TEMPERATURE AND RATE

- The Rate of Reaction depends on Temperature.

Recall:

- k (rate constant) is temperature dependent.
- In most cases k increases with temperature

Example: $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$

Temperature	**k**
25^0 C	$4.9 \times 10^{-6}\ M^{-1}s^{-1}$
35^0 C	$15 \times 10^{-6}\ M^{-1}s^{-1}$

NOTE:

- In this case, **"k"** (the Rate Constant) is more than tripled for a 10^0 C increase in temperature.
- Consequently, for this reaction, the Reaction Rate is also more than tripled for a 10^0 C increase in temperature.

Why?

COLLISION THEORY

- Collision theory states that for a reaction to occur, the reactant molecules must collide:
  - with an **energy** greater that some minimum value, called Activation Energy (E_a)

and

  - with the **proper orientation**
  - **"k"** is shown to depend on 3 factors:

$$k = Z\ f\ p$$

rate constant | collision frequency | fraction of collisions with $E > E_a$ | fraction of collisions with proper orientation

For the previous example:

$$NO\ (g) + Cl_2\ (g) \longrightarrow NOCl\ (g) + Cl\ (g)$$

Z = collision frequency – (depends on temperature)

- (As **"t"** increases —> molecules move faster —> molecules collide more often)
- Root-mean-square (r m s) ≈ average molecular speed = u

$$\mathbf{u} = \sqrt{\frac{\mathbf{3RT}}{\mathbf{M_m}}}$$

- This relationship shows that :
  - At 25^0C, a 10^0C increase in temperature, increases Z by 2 %
  - This does not explain the large increase in rate with temperature

f = fraction of molecules with E > E_a

$$f = e^{-\frac{E_a}{RT}}$$

e = 2.718
R = 8.31 J/molK
E_a= 8.5 x 10^4 J/mol

For: $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$

At : 25^0 C (298K) f = 1.2 x 10^{-15}

35^oC (308) f = 3.8 x 10^{-15}

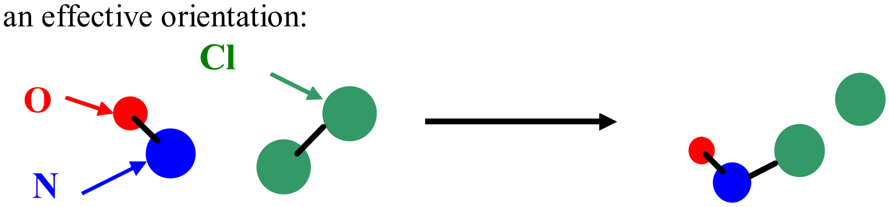
NOTE: 1. "f " triples with a 10^0C increase in temperature

2. The Effect of E_a is impressive:

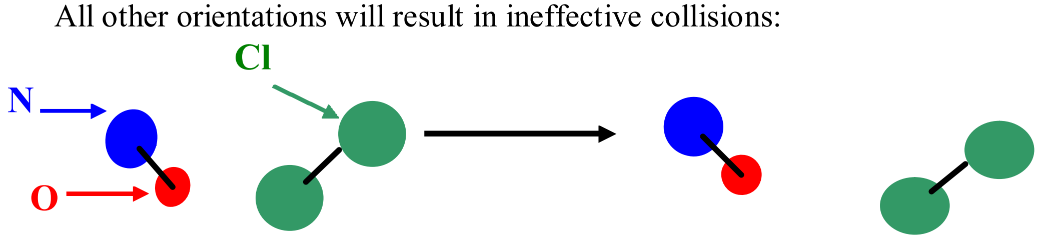
- If E_a is large —>"f" is small" —> "k" is small—>reaction is slow
- If E_a is small —>"f" is large" —> "k" is large—>reaction is fast

p = fraction of collisions with proper orientation

- The only effective orientation is the one in which:
  - The NO molecules approaches with N atom toward Cl_2
  - The angle of approach is about that expected for the formation of bonds in NOCl (slightly less than 120^0)
  - See below an effective orientation:

