

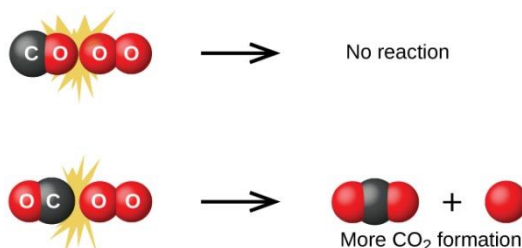
Collision Theory

- Atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds.

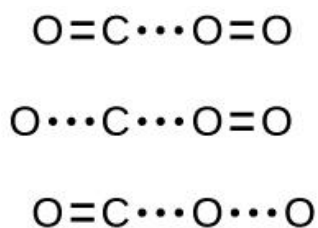
Collision Theory explains those kinds of observation base on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:
2. The reacting species must collide in an orientation that allows contact between atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shell so that the electrons can rearrange and form new bonds (new chemical species)

Let's exam the two collisions that might take place between carbon monoxide and oxygen molecules.



In addition of proper orientation, collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an activated complex at the transition state.

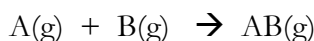


Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed.

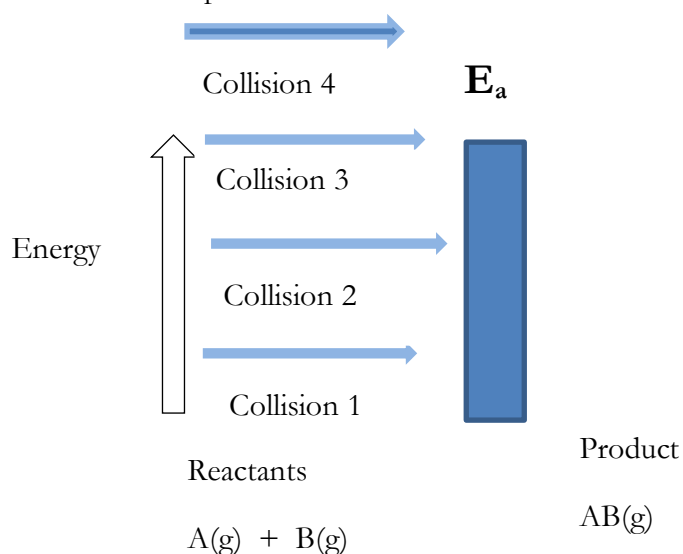
Collision theory explains why most reaction rates increase as concentration increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit volume. More collisions mean a faster reaction rate, assuming the energy of collision is adequate.

**Example:**

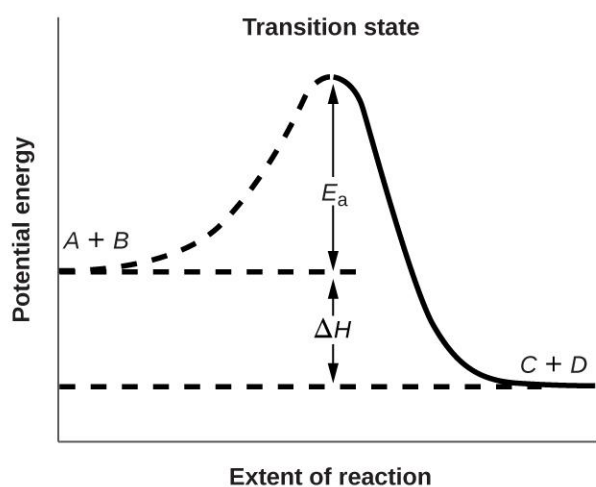
Consider the reaction



Which collision(s) could lead to the product?



### 14.7 -14.8 Reaction rates and Temperature: The Arrhenius Equation



This graph shows the potential energy relationships for the reaction  $A + B \rightarrow C + D$ . The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion represents the energy of the system with a molecule of C and molecule of D present.

