N11 - KINETICS

Collision Theory and More

Link to YouTube Presentation: https://youtu.be/OgoI25FK9_M

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Collision Theory and More

Target: I can use Collision Theory to describe how factors like temperature, concentration, and catalysts affect the speed of a reaction.

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

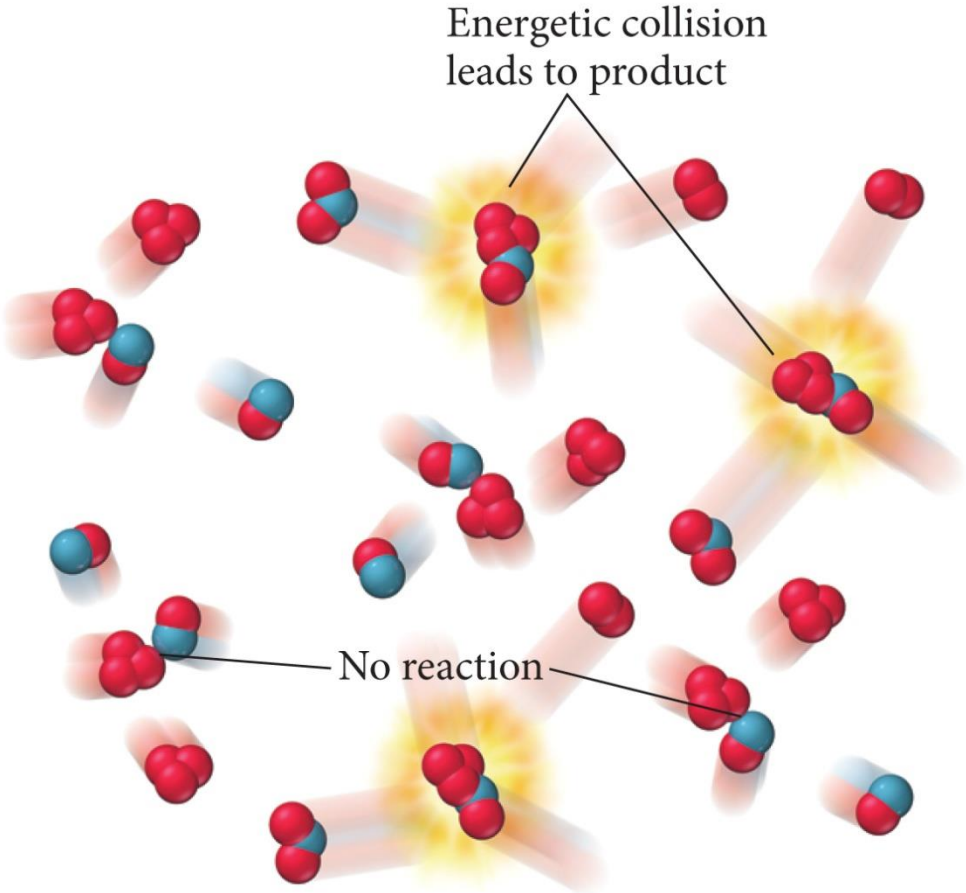
The # of species that must collide to produce the rxn indicated by that step

- **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
$A \rightarrow$ products	Unimolecular	Rate = $k[A]$
$A + A \rightarrow$ products ($2A \rightarrow$ products)	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow$ products		Rate = $k[A][B]$
$A + A + B \rightarrow$ products ($2A + B \rightarrow$ products)	Termolecular	Rate = $k[A]^2[B]$
$A + B + C \rightarrow$ products		Rate = $k[A][B][C]$

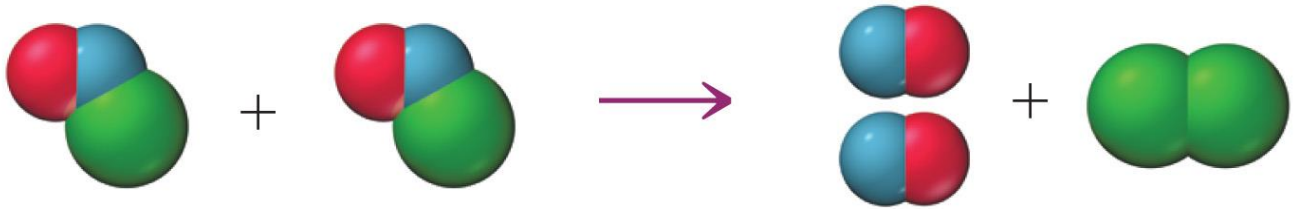
Effective Collisions- Kinetic Energy Factor

