

Reaction Mechanisms

Reaction Mechanism:

- A step by step sequence of elementary reaction by which the overall chemical change occurs.
- Describes at a molecular level how reactants react to form products step by step
- Almost all reactions occur in a series of small steps called elementary reactions.

Elementary reactions:

- Involve the dissociation of one particle or the collision of two or three particles
- Must add up to give the net or balanced equation
- During each elementary step, reactant bonds are broken at the same time that product bonds are formed

Molecularity:

- The number of molecular species that are involved in a single reaction step
- A theoretical concept which can only be applied to elementary reactions

Unimolecular: a reaction involving one molecular species ($A \rightarrow \text{products}$)

Bimolecular: a reaction involving two molecular species ($A + A \rightarrow \text{products}$; or $A + B \rightarrow \text{products}$)

Termolecular: a reaction involving three molecular species ($A + A + B \rightarrow \text{products}$; or $A + B + C \rightarrow \text{products}$)

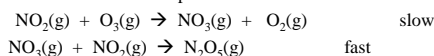
Rate Determining Step (RDS)

- The slowest step in a chemical reaction which also determines the rate of reaction

Intermediate

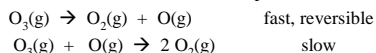
- A short lived molecular species that is formed in one elementary step and consumed in a subsequent elementary step. Does not appear in the net reaction or rate law.

1. A reaction mechanism for the destruction of ozone in polluted air is as follows:



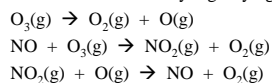
Write a balanced equation for the overall reaction. Define the molecularity of each elementary reaction, and write the rate law for this process. Identify intermediates and catalysts, if any.

2. The reaction mechanism for the destruction of ozone in the stratosphere is shown below.



Write a balanced equation for the overall reaction. Define the molecularity of each elementary reaction, and write the rate law for this process. Identify intermediates and catalysts, if any.

3. The reaction mechanism for the destruction of ozone by high flying aircraft is as follows:



Write a balanced equation for the overall reaction. Define the molecularity of each elementary reaction, and write the rate law for this process. Identify intermediates and catalysts, if any.

Collision Theory

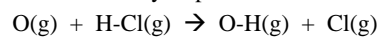
Product formation can only take place when there are “effective” collision between reactants

- Not all collisions result in a chemical reaction.
- Collisions that result in a chemical reaction are called “ effective collisions”

Two conditions for product formation must be met for molecular collisions to be effective:

- 1.
- 2.

Example: Consider the elementary step shown below.

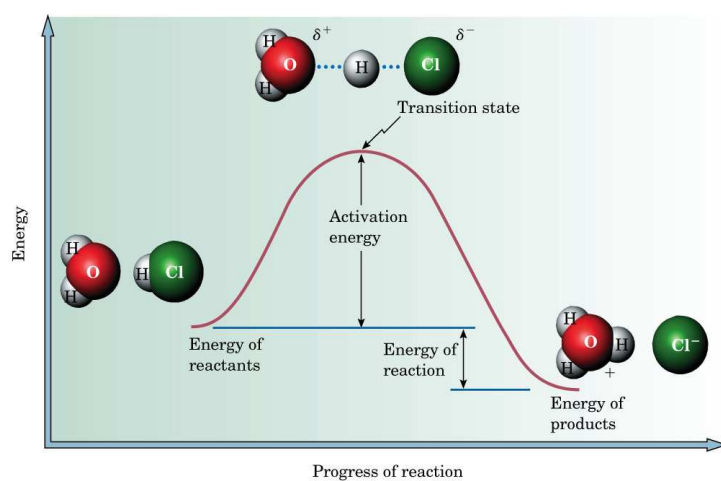


Activation Energy (E_a) the minimum energy necessary for a specific reaction to occur

Energy Level Diagram shows the reaction progress vs. Potential Energy (P.E)