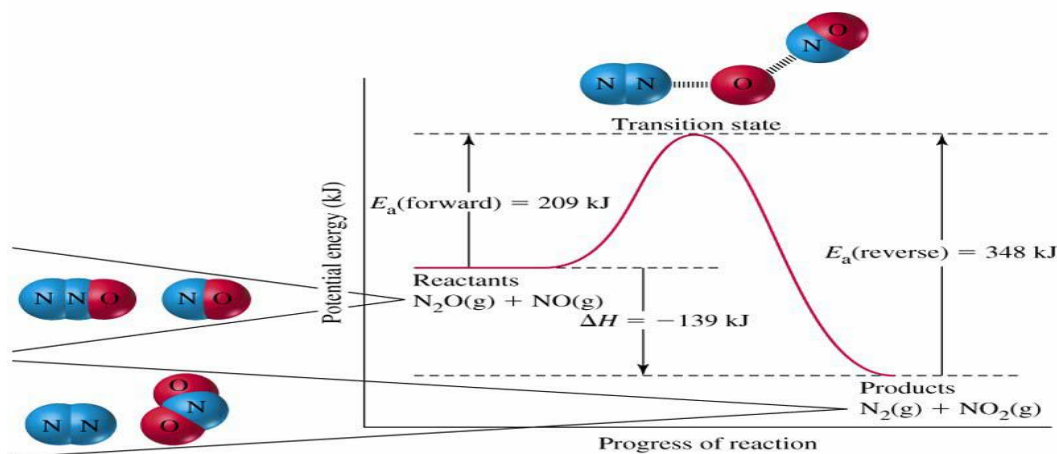
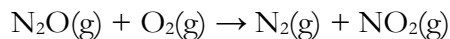
The **activation energy** is the amount of energy needed to convert reactants into the activated complex. The height of the energy barrier

- Every reaction has its own activation energy – some larger, some smaller – usually expressed in units of **kJ/mol**
- Think of the activation of energy as representing a barrier that reactants must pass in order to become products.
- All else being equal, a larger activation energy means a slower reaction

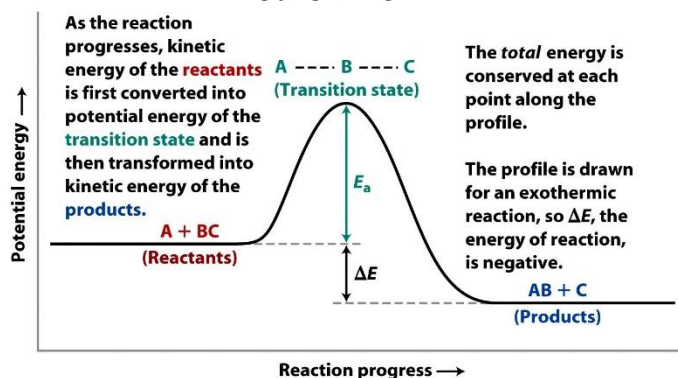
The value of  $E_a$  depends on the particular reaction.

- (1) In order to form products, bonds must be broken in the reactants.
- (2) Bond breakage requires energy.
- (3) Molecules moving too slowly, with too little kinetic energy, don't react when they collide.

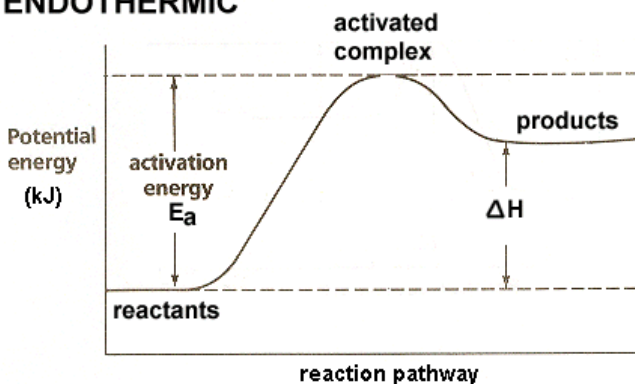
Consider the reaction



### Exothermic



### ENDOTHERMIC



Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:

- (1) The number of collisions per unit time.
- (2) The fraction of collisions that occur with the correct orientation.
- (3) The fraction of the colliding molecules that have an energy greater than or equal to  $E_a$ .

