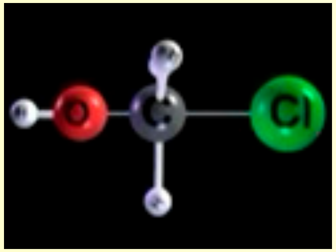
Reaction Mechanisms

- The balanced chemical equation provides information about the beginning and end of reaction.
- The reaction mechanism gives the path of the reaction.
- Mechanisms provide a very detailed picture of which bonds are broken and formed during the course of a reaction.

Elementary Steps

- Elementary step: any process that occurs in a single step.

- Molecularity: the number of reactant molecules present in an elementary step.
  - Unimolecular: one molecule in the elementary step,
  - Bimolecular: two molecules in the elementary step, and
  - Termolecular: three molecules in the elementary step.
- It is not common to see termolecular processes (statistically improbable).



Multistep Mechanisms

- Some reaction proceed through more than one step:

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

- Notice that if we add the above steps, we get the overall reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

- If a reaction proceeds via several elementary steps, then the elementary steps must add to give the balanced chemical equation.
- Intermediate: a species which appears in an elementary step which is not a reactant or product. It is produced in one step and consumed in a later step.

Rate Laws for Elementary Steps

- The rate law of an elementary step is determined by its molecularity:
  - Unimolecular processes are first order,
  - Bimolecular processes are second order, and
  - Termolecular processes are third order.

Rate Laws for Multistep Mechanisms

- Rate-determining step: is the slowest of the elementary steps.

Rate Laws for Elementary Steps

TABLE 14.3 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

Rate Laws for Multistep Mechanisms

- Therefore, the rate-determining step governs the overall rate law for the reaction.

Mechanisms with an Initial Fast Step

- It is possible for an intermediate to be a reactant.
- Consider

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

- The experimentally determined rate law is

$$\text{Rate} = k[NO]^2[Br_2]$$

- Consider the following mechanism

Step 1: $NO(g) + Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2(g)$ **(fast)**

Step 2: $NOBr_2(g) + NO(g) \xrightarrow{k_2} 2NOBr(g)$ **(slow)**

- The rate law is (based on Step 2):

$$\text{Rate} = k_2[NOBr_2][NO]$$

- The rate law should not depend on the concentration of an intermediate (intermediates are usually unstable).
- Assume $NOBr_2$ is unstable, so we express the concentration of $NOBr_2$ in terms of NO and Br_2 assuming there is an equilibrium in step 1 we have

$$[NOBr_2] = \frac{k_1}{k_{-1}}[NO][Br_2]$$

- By definition of equilibrium:

$$k_1[\mathrm{NO}][\mathrm{Br_2}] = k_{-1}[\mathrm{NOBr_2}]$$

- Therefore, the overall rate law becomes

$$\mathrm{Rate} = k_2 \frac{k_1}{k_{-1}}[\mathrm{NO}][\mathrm{Br_2}][\mathrm{NO}] = k_2 \frac{k_1}{k_{-1}}[\mathrm{NO}]^2[\mathrm{Br_2}]$$

- Note the final rate law is consistent with the experimentally observed rate law.

Example

- $NO + Cl_2 \rightleftharpoons NOCl_2$ (fast)
- $NOCl_2 + NO \rightleftharpoons 2\,NOCl$ (slow)

1. Write the overall equation.
2. Determine the rate law.

Example

- At low temperatures, the rate law for the reaction

$CO\ (g) + NO_2\ (g) \rightarrow CO_2\ (g) + NO\ (g)$

Is Rate = $k[NO_2]^2$. Show why or why not each of the following mechanisms is consistent with that rate law for this reaction.

a) 1. $CO + NO_2 \rightarrow CO_2 + NO$

b) 1. $2\ NO_2 \rightleftharpoons N_2O_4$ (fast)

2. $N_2O_4 + 2\ CO \rightleftharpoons 2\ CO_2 + 2\ NO$ (slow)

c) 1. $2\ NO_2 \rightarrow NO_3 + NO$ (slow)

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

d) 1. $2\ NO_2 \rightarrow 2\ NO + O_2$ (slow)

2. $2\ CO + O_2 \rightarrow 2\ CO_2$ (fast)

Catalysis

- A catalyst changes the rate of a chemical reaction.
- There are two types of catalyst:
  - homogeneous, and
  - heterogeneous.
- Chlorine atoms are catalysts for the destruction of ozone.