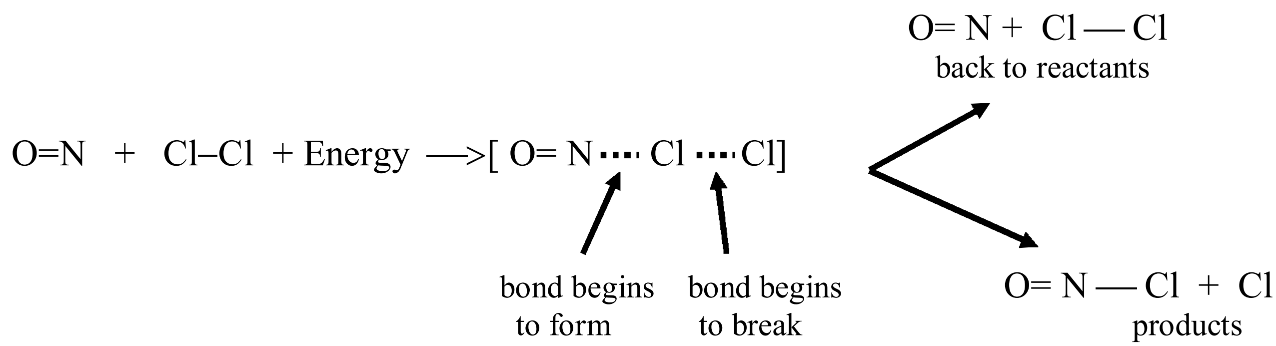


  - All other orientations will result in ineffective collisions:



TRANSITION STATE THEORY

- This theory explains the reaction resulting from the collision of 2 molecules, in terms of an ***activated complex***.
- An Activated Complex (***Transition State***) is an unstable grouping of atoms that can break up to form products:



- Which bond breaks depends on where the absorbed energy is concentrated.

POTENTIAL – ENERGY DIAGRAMS FOR REACTIONS

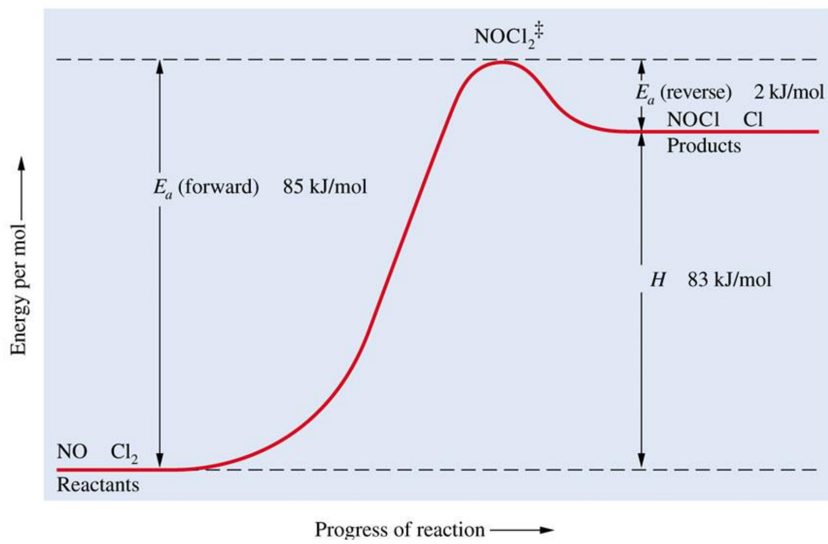
I. Endothermic Reactions

Reactants + 83 kJ/mol ——> Products $\Delta H = + 83$ kJ/mol

Energy of Reactants < Energy of Products

Example: NO + Cl_2 ——> $NOCl_2^*$ ——> NOCl + Cl

activated complex



NOTEs:

1. Sum of (Kinetic Energy + Potential Energy) is constant throughout the reaction. (Law of Conservation of Energy)
2. From: Reactants ———> Activated Complex
   (NO + Cl_2) ($NOCl_2^*$)

   - Potential Energy increases (outer electrons of molecules repel, as molecules get closer)
   - Kinetic Energy decreases (molecules slow down)
   - Kinetic Energy changes into Potential Energy
3. The reaction will yield product only if : PE(max) ≥ Activation Energy (Ea). This will only occur if reactant molecules possess sufficient KE to start with.

