

# **N11 - KINETICS**

**Collision Theory  
and More**

# Rate Laws

Reaction Mechanism - The series of elementary steps by which a chemical reaction occurs.

# Collision Model

**Key Idea:** Molecules must collide to react. However, only a small fraction of collisions produces a reaction. Why?



# Collision Model

Collisions must have sufficient energy to produce the reaction (must equal or exceed the activation energy).

Colliding particles must be correctly oriented to one another in order to produce a reaction.

# Molecularity

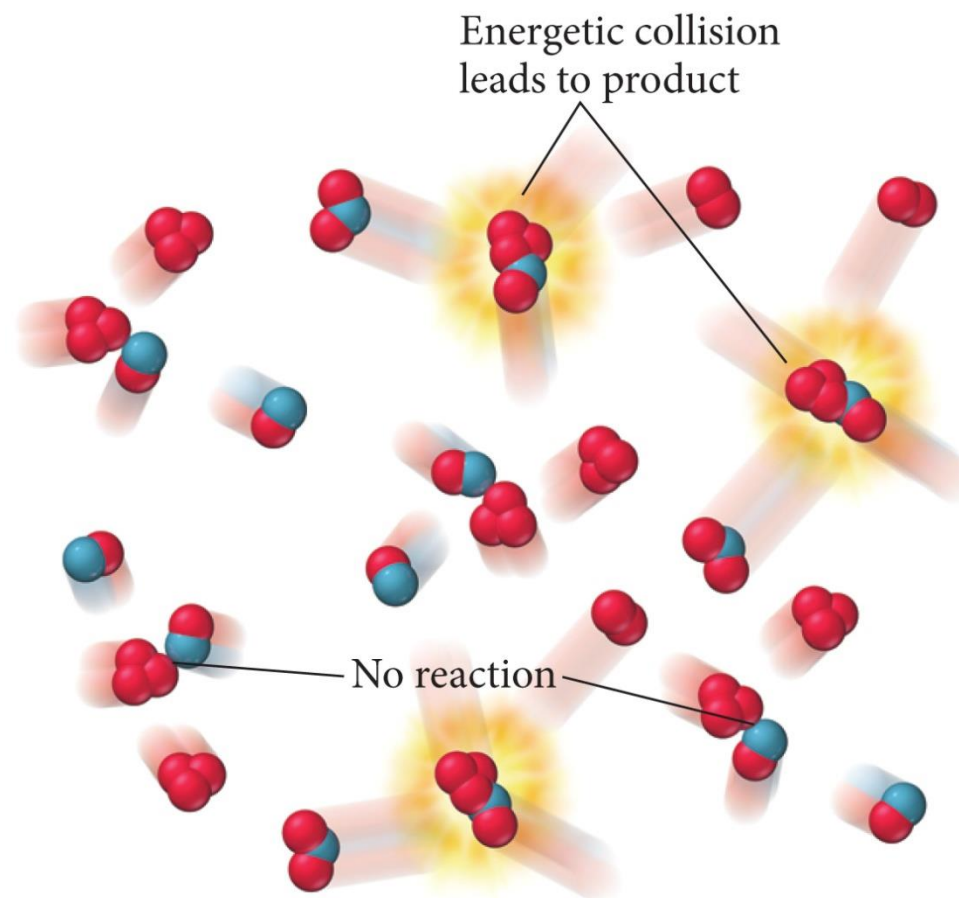
The # of species that must collide to produce the rxn indicated by that step

- **Unimolecular step** - a reaction involving one molecule
- **Bimolecular step** - reaction involving the collisions of two species
- **Termolecular step** - reaction involving the collisions of three species