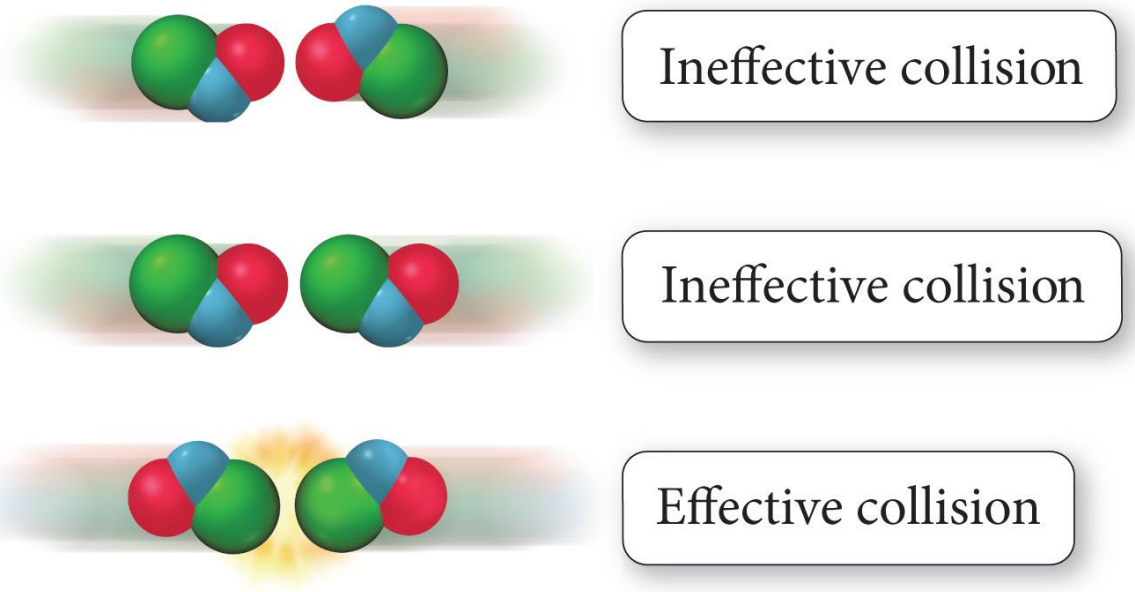
For a collision to lead to overcoming the energy barrier, the reacting molecules must have sufficient kinetic energy so that when they collide the activated complex can form.



Effective Collisions - Orientation Factor

$$NOCl(g) + NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$





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.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ is about 12 times faster than

$CD_4 + Cl_2 \rightarrow CD_3Cl + DCl$ because the C—H bond is weaker and less stable than the C—D bond.

$CH_4 + X_2 \rightarrow CH_3X + HX$ occurs about 100x faster with F_2 than Cl_2 because the A_E for F_2 is 5 kJ/mol, but for 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:

$$k = Ae^{\left(\frac{-Ea}{RT}\right)}$$

T = temperature in kelvins.

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

A = called the frequency factor, the rate the reactant energy approaches the Ea

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

The Arrhenius Equation Rearranged

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

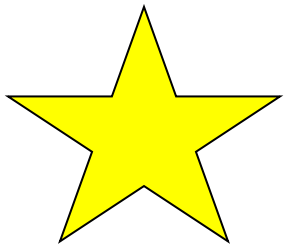
- Simplifies solving for E_a
- $-E_a / R$ is the slope when graphing ln(k) vs. (1/T)
- ln(A) is the y-intercept
- Graphing ln(k) vs (1/T) and taking line of best fit can quickly yield a slope

Arrhenius Equation – Two Point Format

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

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

Or...