   KE (reactants) ———> PE max (of activated complex) ≥ Activation Energy (E_a)
4. Comparing the forward and the reverse reactions.

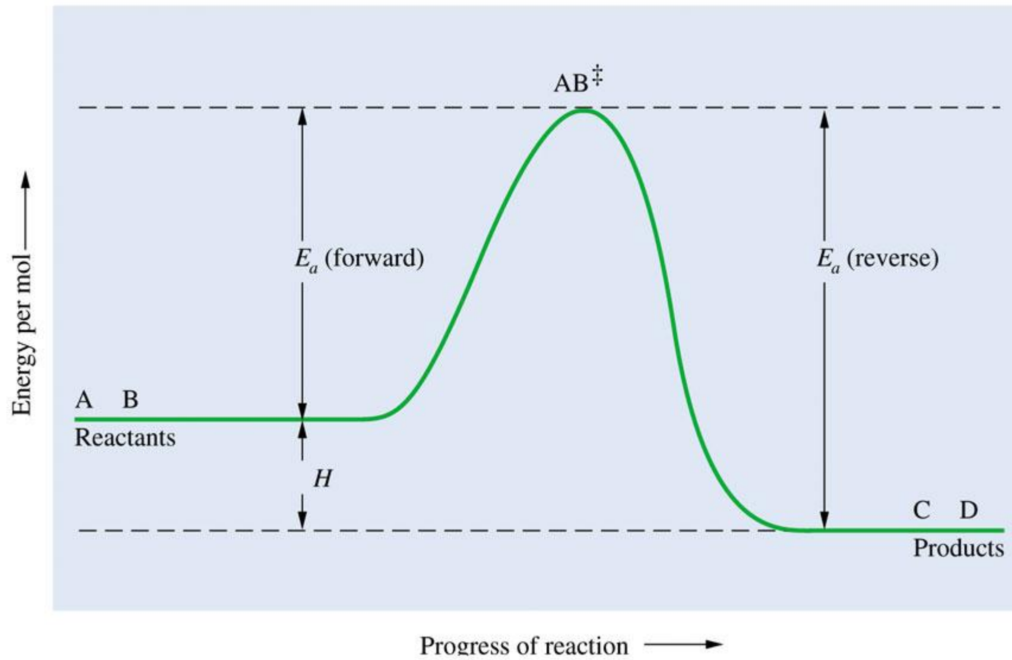
Forward Rxn		Reverse Reaction
NO + Cl_2 —> NOCl + Cl		NOCl + Cl —> NO + Cl_2
Ea = 85 kJ/mol	>>>>>>>>>>>>>	Ea = 2 kJ/mol
k is much smaller		k is much larger
Reaction is much slower		Reaction is much faster

II. **Exothermic Reactions**

Reactants – ΔH ——> Products ΔH is negative

Energy of Reactants > Energy of Products

Example: A + B ——> C + D+ Energy



ARRHENIUS EQUATION

$$k = A\,e^{-\frac{Ea}{RT}}$$

e = 2.718
Ea = Activation Energy
R = gas constant = 8.31 J/K x mol
T = absolute temperature
A = frequency factor

- The equation expresses the dependence of k on temperature.