Homogeneous Catalysis

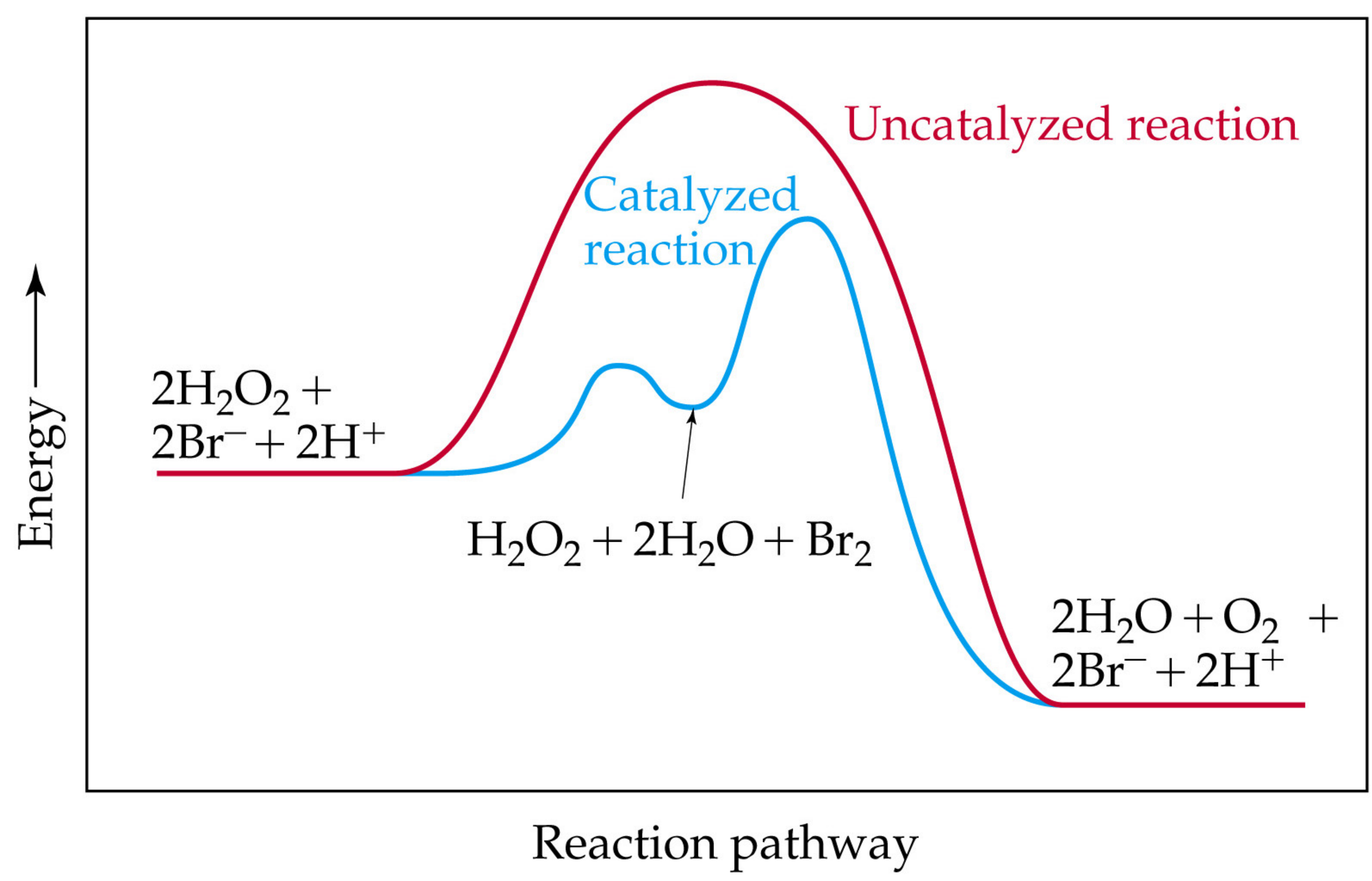
- The catalyst and reaction is in one phase.