Typically, as the temperature increases, the rate of reaction increases. Rate constant for most chemical reactions closely follow an **Arrhenius equation at one particular temperature**

$$k = Ae^{-E_a/RT}$$

The Frequency factor represents the number of approaches to the activation barrier per unit of time

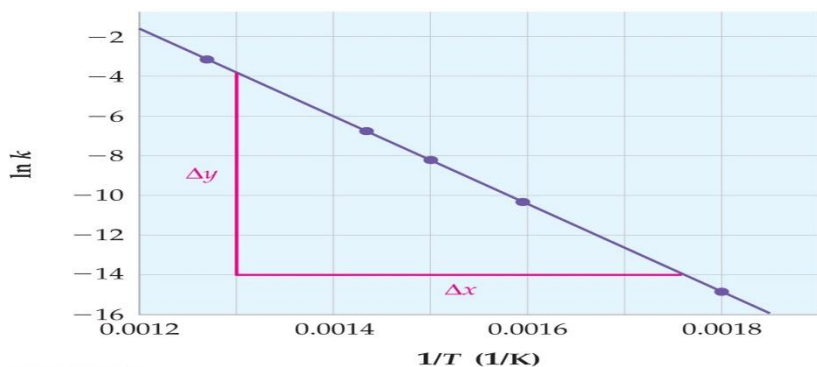
The exponential factor is a number between 0 and 1 that represents the fraction of molecules that have enough energy to make it over the activation barrier on a given approach.

$k$	rate constant
$A$	collision frequency factor ( $\text{s}^{-1}$ )
$E_a$	activation energy
$R$	gas constant = $8.314 \text{ J/K mol}$
$T$	temperature (K)

$$\ln(k) = \ln(A) + \ln\left[e^{-E_a/RT}\right]$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \xrightarrow{\text{rearrange the equation}} \ln(k) = \left[\frac{-E_a}{R}\right]\left[\frac{1}{T}\right] + \ln(A)$$

$$y = mx + b$$



A typical plot used to calculate the activation energy from the Arrhenius equation. In this plot of  $\ln k$  vs.  $1/T$  will have a slope of  $-E_a/R$  and a y-intercept of  $\ln A$ .

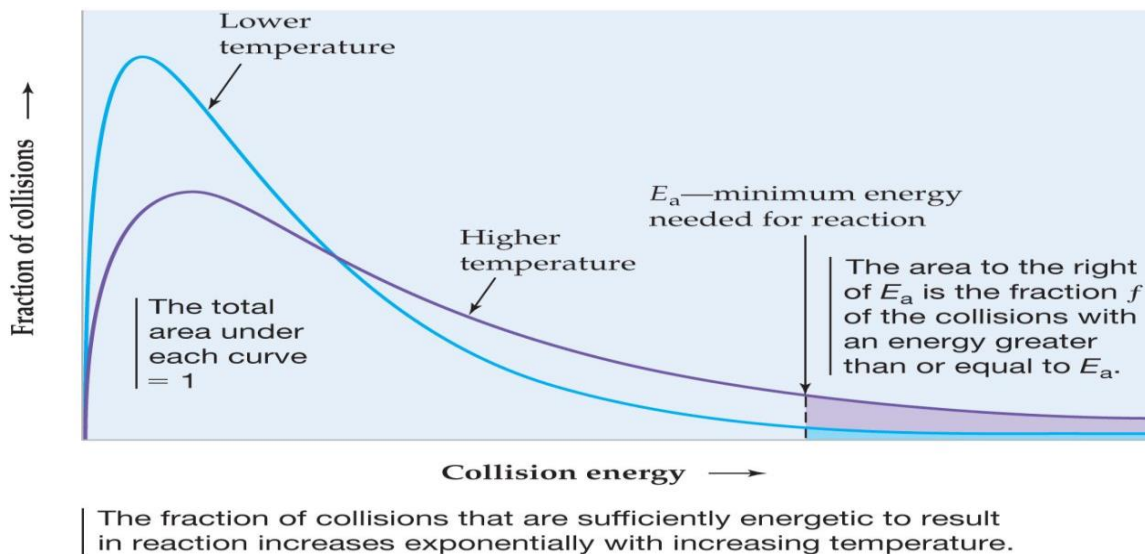
**Example:** The rate constant ( $k$ ) for a reaction was measured as function of temperature. A plot of ( $\ln k$ ) versus  $1/T$  (in  $K$ ) is linear and has a slope of  $-7445K$ . Calculate the activation of energy in  $kJ/mol$