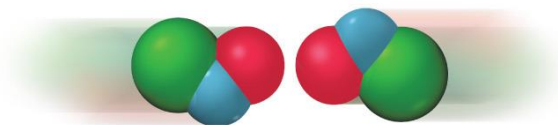
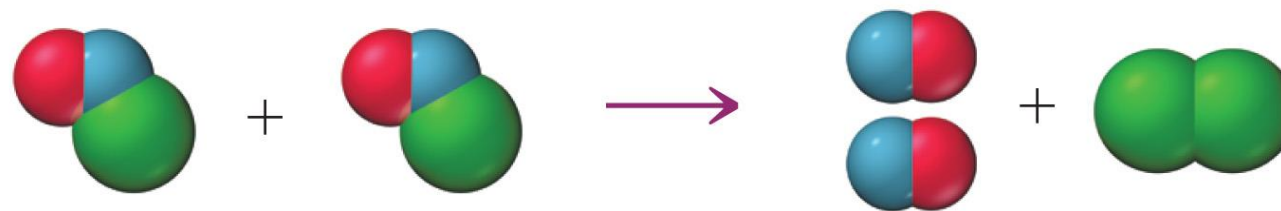
Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	Unimolecular	Rate = $k[A]$
$A + A \rightarrow \text{products}$ ( $2A \rightarrow \text{products}$ )	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow \text{products}$		Rate = $k[A][B]$
$A + A + B \rightarrow \text{products}$ ( $2A + B \rightarrow \text{products}$ )	Termolecular	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{products}$		Rate = $k[A][B][C]$

# Effective Collisions: Kinetic Energy Factor

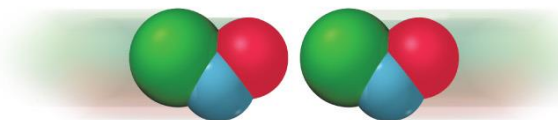
For a collision to lead to overcoming the energy barrier, the reacting molecules must have sufficient kinetic energy so that when they collide the activated complex can form.



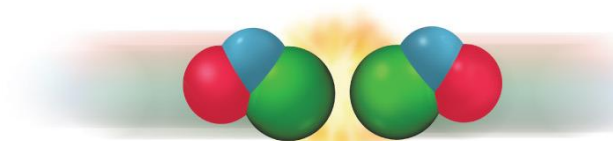
# Effective Collisions: Orientation Factor



Ineffective collision



Ineffective collision



Effective collision

# Molecular Interpretation of Factors Affecting the Rate – Reactant Nature

- Reactions generally occur faster in solution than in pure substances.
  - Mixing gives more particle contact.
  - Particles are separated, allowing more effective collisions per second.
  - Forming some solutions breaks bonds that need to be broken.



# Molecular Interpretation of Factors Affecting the Rate – Reactant Nature

Some materials undergo similar reactions at different rates either because they have a

- 1) Higher initial potential energy and are therefore closer in energy to the activated complex, or
- 2) Because their reaction has a lower activation energy.

$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$  is about 12 times faster than  
 $\text{CD}_4 + \text{Cl}_2 \rightarrow \text{CD}_3\text{Cl} + \text{DCI}$  because the C–H bond is weaker and less stable than the C–D bond.

$\text{CH}_4 + \text{X}_2 \rightarrow \text{CH}_3\text{X} + \text{HX}$  occurs about 100x faster with  $\text{F}_2$  than  $\text{Cl}_2$  because the  $A_E$  for  $\text{F}_2$  is 5 kJ/mol, but for  $\text{Cl}_2$  is 17 kJ/mol.

# Molecular Interpretation of Factors Affecting the Rate – Concentration

- Reaction rate generally increases as the concentration or partial pressure of reactant molecules increases.
  - Except for zero order reactions
- More molecules leads to more molecules with sufficient kinetic energy for effective collision.
  - Distribution the same, just bigger curve

# Molecular Interpretation of Factors Affecting the Rate – Temperature

- Increasing the temperature raises the average kinetic energy of the reactant molecules.
- There is a minimum amount of kinetic energy needed for the collision to be converted into enough potential energy to form the activated complex.
- Increasing the temperature increases the number of molecules with sufficient kinetic energy to overcome the activation energy.

# Effect of Temperature on Rate

- Changing the temperature changes the rate constant of the rate law.
- Svante Arrhenius investigated this relationship and showed the following:

$$k = A \left( e^{\frac{-E_a}{RT}} \right)$$

$T$  is the temperature in kelvins.

$R$  is the gas constant in energy units, 8.314 J/(mol · K).

$A$  is called the frequency factor, the rate the reactant energy approaches the  $E_a$

$E_a$  is the activation energy, the extra energy needed to start the molecules reacting.