Catalysis

- Hydrogen peroxide decomposes very slowly:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

- In the presence of the bromide ion, the decomposition occurs rapidly:
  - $2Br^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow Br_2(aq) + 2H_2O(l)$.
  - $Br_2(aq)$ is brown.
  - $Br_2(aq) + H_2O_2(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + O_2(g)$.
  - Br^- is a catalyst because it can be recovered at the end of the reaction.
- Generally, catalysts operate by lowering the activation energy for a reaction.


Uncatalyzed reaction
Catalyzed reaction
$2H_2O_2$ +
$2Br^- + 2H^+$
$H_2O_2 + 2H_2O + Br_2$
$2H_2O + O_2$ +
$2Br^- + 2H^+$
Energy
Reaction pathway

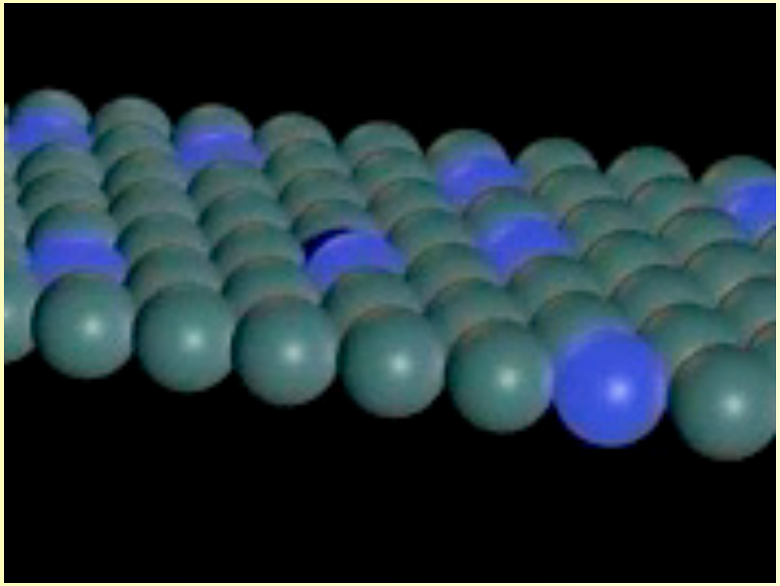
- Catalysts can operate by increasing the number of effective collisions.
- That is, from the Arrhenius equation: catalysts increase k by increasing A or decreasing E_a.
- A catalyst may add intermediates to the reaction.
- Example: In the presence of Br^-, $Br_2(aq)$ is generated as an intermediate in the decomposition of H_2O_2.

- When a catalyst adds an intermediate, the activation energies for both steps must be lower than the activation energy for the uncatalyzed reaction. The catalyst is in a different phase than the reactants and products.

Heterogeneous Catalysis

- Typical example: solid catalyst, gaseous reactants and products (catalytic converters in cars).
- Most industrial catalysts are heterogeneous.