Example: Activation of energy of a reaction is  $56.8 kJ/mol$  and frequency factor is  $1.5 \times 10^{11}/s$ . Calculate the rate constant of reaction at  $25.0^\circ C$

## Effecting of Temperature

When the temperature is increased the term  $E_a/RT$  gets smaller. This means in turn, that the term  $e^{-E_a/RT}$  gets bigger. As the temperature increases, the number of molecules having enough thermal energy to surmount the activation energy barrier increases. At any given temperature, the atoms or molecules in a gas sample will have a range of energies. The higher the temperature, the wider the energy distribution and the greater the average energy. The

fraction of molecules with enough energy to surmount the activation energy barrier and react increases sharply as the temperature rises.



### Using two-point form of the Arrhenius Equation

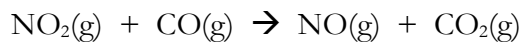
In some case, when either data are limited or plotting capabilities are absent, we can calculate the activation energy of a reaction by measuring the rate constant at **two temperatures**:

Writing the Arrhenius equation for each temperature then subtract the first equation from the second equation

$$\ln k_1 = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T_1} \right) + \ln A \quad \ln k_2 = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T_2} \right) + \ln A$$

$$\ln \left( \frac{k_2}{k_1} \right) = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Example: Consider the reaction between nitrogen dioxide and carbon monoxide



The rate constant at 701 K is measured as  $2.57 \text{ M}^{-1}\text{s}^{-1}$  and that at 895 K is measured as  $5.67 \text{ M}^{-1}\text{s}^{-1}$ . Find the activation of energy in kJ/mol

**Example:** The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

## 14.9 – Reaction Mechanism

A balanced chemical equation defines the identities of reactants and the products as well as the stoichiometry (mole-mole ratios) between them but says nothing about the process by which reactants are actually transformed into the products. A **mechanism** for a reaction is a collection of elementary processes (also called elementary steps or elementary reactions) that explains how the overall reaction proceeds.

A mechanism is a proposal from which you can work out a rate law that agrees with the observed rate laws. The fact that a mechanism explains the experimental results is not a proof that the mechanism is correct. A mechanism is our rationalization of a chemical reaction, and devising mechanism is an excellent academic exercise. For that reason, although chemists can definitely rule out some propose mechanism, they can never definitely “prove” that a proposed mechanism is the correct set of step that a reaction is actually using.

The number of particle involved in an elementary step is called the **molecularity**, and in general, we consider only the molecularity of 1, 2, and 3.

**Unimolecular reaction:** is an elementary reaction that involves a single reactant molecule

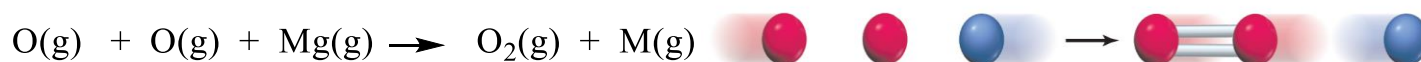


The asterisk on  $\text{O}_3$  indicates that the ozone molecule is an energetically excited state. It has absorbed ultraviolet light from the sun, causing the bond to break without any collision.

**Bimolecular reaction:** is an elementary reaction that results from an energetic collision between reactants atoms or molecules.



**Termolecular reactions:** which involves three atoms or molecule and not common in mechanism. Three particles collide simultaneously only infrequently. When a reaction mechanism includes a termolecular step, it is generally a “slow” reaction since three-body collision occurs only infrequently.



**Facts about a reaction mechanism:**

1. The sum of the fundamental steps in the mechanism must equal the correct overall reaction.
2. The rate of the reaction, and therefore the rate law for the reactions are determined by the rate of the *slow step*.
3. The rate law for an elementary reaction follows directly from its molecularity because an **elementary reaction is an individual molecular event**.

