

# Rates of Reactions

## Chapter – 6

Mr. V



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# Chemical Kinetics

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- ◆ It is the branch of chemistry which deals with the rate and mechanism of chemical reactions.

# Rate

- ◆ The rate of a reaction may be defined as the change in the concentration of any one of the reactants or products per unit time.
- ◆ Unit of rate:

$$\text{Unit of rate} = \text{mol L}^{-1}\text{time}^{-1}$$

# Average Rate

- ◆ Total change in concentration by total time taken is known as average rate.

$$\text{Average rate} = \frac{[\text{Total change in concentration}]}{[\text{Total time taken}]}$$

# Instantaneous rate

$$\frac{dx}{dt}$$

- ◆ The rate of change of concentration of any one of the reactants or products at that particular instant of time.

For the reaction  $A \rightarrow B$

$$\text{Rate of reaction} = -\frac{d[A]}{dt}$$

$$\text{Rate of reaction} = \frac{d[B]}{dt}$$



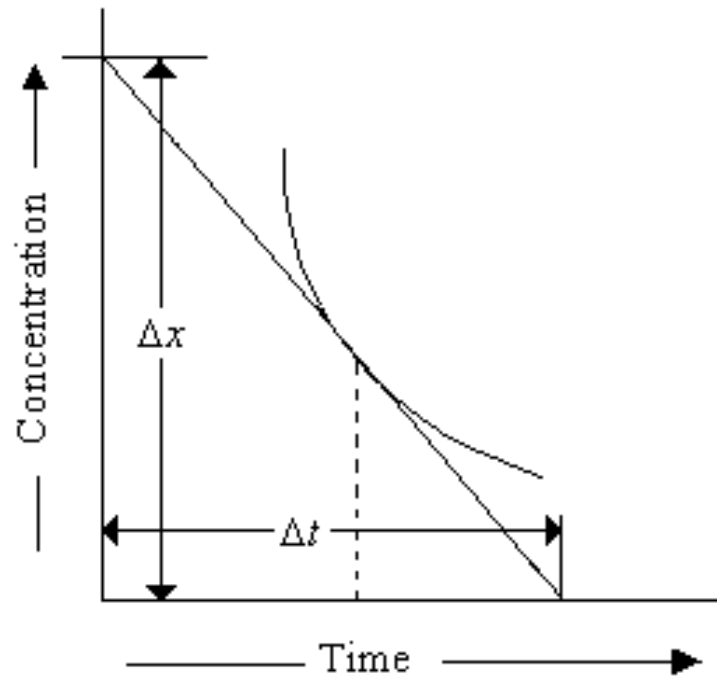
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# Rate from Graph

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- ◆ The rate can be determined by finding the slope of the tangent to the curve at the point corresponding to that instant of time.

# Rate Graph



# Examples of differential rates



$$\text{Differential rate for A} = -\frac{d[A]}{dt}$$

$$\text{Differential rate for B} = -\frac{d[B]}{dt}$$

$$\text{Differential rate for C} = +\frac{d[C]}{dt}$$

$$\text{Differential rate for D} = +\frac{d[D]}{dt}$$

# Law of Mass Action

- ◆ This law gives the theoretical dependence of rate of reaction on concentration.

Law of mass action



$$\text{Rate}_f = k' [A]^a [B]^b$$

$$\text{Rate}_b = k'' [C]^c [D]^d$$

At equilibrium  $\text{Rate}_f = \text{Rate}_b$

# Rate law

- ◆ The rate law is an experimentally determined factor. It does not depend on the law of mass action. The dependence of rate of the different concentration terms is expressed using order of a reaction.

# Order of reaction

- ◆ It may be defined as the sum of the powers to which the concentration terms are raised in a rate law expression.



$$\text{Rate} = k [A]^x [B]^y$$

$$\text{order 'n' of the reaction} = x + y$$



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# Different orders

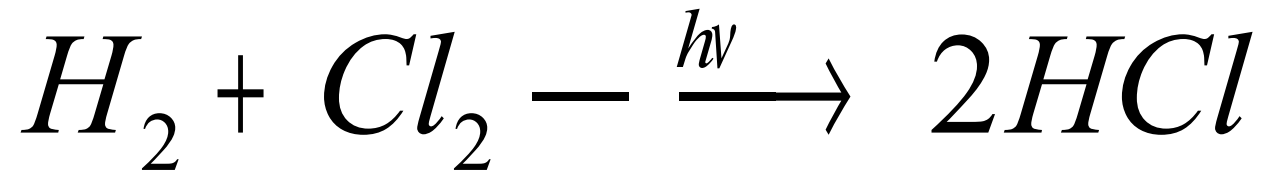
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- ◆ Zero order
- ◆ First order
- ◆ Second order
- ◆ Third order
- ◆ Fractional order

# Zero order reaction

- ◆ **A zero order reaction** is independent of the concentration of reactants.
- ◆ The rate of the reaction does not depend on the concentration terms or in other words an increase in the quantity of the reactants does not increase the rate of the reaction.
- ◆ Photochemical formation of HCl from hydrogen and chlorine is a zero order reaction.