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

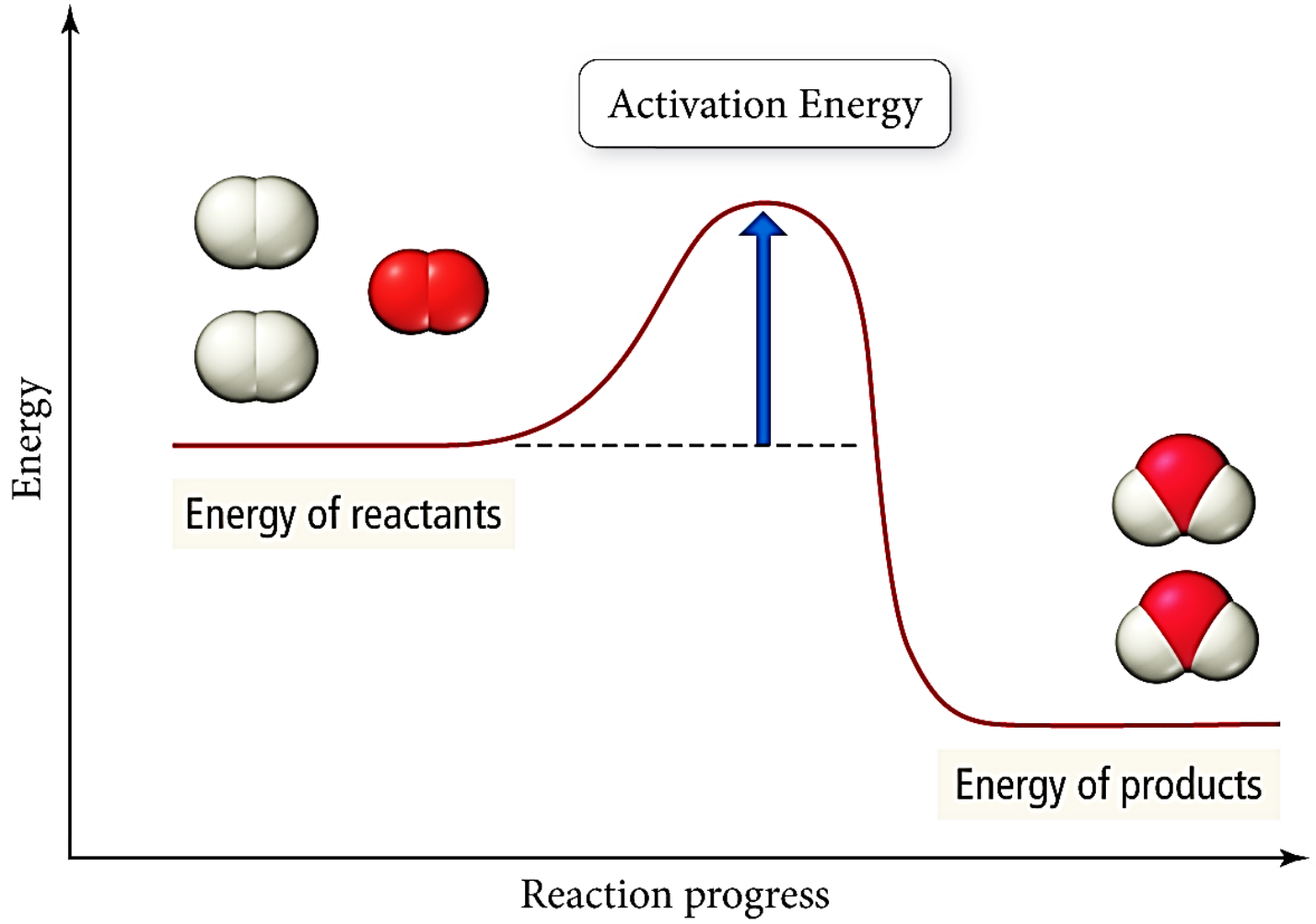
Arrhenius Equation – Exponential Factor

$$k = Ae^{\left(\frac{-Ea}{RT}\right)}$$

- 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.