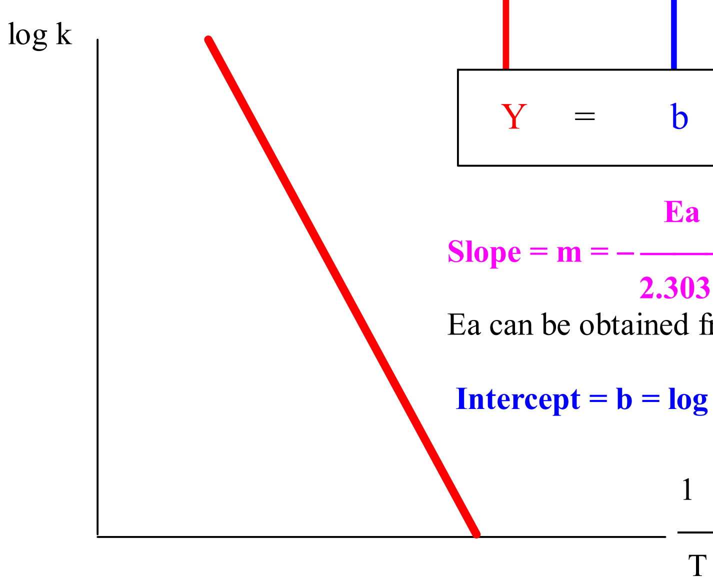
  A = frequency factor

  - A is related to the frequency of collisions (Z) with proper orientation (p)
  - A depends slightly on temperature (but can be ignored)

$$\ln k = \ln A - \frac{Ea}{RT} \qquad \log k = \log A - \frac{Ea}{2.303\,RT}$$

$$\log k = \log A - \left(\frac{Ea}{2.303\,R}\right)\left(\frac{1}{T}\right)$$

$$Y = b + m\,x$$



Slope = m = $-\dfrac{Ea}{2.303\,R}$

Ea can be obtained from the slope

Intercept = b = log A

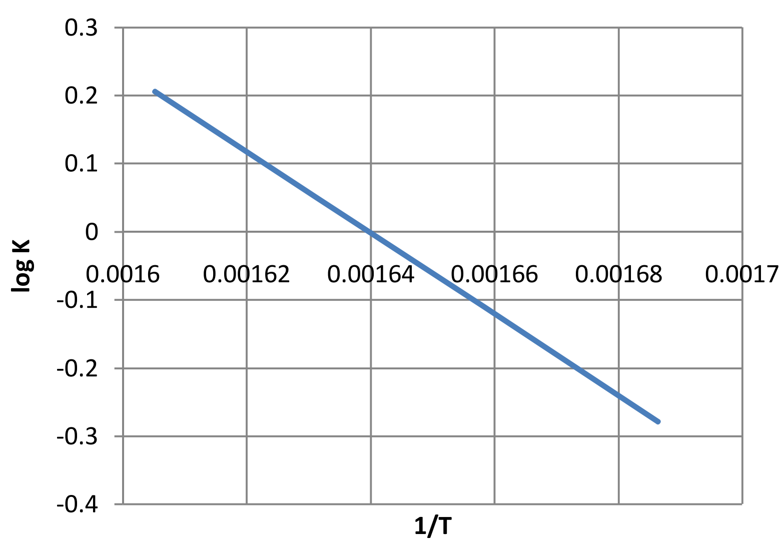
Examples:

1. Sketch a potential energy diagram for the decomposition of nitrous oxide:

$$2\ N_2O\ (g)\ \rightarrow\ 2\ N_2\ (g)\ +\ O_2\ (g)$$

The activation energy for the forward reaction is 251 kJ; the ΔH° is +167 kJ. What is the activation energy for the reverse reaction? Label the diagram appropriately.

2. The rate constant for a particular reaction was studies at various temperatures and a plot of log k vs. 1/T was obtained as shown below. Determine the activation energy of this reaction based on the graph below.



REACTION MECHANISMS

- Reaction Mechanisms show the steps involved in the change from Reactants to Products
- Mechanisms consist of a set of "**Elementary Reactions**" whose overall effect is the Net Chemical Equation.