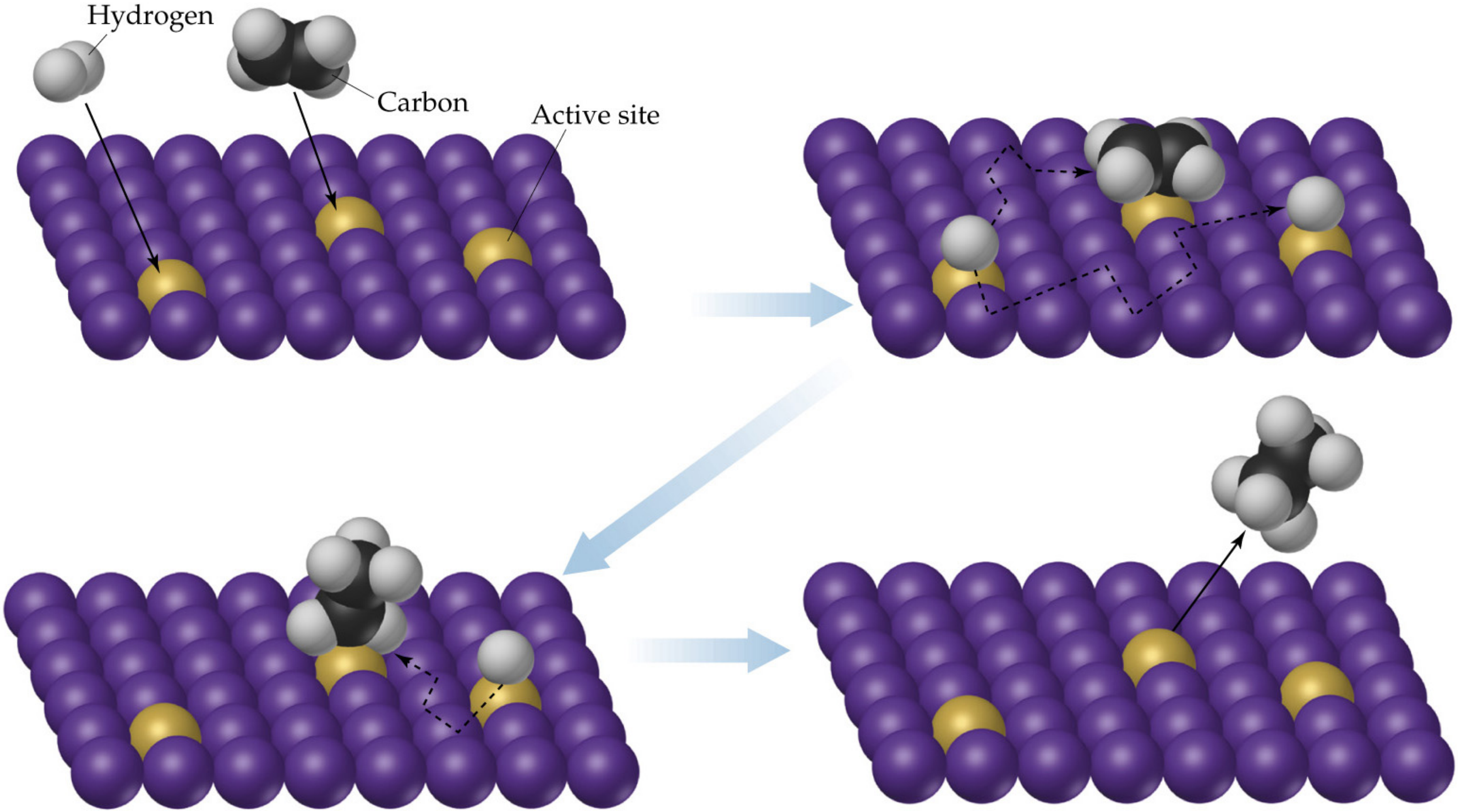
- First step is adsorption (the binding of reactant molecules to the catalyst surface).
- Adsorbed species (atoms or ions) are very reactive.
- Molecules are adsorbed onto active sites on the catalyst surface.



Example

- $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
- $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$ (fast)

1. What is the overall equation?
2. What is the catalyst?
3. What is the intermediate?
4. What is the rate law?


Hydrogen
Carbon
Active site

- Consider the hydrogenation of ethylene:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g), \Delta H = -136 \text{ kJ/mol.}$$

  - The reaction is slow in the absence of a catalyst.
  - In the presence of a metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.
  - First the ethylene and hydrogen molecules are adsorbed onto active sites on the metal surface.
  - The H-H bond breaks and the H atoms migrate about the metal surface.