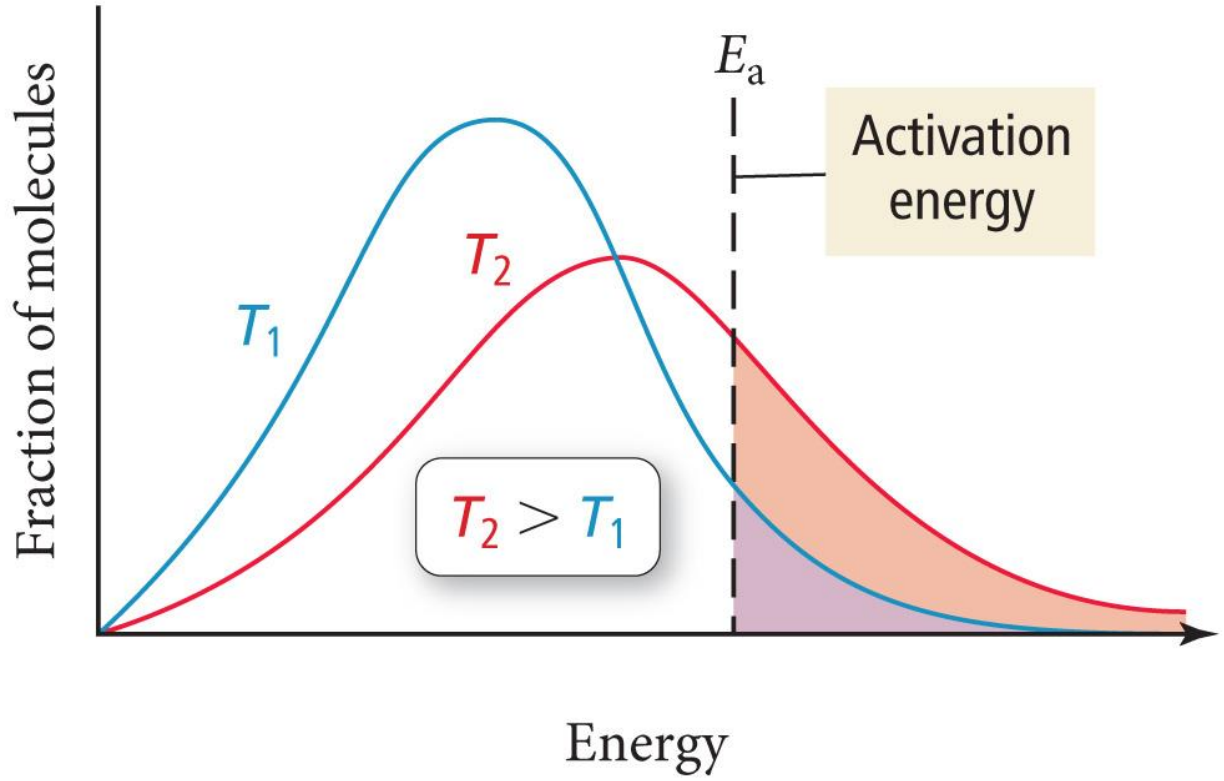
Activation Energy

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$$



Thermal Energy Distribution

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



Catalysts

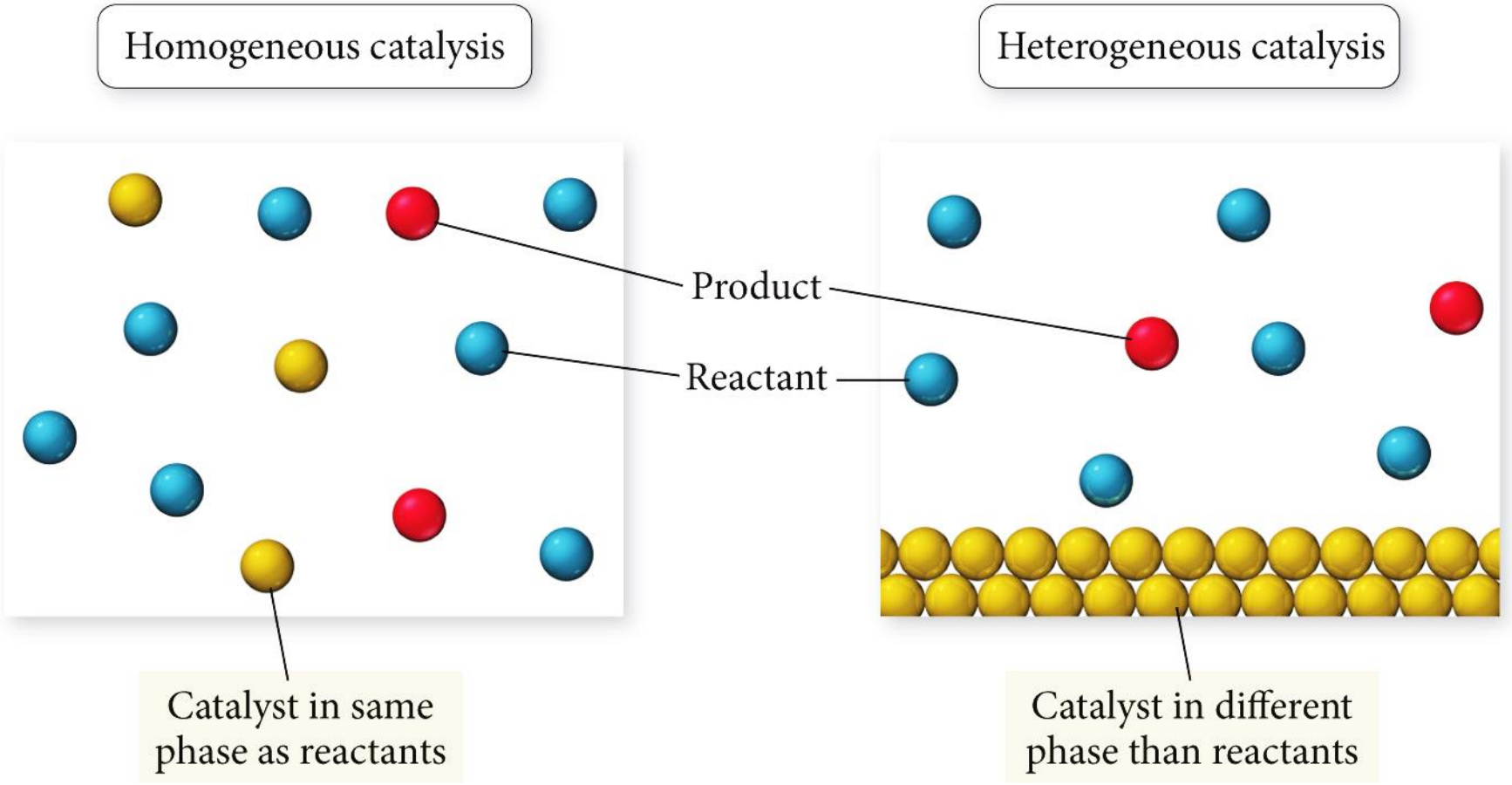
Catalyst - A substance that speeds up a reaction without being consumed during the reaction.