Elementary Reactions:

- **Elementary reactions** are single molecular events that result in a reaction and are caused by molecular collisions

NO_2 (g) + CO (g) ——> NO (g) + CO_2 (g) Net Chemical Equation

Below 500K, this reaction takes place in 2 steps:

Elementary Reaction 1: NO_2 + NO_2 ——> NO_3 + NO
Reaction intermediate (short-lived)

Elementary Reaction 2: NO_3 + CO ——> NO_2 + CO_2

- Adding the steps (Elementary Reactions) yields the Overall Equation:

~~NO_2~~ + NO_2 ——> ~~NO_3~~ + NO

~~NO_3~~ + CO ——> ~~NO_2~~ + CO_2

NO_2 + CO ——> NO + CO_2 Overall Equation

Example 1:

The decomposition of Ozone (O_3) is believed to occur in 2 steps:

Elementary Reaction 1: $O_3 \rightleftharpoons O_2 + O$

Elementary Reaction 2: $O_3 + O \longrightarrow 2O_2$

Identify any Reaction Intermediate:
What is the Overall equation?

Example 2:

Sodium hydrogen carbonate (**$NaHCO_3$**), also called sodium bicarbonate can been synthesized through a sequence of 3 elementary steps:

$$CO_2\,g) \quad + \quad H_2O \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) \quad + \quad NH_4OH \longrightarrow NH_4HCO_3\,(aq) + H_2O\,(l)$$

$$NH_4HCO_3\,(aq) + NaCl\,(aq) \longrightarrow \mathbf{NaHCO_3\,(s)} + NH_4Cl\,(aq)$$

Identify the Reaction Intermediates:

Write the Overall Equation:

$$CO_2\,g) \quad + \quad H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) \quad + \quad NH_4OH \longrightarrow NH_4HCO_3\,(aq) + H_2O\,(l)$$

$$NH_4HCO_3\,(aq) + NaCl\,(aq) \longrightarrow \mathbf{NaHCO_3\,(s)} + NH_4Cl\,(aq)$$

MOLECULARITY

- **Molecularity** is the number of molecules on the reactant side of an Elementary Reaction.

Unimolecular Reactions:

- **Unimolecular** reactions are Elementary Reactions that involve **ONE** reactant molecule.
- These are commonly the decomposition reactions of unstable species.

Example: $O_3^* \longrightarrow O_2 + O$
excited molecule

Bimolecular Reactions:

- Bimolecular reactions are Elementary Reactions that involve **TWO** reactant molecules.
- These are very common reactions.

  Example: O=N + Cl–Cl ⟶ O=N–Cl + Cl

Termolecular Reactions:

- **Termolecular** reactions are Elementary Reactions that involve **THREE** reactant molecules.
- These are less common because the chance of three molecules coming together with the right orientation is unlikely.

Example 1:
What is the molecularity of each of the following elementary reactions?

$O + O_2 + N_2 \longrightarrow O_3 + N_2^*$

$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$

$Cl + H_2 \longrightarrow HCl + H$

$CS_2 \longrightarrow CS + S$

Rate Equation for an Elementary Reaction

I. For an Overall Reaction, the Rate Law cannot be predicted by the Overall Equation

Reasons:

- The majority of reactions consist of several elementary steps.
- The Rate Law is the combined result of the elementary steps
- The rate of all the elementary reactions must be known in order to predict the rate law for the overall equation.

II. For an Elementary Reaction, the Rate Law can be written directly from the Elementary Equations

- The rate of an elementary reaction is proportional to the product of the concentrations of each reactant molecule.

1. Unimolecular Elementary Reactions

$A \longrightarrow B + C$ Rate = k [A]

2. Bimolecular Elementary Reactions

$A + B \longrightarrow C + D$ Rate = k [A] [B]

Reason:

- The frequency of collisions is proportional to the number of A molecules (n_A) and the number of B molecules (n_B)

3. Termolecular Elementary Reactions

$A + B + C \longrightarrow D + E$ Rate = k [A] [B] [C]

Examples:

Write Rate Equations for each of the elementary reactions shown below

:

1) $O_3 + NO \longrightarrow O_2 + NO_2$

Rate =

2) $CS_2 \longrightarrow CS + S$

Rate =

3) $2NO_2 \longrightarrow N_2O_4$ or $NO_2 + NO_2 \longrightarrow N_2O_4$

Rate =

NOTE:

- For Elementary Reactions **ONLY,** the coefficients of the balanced chemical elementary reaction are the exponents to which the concentrations of the reactants are raised.