# The Arrhenius Equation Rearranged

$$\ln(k) = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln(A)$$

- Simplifies solving for  $E_a$
- $-E_a / R$  is the slope when graphing  $\ln(k)$  vs.  $(1/T)$
- $\ln(A)$  is the y-intercept
- $E_a = -R(\text{slope})$
- Graphing  $\ln(k)$  vs  $(1/T)$  and taking line of best fit can quickly yield a slope

# Arrhenius Equation – Exponential Factor

- The exponential factor in the Arrhenius equation is a number between 0 and 1.
- Represents the fraction of reactant molecules with sufficient energy so they can make it over the energy barrier.
  - The higher the energy barrier (larger  $E_A$ ), the fewer molecules that have sufficient energy to overcome it.
- That extra energy comes from converting the kinetic energy of motion to potential energy in the molecule when the molecules collide.
  - Increasing the temp increases the average kinetic energy of the molecules.
  - Therefore, increasing the temp will increase the number of molecules with sufficient energy to overcome the energy barrier.
  - Therefore, increasing the temperature will increase the reaction rate.

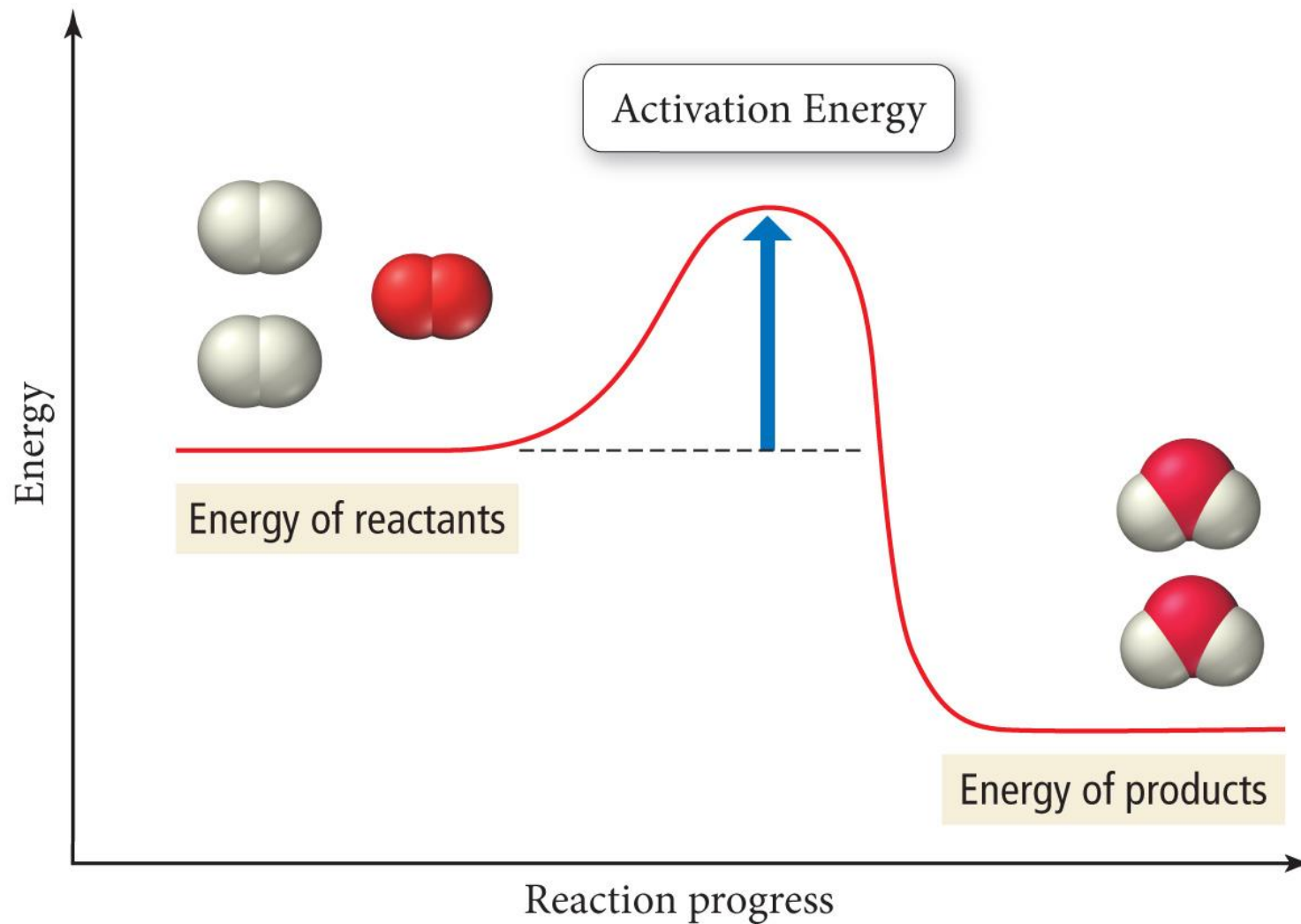
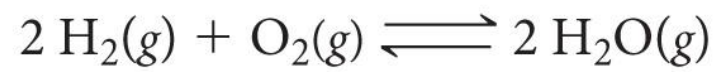
$$k = A \left( e^{\frac{-E_a}{RT}} \right)$$

