Heterogeneous Catalysis

Homogeneous: catalyst and reactants in solution
Heterogeneous: reaction occurs on a catalytic surface