- When an H atom collides with an ethylene molecule on the surface, the C-C π bond breaks and a C-H σ bond forms.
- When C_2H_6 forms it desorbs from the surface.
- When ethylene and hydrogen are adsorbed onto a surface, less energy is required to break the bonds and the activation energy for the reaction is lowered.

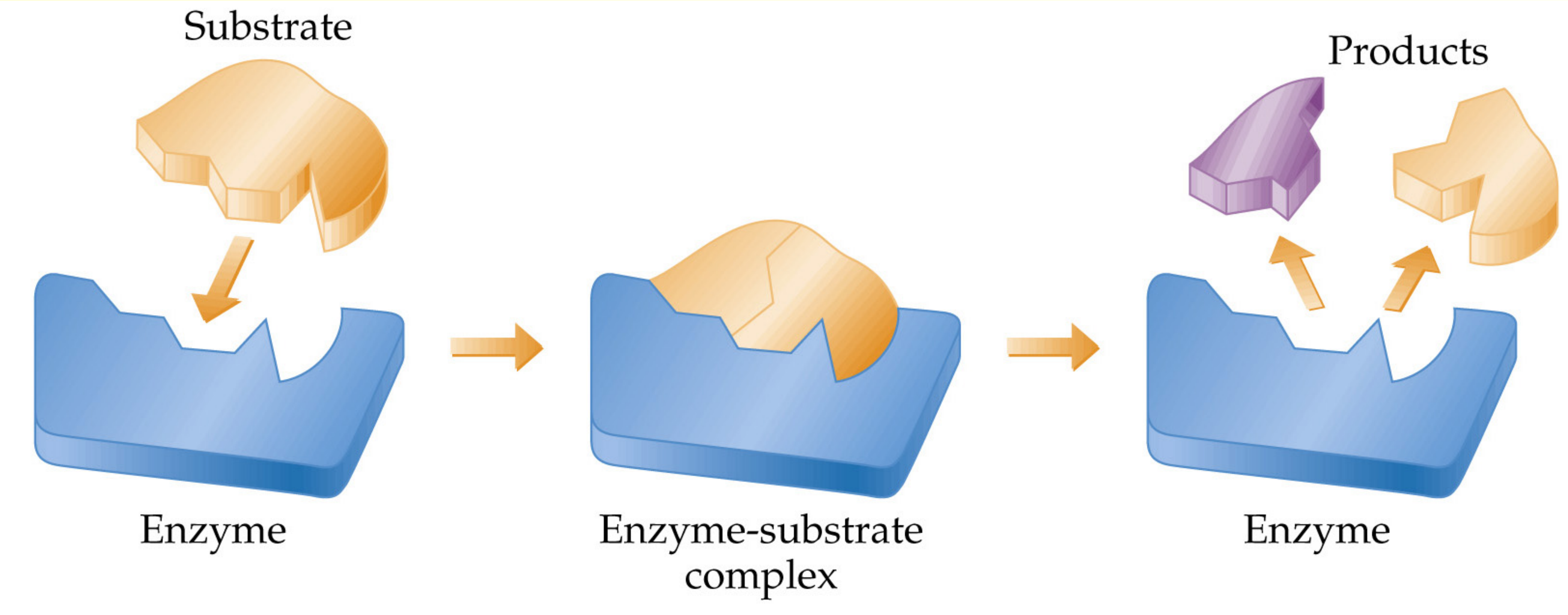
Enzymes

- Enzymes are biological catalysts.
- Most enzymes are protein molecules with large molecular masses (10,000 to 10^6 amu).

- Enzymes have very specific shapes.
- Most enzymes catalyze very specific reactions.
- Substrates undergo reaction at the active site of an enzyme.
- A substrate locks into an enzyme and a fast reaction occurs.
- The products then move away from the enzyme.

- Only substrates that fit into the enzyme “lock” can be involved in the reaction.
- If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (enzyme inhibitors).
- The number of events (turnover number) catalyzed is large for enzymes (10^3 - 10^7 per second).

Enzymes


Substrate
Products
Enzyme
Enzyme-substrate complex
Enzyme