**TABLE 13.5 Rate Laws for Elementary Reactions**

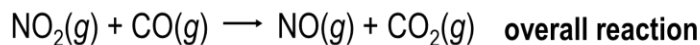
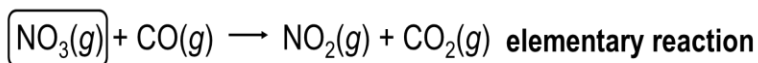
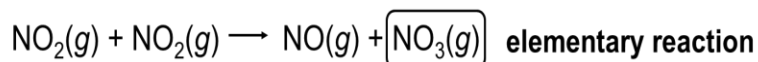
Elementary Reaction	Molecularity	Rate Law
$A \rightarrow \text{Products}$	Unimolecular	$\text{Rate} = k[A]$
$A + A \rightarrow \text{Products}$	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{Products}$	Bimolecular	$\text{Rate} = k[A][B]$
$A + A + B \rightarrow \text{Products}$	Termolecular	$\text{Rate} = k[A]^2[B]$
$A + B + C \rightarrow \text{Products}$	Termolecular	$\text{Rate} = k[A][B][C]$

## 14.11 – Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an **elementary reaction is an individual molecular event**.

**Example:** Consider the reaction of  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

Experimental evidence suggests that the reaction between  $\text{NO}_2$  and  $\text{CO}$  takes place by a two-step mechanism:



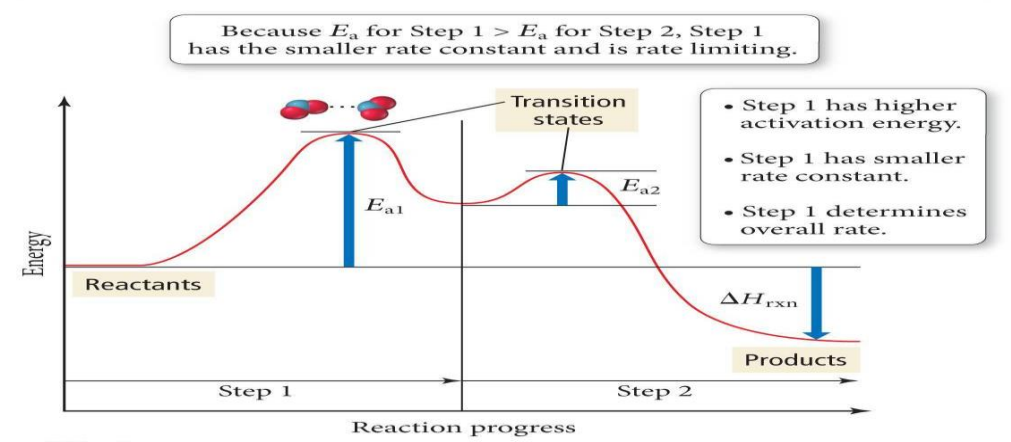
Do the steps of the proposed mechanism add up to the overall reaction? \_\_\_\_\_

Which molecule(s) were not appear in the overall reaction? \_\_\_\_\_

A **reactive intermediate** is formed in one step and consumed in a subsequent step.

**Rate of overall reaction is equal to the rate-determining step**

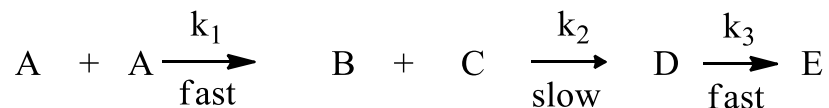
**Energy Diagram for a Two-Step Mechanism**



For mechanism in which there are two or more elementary steps, one of the step is often much slower than any of the others. This step is called the “**rate-determining step**”.

**Rate-Determining Step:** The slow step in a reaction mechanism since it acts as a bottleneck and limits the rate at which reactants can be converted to products

The orders of the reactants observed in the rate law are related to the mechanism of the reaction, including the identity of the rate-determining step.

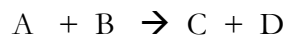


Identify the rate-determining step from the question above. How do you know?