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



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:

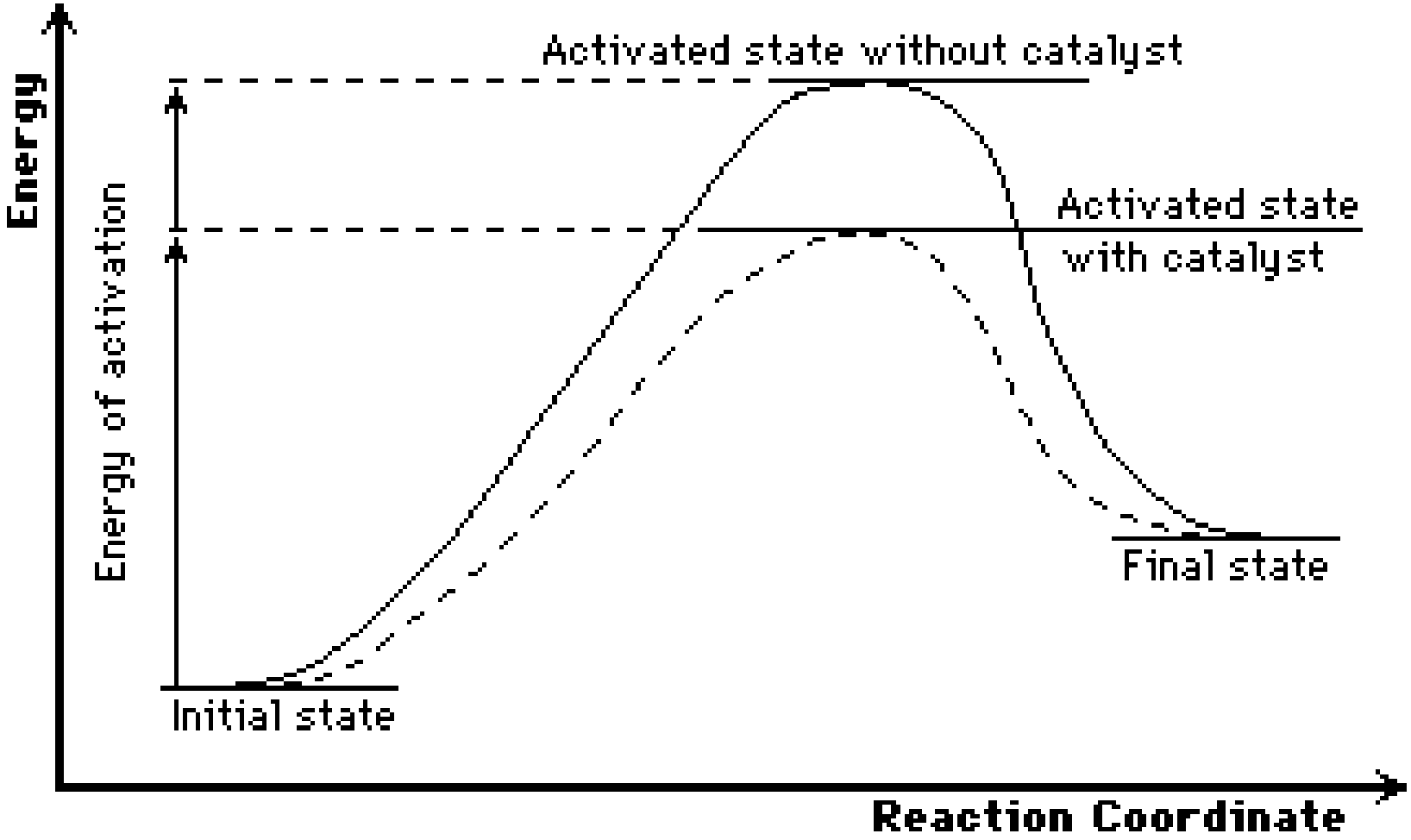
$O_{3(g)} + O_{(g)} \rightarrow 2\ O_{2(g)}$ **Very Slow**

Mechanism with catalyst:

$Cl_{(g)} + O_{3(g)} \Leftrightarrow O_{2(g)} + ClO_{(g)}$ **Fast**

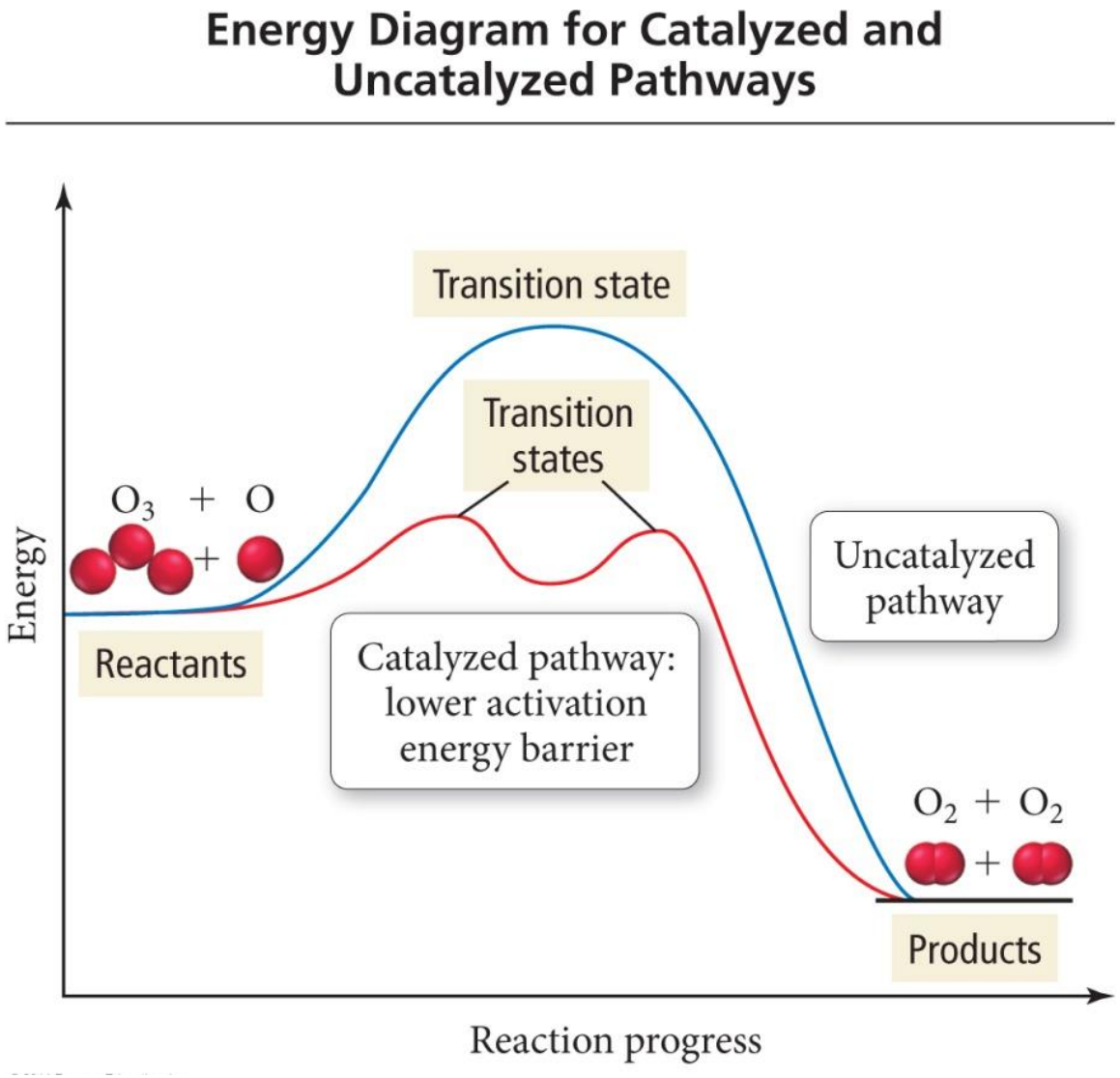
$ClO_{(g)} + O_{(g)} \rightarrow O_{2(g)} + Cl_{(g)}$ **Slow**