# Arrhenius Equation – Two Point Format

If you only have two (T, *k*) data points, the following form of the Arrhenius equation can be used:

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

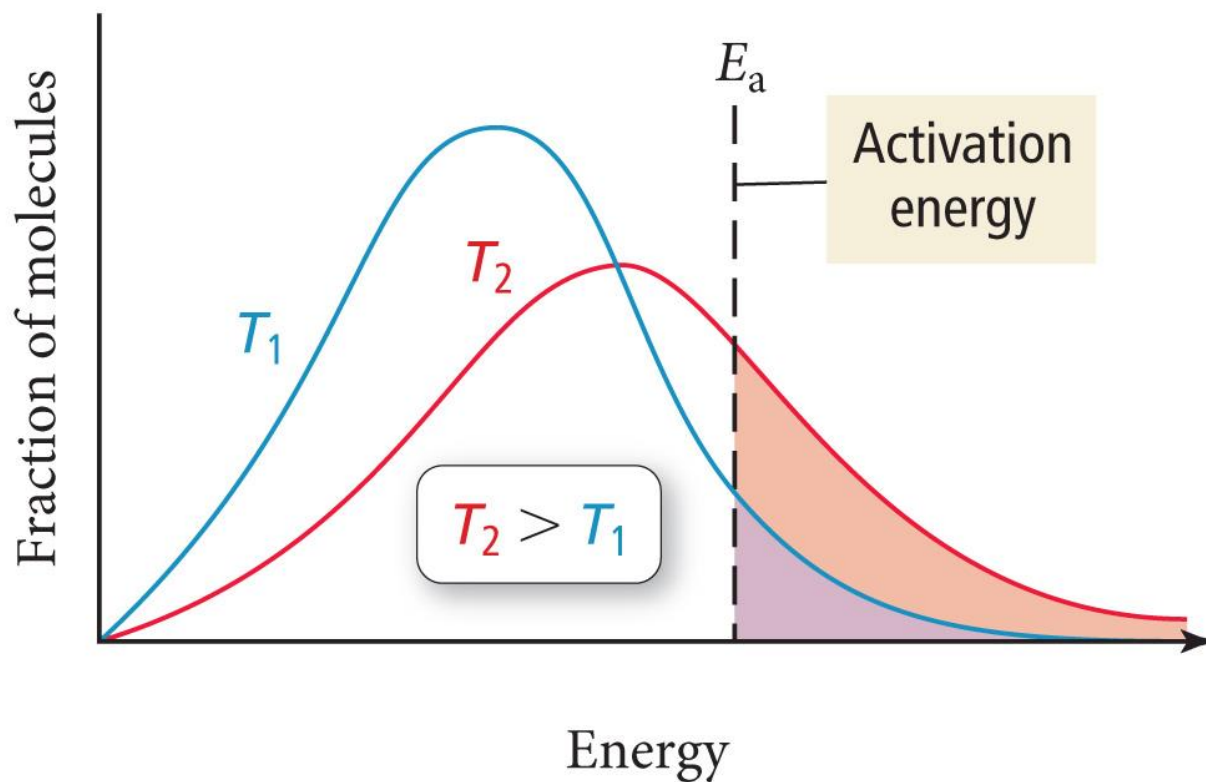
# Activation Energy





# Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



# Catalysts

**Catalyst** - A substance that speeds up a reaction without being consumed during the reaction.

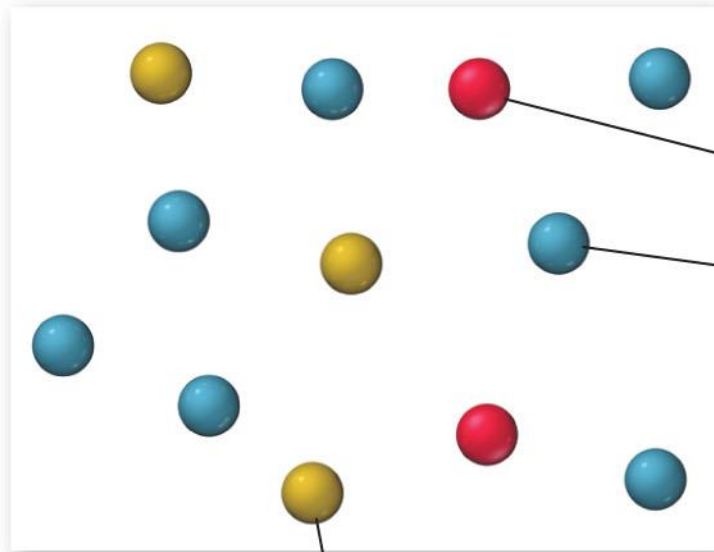
**Enzyme** - A large molecule (usually a protein) that catalyzes biological reactions.