## Rate Laws for Overall Reactions

**Example:** Two students proposed a mechanism for the given reaction below. Who proposed the correct one?



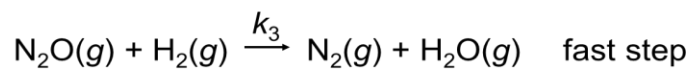
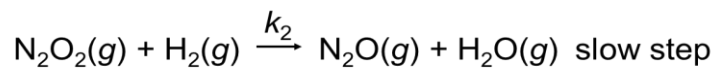
*Rate law from experiment: Rate = k [B]<sup>2</sup>*

*Rate law predicted by "student 1" proposed mechanism: Rate = k [A][B]*

*Rate law predicted by "student 2" proposed mechanism: Rate = k [B]<sup>2</sup>*

**Example:** Write a rate law for the reaction below

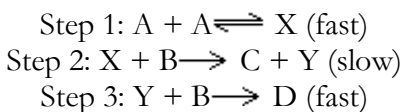
### Multistep Reactions with an Initial Fast Step



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overall reaction

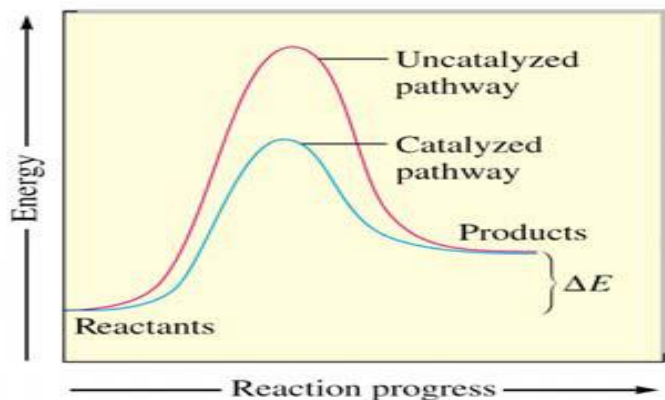
**Example:** Consider the following elementary steps for the reaction of  $2A + 2B \rightarrow C + D$



Is the mechanism consistent with the rate law?  $\text{Rate} = k[A]^2[B]$

### 14.12 – Catalyst

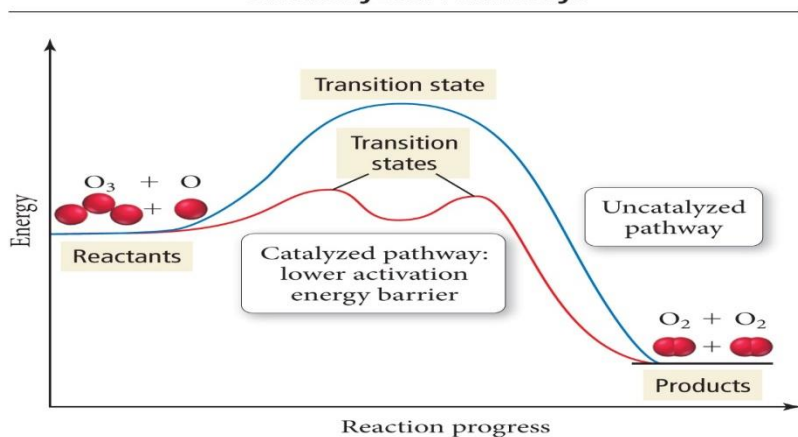
Reaction rates are affected not only by reactant concentrations and temperature but also by the presence of catalysts.



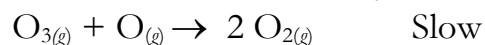
**Catalyst:** A substance that increases the rate of a reaction without itself being consumed in the reaction. A catalyst is used in one step and regenerated in a later step

How does it work? A catalyst accelerates the rate of a reaction by making available different, more efficient mechanism for the conversion of reactants to products.