Lowering of E_A by a Catalyst

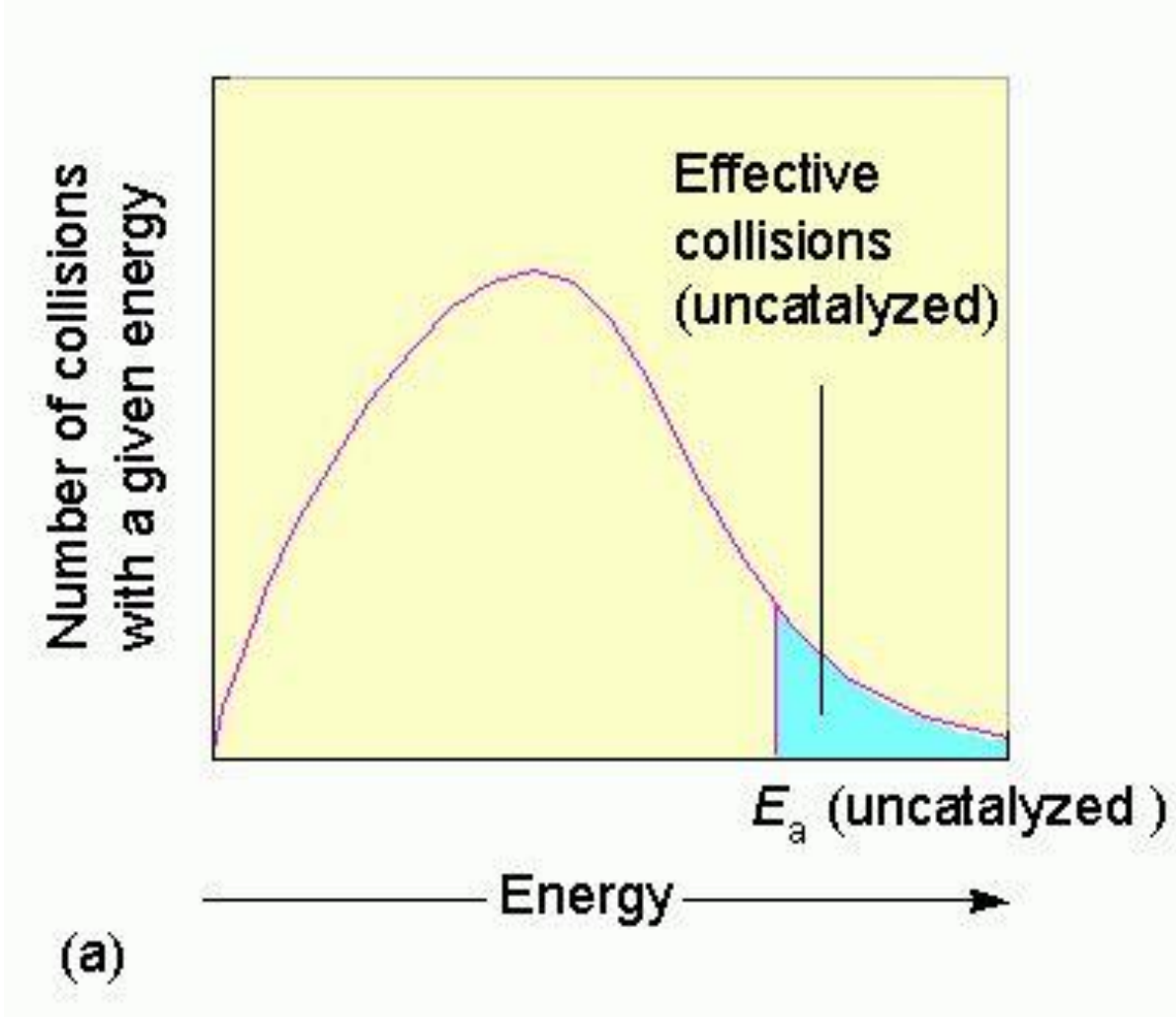


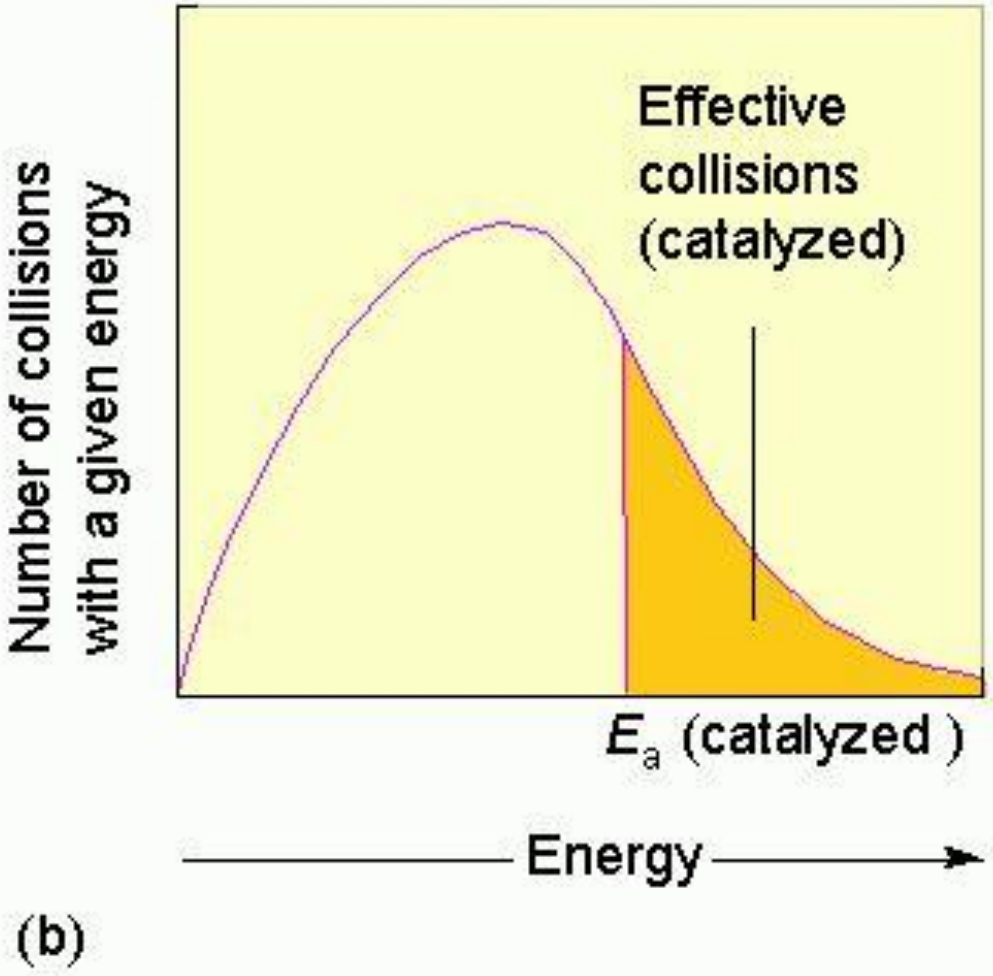
Energy Profile of a Catalyzed Reaction

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



Catalysts Increase the # of Effective Collisions





Molecular Interpretation of Factors Affecting the Rate – Catalysts

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

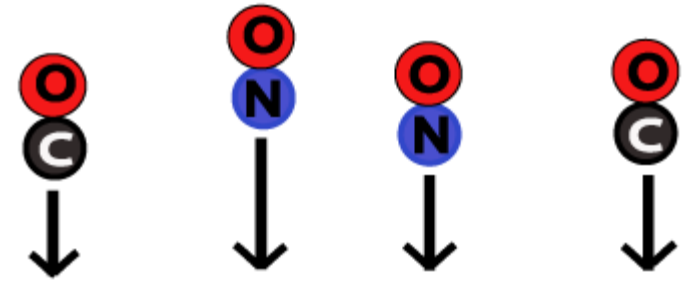
- **Homogeneous catalysts** react with one of the reactant molecules to form a more stable activated complex with a lower activation energy.
- **Heterogeneous catalysts** hold one reactant molecule in proper orientation for reaction to occur when the collision takes place.