**Homogeneous catalyst** - Present in the same phase as the reacting molecules.

**Heterogeneous catalyst** - Present in a different phase than the reacting molecules.

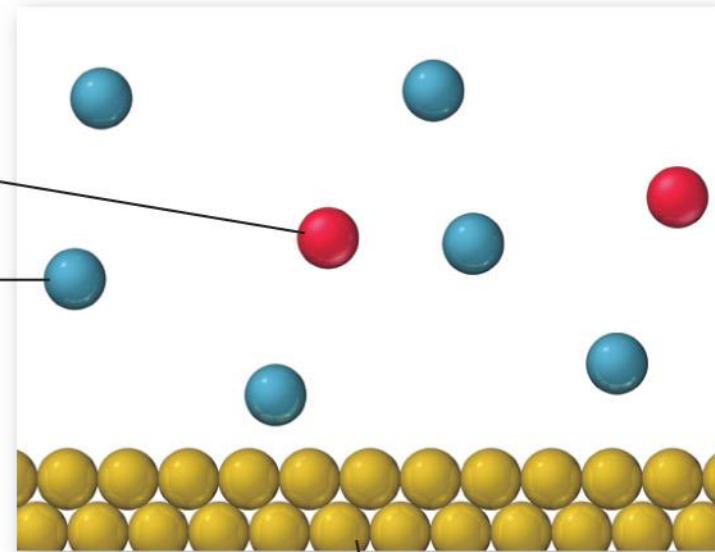
# Types of Catalysts

Homogeneous catalysis



Catalyst in same phase as reactants

Heterogeneous catalysis



Catalyst in different phase than reactants

Product

Reactant

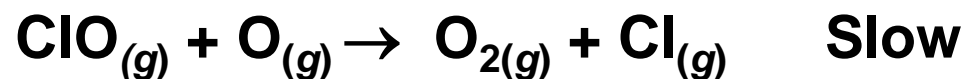
# Catalysts

- Catalysts work by providing an alternative mechanism for the reaction with a lower activation energy.
- Catalysts are consumed in an early mechanism step, and then re-made in a later step.