Indicates the relative energy of the following:

i) reactants, ii) transition state (TS), and iii) products

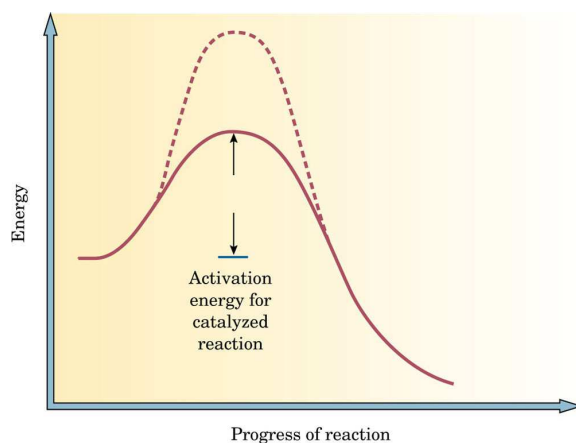


© 2007 Thomson Higher Education

Catalyst

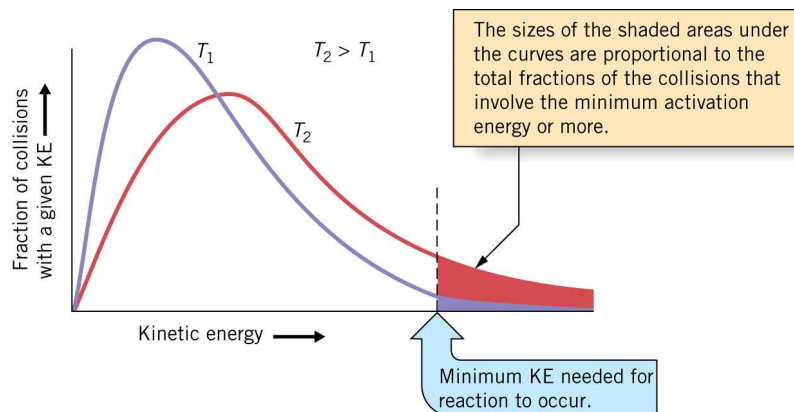
A substance that is added to increase the rate of a chemical reaction without being used up during the reaction

- A catalyst is reacted in one elementary step, and produced in the same form in a subsequent step.
- Speeds up the chemical reaction by providing an alternative mechanism for the reaction that lowers the Activation Energy → more collisions have enough energy to overcome the activation energy barrier → reaction rate increases



Temperature

As temperature increases, Kinetic Energy increases, leading to higher reaction rates



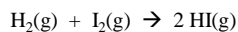
The Arrhenius Equation

Temperature is included in the rate law via the rate constant, k . Arrhenius discovered that the temperature dependence of the rate constant, could be described by an exponential equation.

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

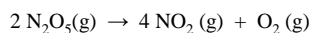
1. Write the straight line form of the Arrhenius Equation.
2. How could the activation energy and pre-exponential factor be graphically obtained?
3. Derive the equation that relates the activation to k at two different temperatures.

1. The rate constants for formation of HI were measured at the two different temperatures shown below. Calculate the activation energy, pre-exponential factor, and specific rate constant for formation of HI at 427 °C.



<u>k</u>	<u>temperature</u>
2.7×10^{-4}	327°C
3.5×10^{-3}	377°C
?	427°C

2. The rate constants for the decomposition of gaseous dinitrogen pentoxide are $3.7 \times 10^{-5} \text{ s}^{-1}$ at 25 °C and $1.7 \times 10^{-3} \text{ s}^{-1}$ at 55 °C.



- a. What is the activation energy for this reaction in kJ/mol? ($1.0 \times 10^2 \text{ kJ/mol}$)
- b. What is the rate constant at 35 °C? ($1.4 \times 10^{-4} \text{ s}^{-1}$)
- c. What is the numerical value of the pre-exponential factor, A ? ($5.5 \times 10^{13} \text{ s}^{-1}$)