THE RATE LAW AND THE MECHANISM

- The Suggested Mechanism for a particular reaction:
  - cannot be observed directly,
  - is a rationalized explanation based on experimental data,
  - is accepted provisionally, and may be replaced by another suggested mechanism based on further experimentation.

- A Suggested Mechanism
  - Is considered **correct** if it **agrees** with the experimentally determined Rate Law
  - Is considered **incorrect** if it **does not agree** with the experimentally determined Rate Law

Example 1:

Overall Equation: $2\ NO_2\ (g) + F_2\ (g) \longrightarrow 2\ NO_2F\ (g)$

Experimental Rate Law: Rate = k $[NO_2]\ [F_2]$

NOTE: 1st order with respect to NO_2
1st order with respect to F_2
2nd order Overall

Predicted Possible Mechanisms:

1. One Single Elementary Reaction

$NO_2 + NO_2 + F_2 \longrightarrow 2\ NO_2F$ (Termolecular)

Predicted Rate Law: Rate: k $[NO_2]^2\ [F_2]$

NOTE: 2nd order with respect to NO_2
1st order with respect to F_2
3rd order overall

- The predicted Rate Law does not agree with the experimental Rate Law
- This mechanism must be incorrect.

2. Two Single Elementary Reactions

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \quad \text{(slow step)}$$

$$NO_2 + F \xrightarrow{k_2} NO_2F \quad \text{(fast step)}$$

Overall: $2\ NO_2 + F_2 \longrightarrow 2\ NO_2F$

Reaction Intermediate: F

NOTE:

- The Rate Law is determined by the slow step
- **THE SLOWEST STEP ——> THE RATE DETERMINING STEP**
- Predicted Rate Law = RATE (rate-determining-step) = $k_1[NO_2]\,[F_2]$

NOTE: 1^{st} order with respect to NO_2
1^{st} order with respect to F_2
2^{nd} order overall

- The predicted Rate Law agrees with the experimental Rate Law
- This mechanism must be correct.

Predicted Rate Law	Experimental Rate Law
RATE $= k_1[NO_2]\,[F_2]$	RATE $= k\,[NO_2]\,[F_2]$

The two Rate Laws are identical if: $k_1 = k$

Example 2:
The following mechanism has been proposed for decomposition of ozone to oxygen gas:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O \quad \text{(fast equilibrium)}$$

$$O_3 + O \xrightarrow{k_2} 2\ O_2 \quad \text{(slow)}$$

Determine the Rate Law based on this mechanism.

CATALYSIS

- A **Catalyst** is a substance that speeds up a reaction without being consumed.
- In theory the catalyst may be used over and over again.
- In practice, however, there is some loss of catalyst through other reactions that occur at the same time (side-reactions).

Importance of Catalysts:
- Catalysts allow reactions to occur much faster.
- Catalysts allow reactions to occur at lower temperatures (energy savings).

Characteristics of Catalysts:
- Catalysts are often quite specific. They increase the rate of some reactions but not others.
- Enzymes (catalysts used in biological organisms) are extremely selective.

How Catalysts Work:
- A catalyst is an active participant in the reaction.
- A catalyst must participate in one step of a reaction and be regenerated in a later step.
- The catalyzed reaction mechanism makes available a reaction path having an **increased overall rate of reaction** by:
  - increasing the frequency factor A, or
  - decreasing the **Activation Energy, Ea** (most dramatic effect)

$$k = A\,e^{-\frac{Ea}{RT}}$$

<u>Examples:</u>

1. The commercial preparation of sulfuric acid, H_2SO_4 from SO_2 (the early process)

NO ← catalyst

First step: $2\ SO_2\ (g) + O_2(g) \longrightarrow 2\ SO_3\ (g)$

Proposed Mechanism:

2NO + $O_2 \longrightarrow 2\ NO_2$
$NO_2 + SO_2 \longrightarrow$ **NO** + SO_3 (must occur **<u>twice</u>** each time the first step occurs once)

~~2NO~~ + $O_2 \longrightarrow$ ~~2NO₂~~
2~~NO₂~~ + 2$SO_2 \longrightarrow$ 2~~NO~~ + 2SO_3

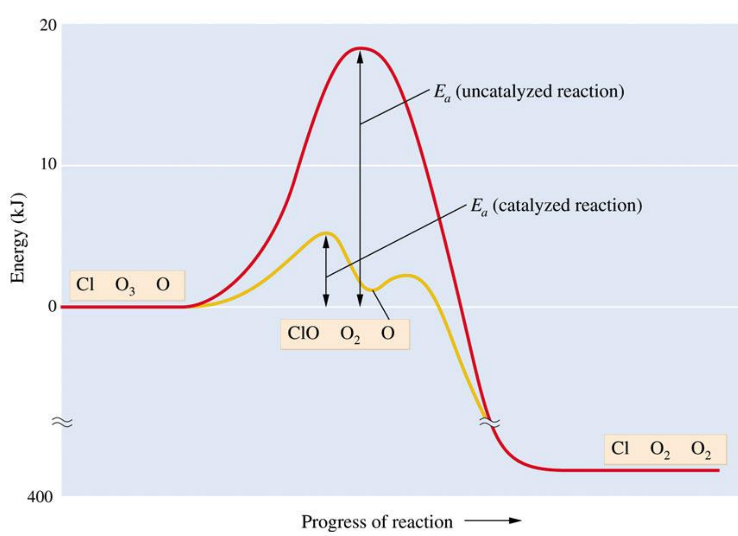
Overall: $2\ SO_2 + O_2 \longrightarrow 2SO_3$

2. The Cl-catalyzed decomposition of ozone (O_3) in the stratosphere
(Cl atoms originate from the decomposition of chloro-fluorocarbons, compounds used as refrigerants and aerosol propellants)

<u>Mechanism of catalyzed reaction</u>:

~~Cl (g)~~ + O_3 (g) ⟶ ~~ClO (g)~~ + O_2 (g)
~~ClO (g)~~ + O (g) ⟶ ~~Cl (g)~~ + O_2 (g)

$O_3\ (g) + O\ (g) \longrightarrow 2\ O_2\ (g)$



HOMOGENEOUS & HETEROGENEOUS CATALYSIS

- **Homogeneous catalysis** is a catalyzed process in which the catalyst is in the same physical phase as the reacting species.

Example:
The commercial preparation of sulfuric acid, H_2SO_4 from SO_2 (the early process)
Catalyst (NO) and reactants (SO_2 and O_2) are all in gaseous phase.

- **Heterogeneous catalysis** is a catalyzed process in which the catalyst exists in a different phase from the reactants.
- In these types the catalyst is usually a solid in contact with a gaseous or liquid solution of reactants.
- Heterogeneous catalysis occurs by the **adsorption** of the reactant molecules to the surface of the solid catalyst.
- **Adsorption** is the attraction of molecules to a surface and it can be of two types:

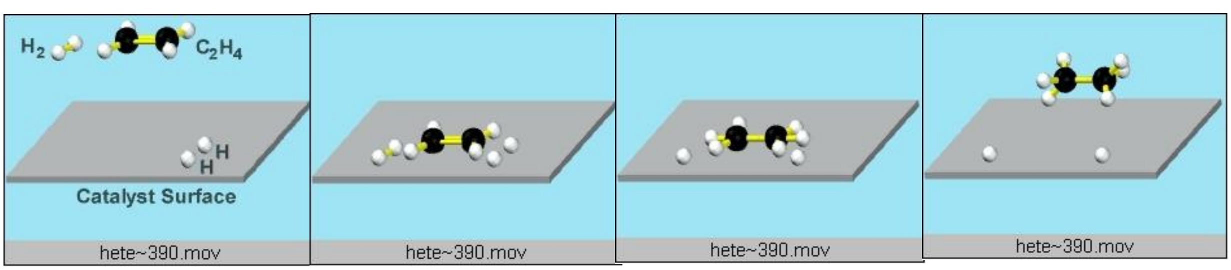
  - Physical Adsorption
    The molecules are attracted to the catalyst surface by weak intermolecular forces.
  - Chemisorption
    The molecules are attached to the catalyst surface by chemical bonds.