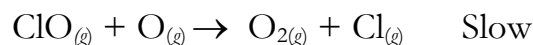
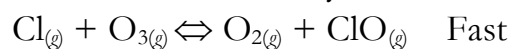
### Energy Diagram for Catalyzed and Uncatalyzed Pathways



Mechanism without catalyst:

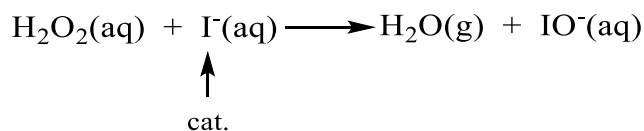


Mechanism with catalyst:



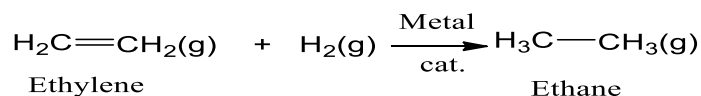
## 14.13– Homogeneous and Heterogeneous Catalysts

**Homogeneous Catalyst:** A catalyst that exists in the same phase as the reactants.



Homogeneous catalysts react with one of the reactant molecules to form a more stable activated complex with a lower activation energy.

**Heterogeneous Catalyst:** A catalyst that exists in a different phase from that of the reactants



Heterogeneous catalysts hold one reactant molecule in proper orientation for reaction to occur when the collision takes place. Sometimes they also help to start breaking bonds

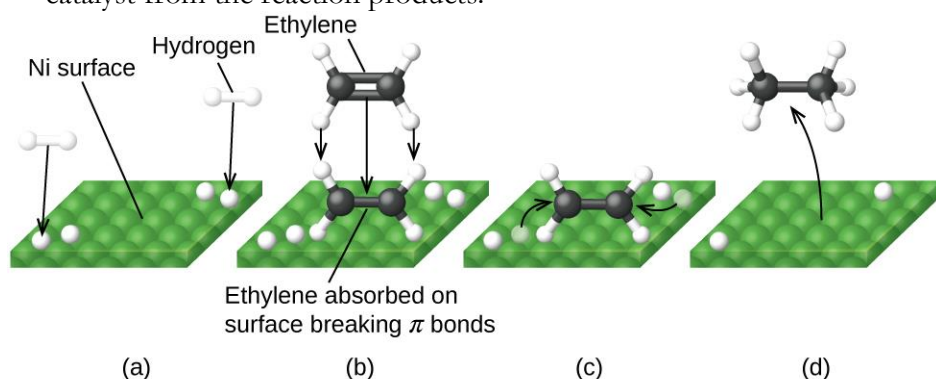
- Mechanism complex and not well understood
- 3 Important steps
  - a. Adsorption of reactants onto the surface of the catalyst
  - b. Conversion of reactants to products on the surface
  - c. Desorption of products from the surface

Adsorption steps.

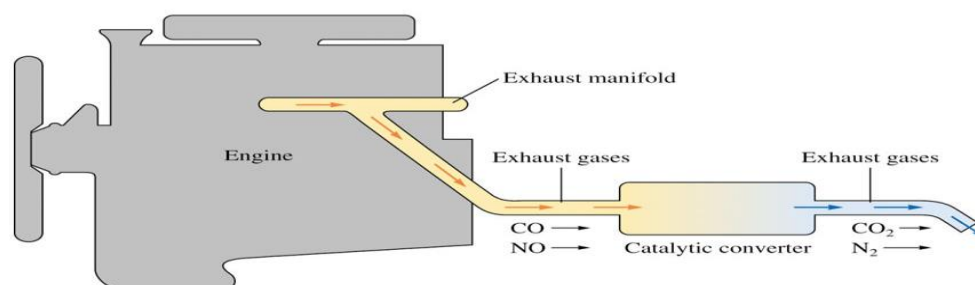
- a. Chemical bonding of reactants to the highly reactive metal atoms on the surface

b. Breaking or weakening of bonds in the reactants

4. Industrial chemical processes use mostly heterogeneous catalysts due to the ease of separation of the catalyst from the reaction products.