## Mechanism without catalyst:



## Mechanism with catalyst:

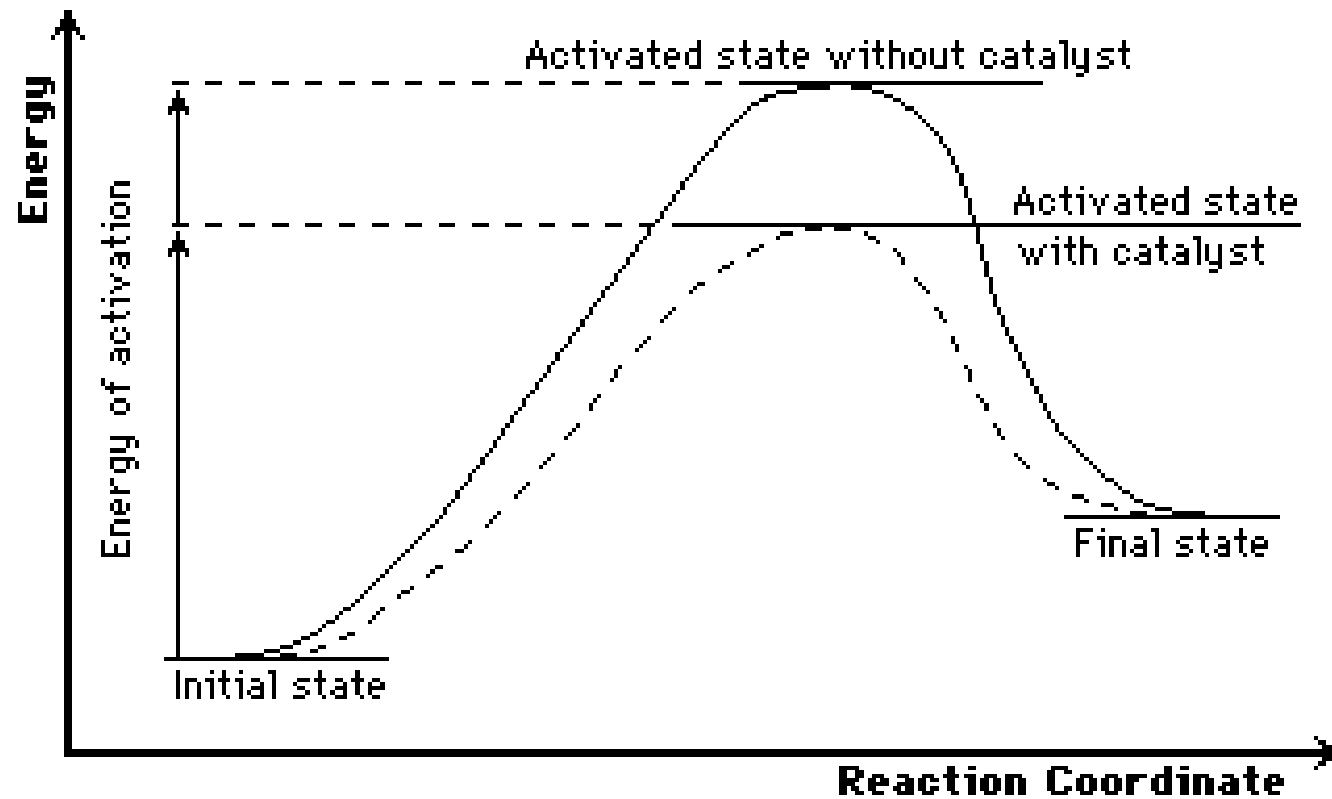


# Molecular Interpretation of Factors Affecting the Rate – Catalysts

Give reactant molecules a different path to follow w/ lower  $E_A$ .