Examples:

3. Surface catalysts are used in the catalytic converters of cars to convert potential atmospheric pollutants (such as CO and NO) into CO_2 and N_2.

2. The catalytic hydrogenation of ethylene:

$$\underset{\text{ethylene}}{C_2H_4\,(g)} \quad + \quad H_2\,(g) \xrightarrow{\text{Pt or Ni}} \underset{\text{ethane}}{C_2H_6\,(g)}$$



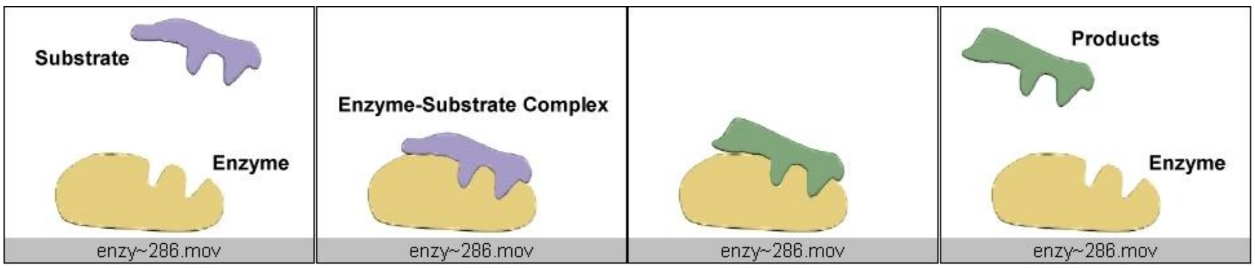
Ethylene and Hydrogen chemisorb to the catalyst surface

Ethane then diffuses of the catalyst surface

ENZYME CATALYSIS

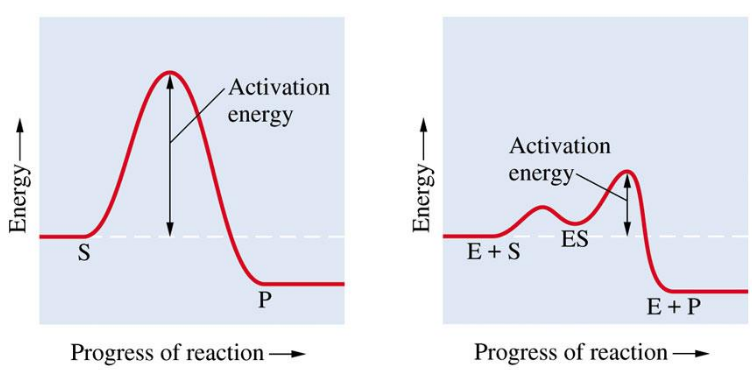
- **Enzymes** are the catalysts of biological organisms.
- Enzymes are huge protein molecules (Molecular Weights over a million amu) that are **highly specific**:
  - Each enzyme acts only on a **specific substance** or a **specific type of substance.**
  - Each enzyme catalyzes a **specific substance** to undergo a **specific reaction.**
- Substrate (S) is the substance whose reaction the enzyme catalyzes.

How an enzyme (E) works



The enzyme molecule folds into a roughly spherical shape with an **active site**	Substrate molecule and enzyme molecule fit into each other like a lock and key	Substrate changes into products, and they diffuse away and the enzyme is regenerated

$$E + S \longrightarrow \underbrace{ES}_{\text{enzyme-substrate complex}} \qquad ES \longrightarrow E + P$$



A B