Used in automobile catalytic converters

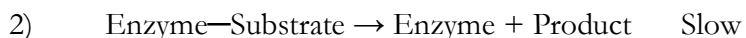
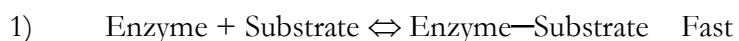


Catalytic converters are used in exhaust systems to provide a site for the oxidation and reduction of toxic by-products (like nitrogen oxides, carbon monoxide, and hydrocarbons) of fuel into less hazardous substances such as carbon dioxide, water vapor, and nitrogen gas

“Catalytic converters” in all modern automobiles utilize a heterogeneous catalysts (usually consisting of Pt or Pd metals and transition metal oxides) to remove pollutants from exhaust stream.

## Enzymes

Enzymes are protein catalysts that, like all catalysts, speed up the rate of a chemical reaction without being used up in the process.



## How Enzymes Work

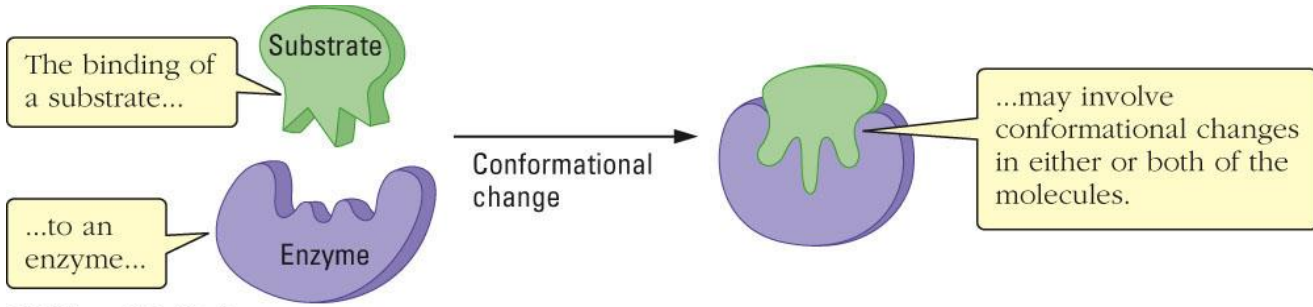
- Enzyme-catalyzed reactions are characterized by the formation of a complex between the enzyme and its substrate (the ES complex)

- Substrate binding occurs in a pocket on the enzyme called the active site

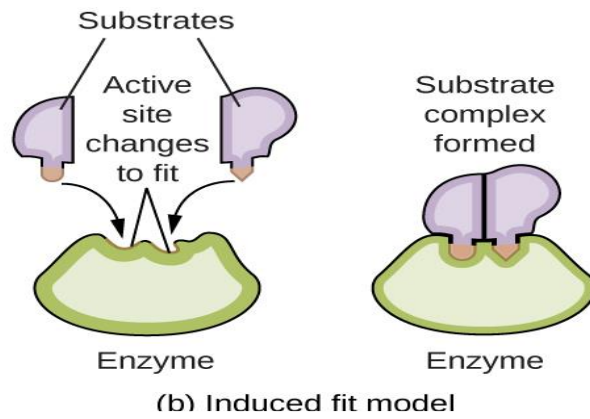
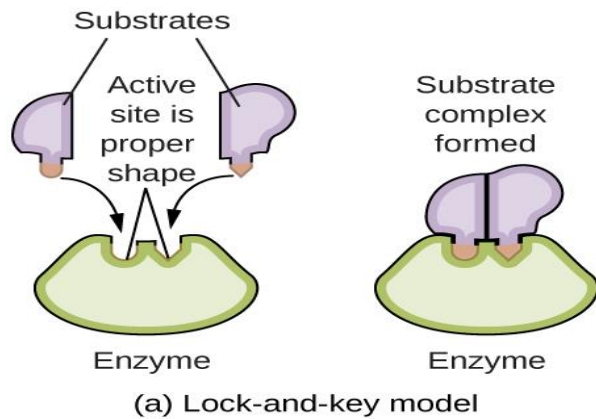
- Enzymes accelerate reactions by lowering the free energy of activation  $E_a$

The equilibrium of the reaction remains unaffected by the enzyme

- Enzymes do this by binding the transition state of the reaction better than the substrate



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Mechanism:



The “lock and key” model – in this model the substrate has a shape matching the enzyme’s active site

The “induced fit model” – the active site has a shape complementary to that of the substrate *after* the substrate is bound