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

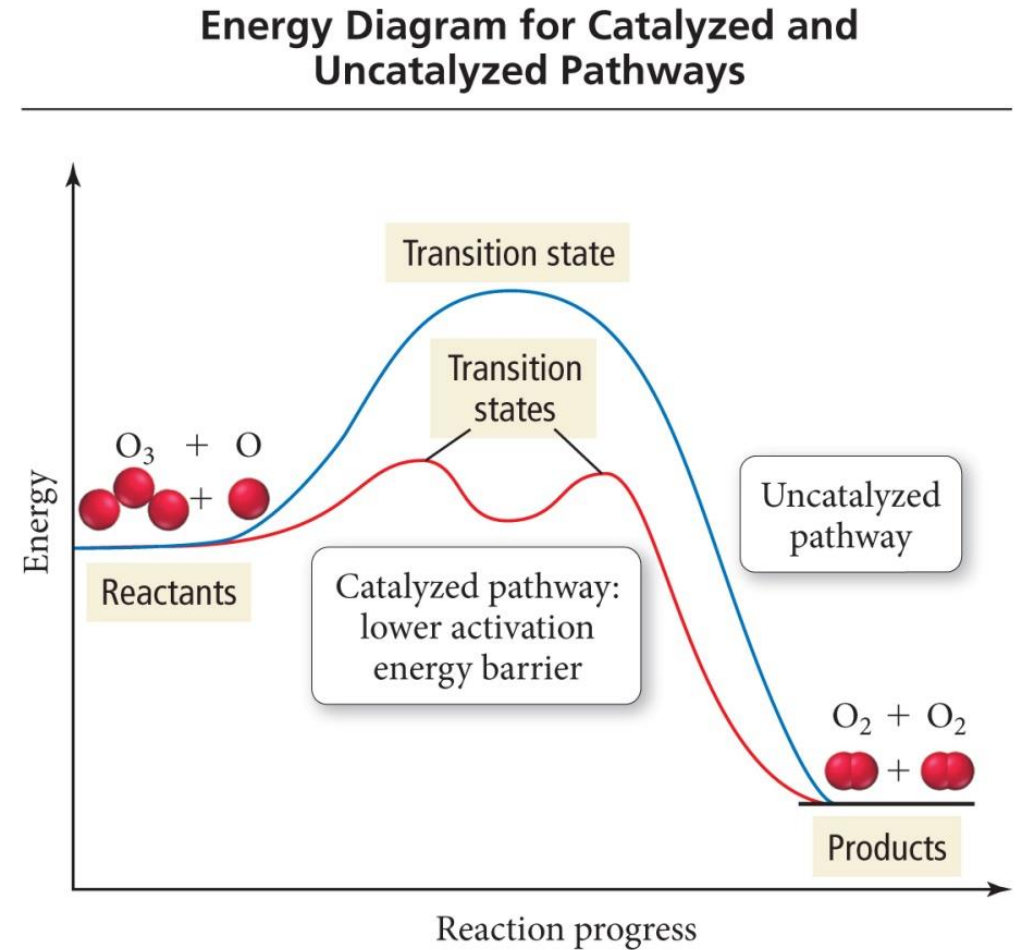
# Lowering of $E_A$ by a Catalyst



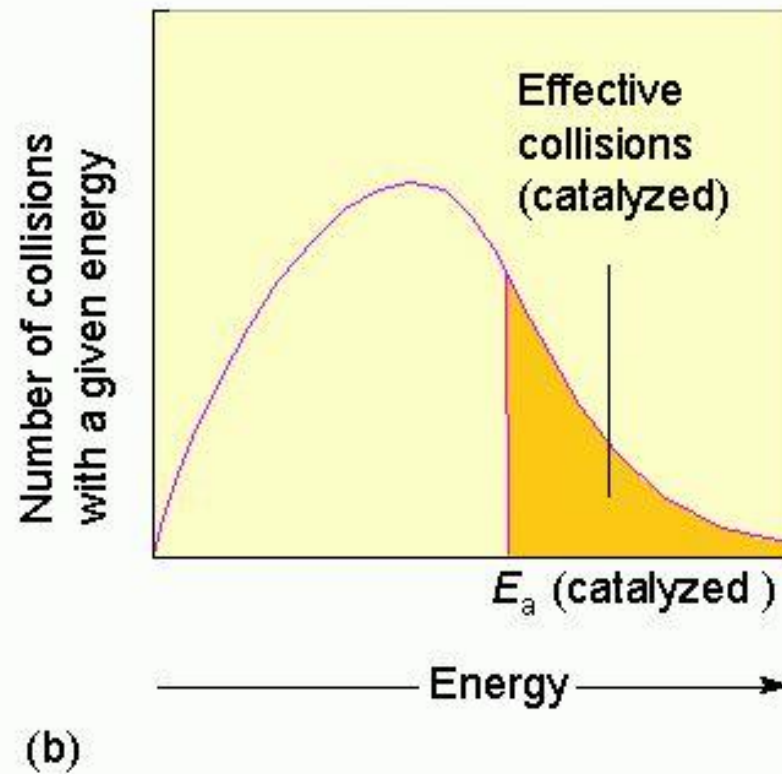
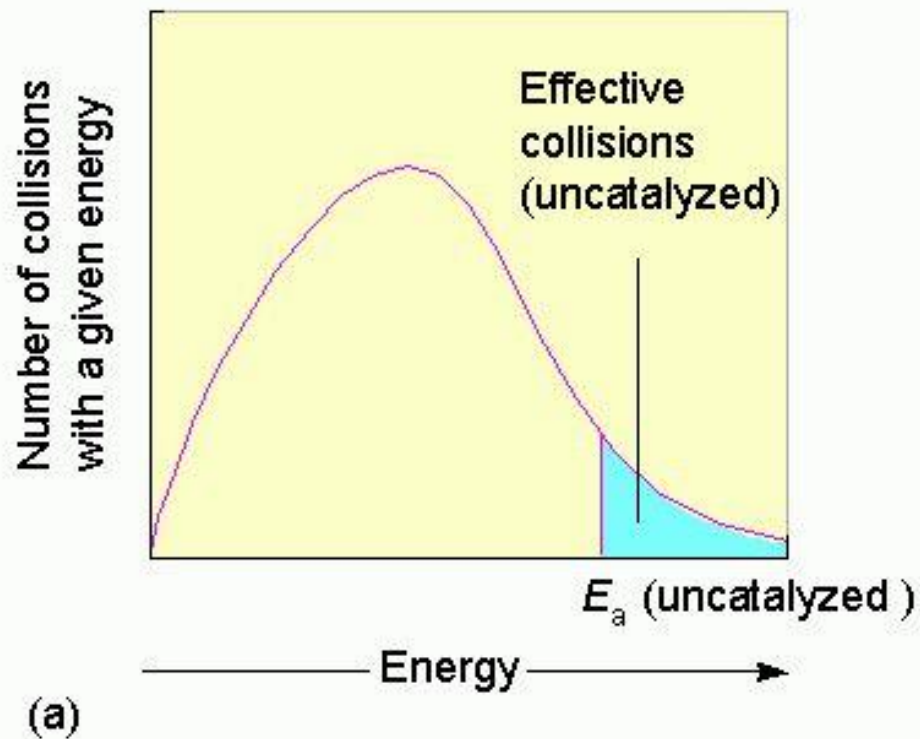
# Energy Profile of a Catalyzed Reaction



Polar stratospheric clouds contain ice crystals that catalyze reactions that release Chlorine from atmospheric chemicals.



# Catalysts Increase the # of Effective Collisions



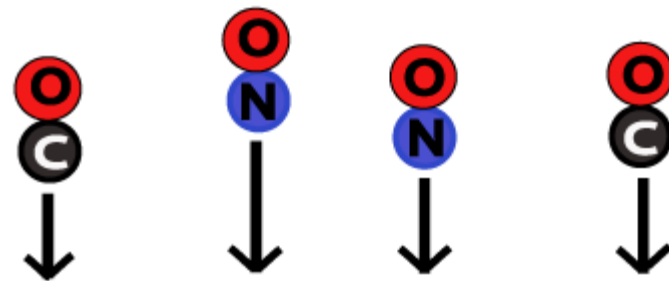


# Heterogeneous Catalysts

## Step #1:

Adsorption and activation of the reactants.

Carbon monoxide and nitrogen monoxide adsorbed on a platinum surface



Platinum

# Heterogeneous Catalysts

## Step #2:

Migration of the adsorbed reactants on the surface.

Carbon monoxide and nitrogen monoxide arranged prior to reacting



Platinum

# Heterogeneous Catalysts

## Step #3:

Reaction of the adsorbed substances.

Carbon dioxide and nitrogen form from previous molecules



Platinum

# Heterogeneous Catalysts

## Step #4:

Escape, or desorption, of the products.