  - Sometimes they also help to start breaking bonds.

Heterogeneous Catalysts

Step #1:

Adsorption and activation of the reactants.

Carbon monoxide and nitrogen monoxide adsorbed on a platinum surface

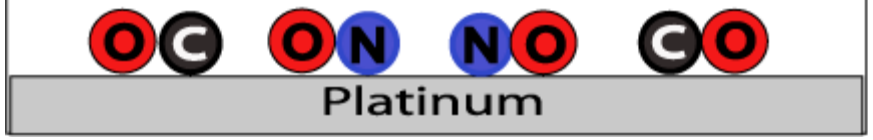


Heterogeneous Catalysts

Step #2:

Migration of the adsorbed reactants on the surface.

Carbon monoxide and nitrogen monoxide arranged prior to reacting



Heterogeneous Catalysts

Step #3:

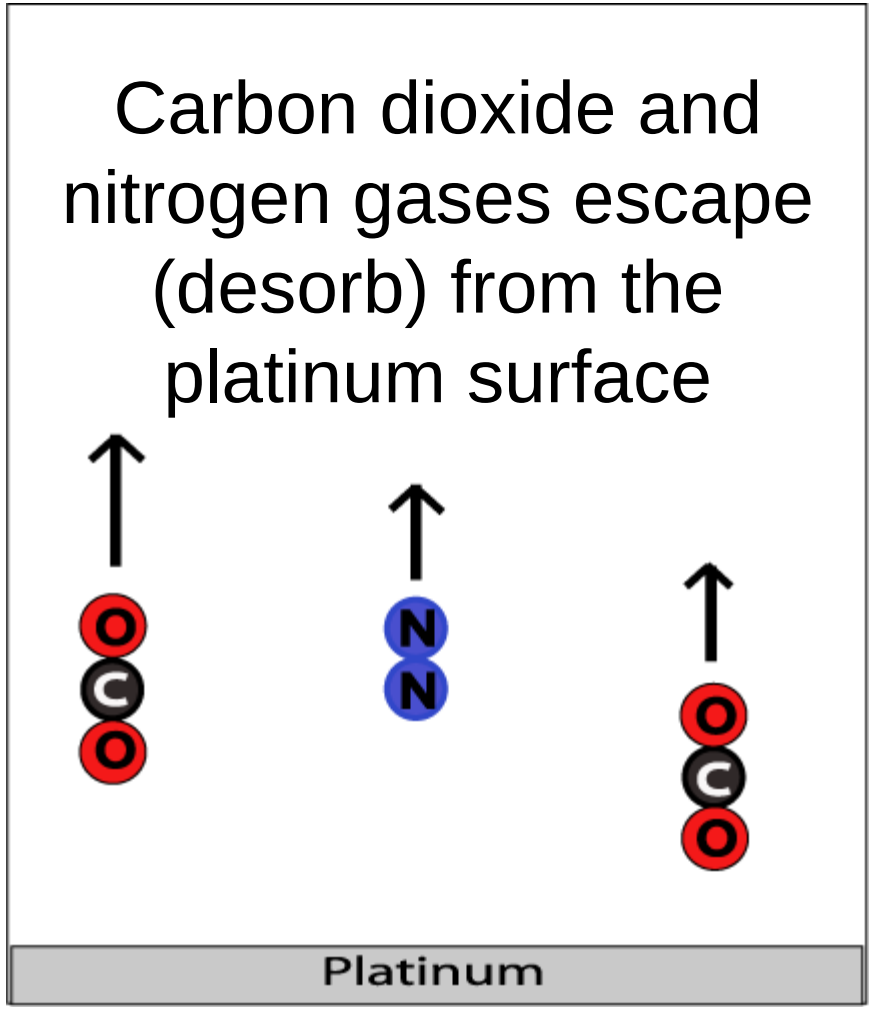
Reaction of the adsorbed substances.

Carbon dioxide and nitrogen form from previous molecules

Heterogeneous Catalysts

Step #4:

Escape, or desorption, of the products.



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