## Example of Zero order



$$Rate = k [H_2]^0 [Cl_2]^0$$

$$Order 'n' = 0 + 0 = 0$$

# Unit for 'k'-Zero order reaction

- ◆ Same as rate

$$\text{Rate} = k [H_2]^0 [Cl_2]^0$$

$$\text{Order 'n'} = 0 + 0 = 0$$

$$k = \frac{\text{Rate}}{[H_2]^0 [Cl_2]^0}$$

$$k = \frac{\text{molL}^{-1}\text{T}^{-1}}{[H_2]^0 [Cl_2]^0}$$

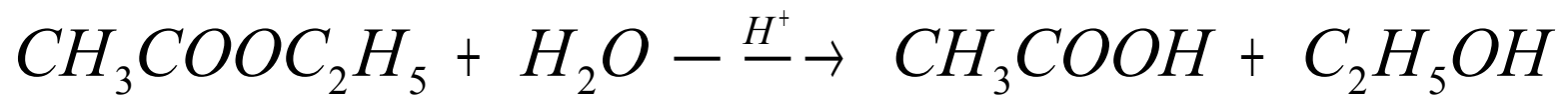
$$k = \text{molL}^{-1}\text{T}^{-1}$$

# First order reaction

- ◆ The rate of a first order reaction depends on one concentration term only.
- ◆ It is possible that there could be more than one reactants involved in the reaction.
- ◆ All nuclear fission reactions are first order decay or disintegration.
- ◆ Hydrolysis of esters: are first order reactions

# Example of first order reaction

- ◆ Hydrolysis of esters

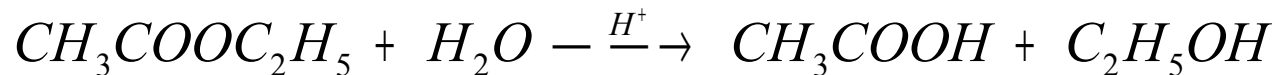


$$Rate = k[CH_3COOC_2H_5]^1$$

$$Order = 1$$

# Unit for 'k' - First order reaction

## ◆ Time<sup>-1</sup>



$$Rate = k[CH_3COOC_2H_5]^1$$

$$Order = 1$$

$$k = \frac{Rate}{[CH_3COOC_2H_5]^1}$$

$$k = \frac{molL^{-1}T^{-1}}{[molL^{-1}]}$$

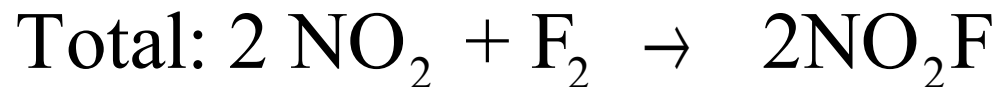
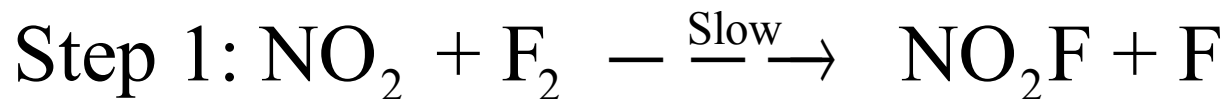
$$k = Time^{-1}$$

# Second order reaction

- ◆ The rate of a second order reaction is dependent on two concentration terms.
- ◆ This depends on the mechanism of the reaction

# Mechanism of reaction

- ◆ Slowest step is the rate determining step in this multi step reaction.



# Example of Second order

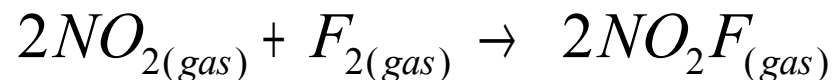


*Experimentally it has been found*

*Rate of reaction  $\propto [NO_2]^1 [F_2]^1$*

*Order 'n' = 1 + 1 = 2*

# Unit for 'k' Second order rxn



Experimentally it has been found

$$\text{Rate of reaction} \propto [NO_2]^1 [F_2]^1$$

$$\text{Order 'n'} = 1 + 1 = 2$$

$$k = \frac{\text{Rate}}{[NO_2]^1 [F_2]^1}$$

$$k = \frac{\text{molL}^{-1}\text{T}^{-1}}{[\text{molL}^{-1}][\text{molL}^{-1}]}$$

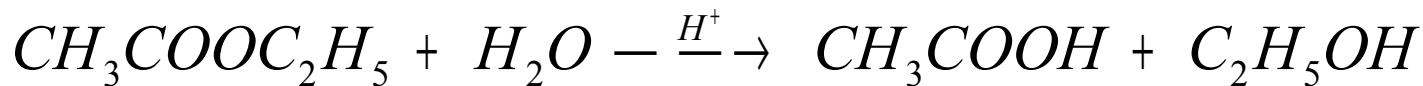
$$k = \text{Lmol}^{-1}\text{T}^{-1}$$

# Molecularity

- ◆ The number of reacting species (atoms, ions or molecules) that must collide with each other simultaneously so as to result in a chemical reaction is called molecularity

# Pseudo Uni-molecular reactions

- ◆ Reactions in which the ORDER is one but molecularity is two is called pseudounimolecular reactions.
- ◆ E.g. Hydrolysis of Esters.



$$Rate = k[CH_3COOC_2H_5]^1$$

$$Order = 1$$

*Molecularity is two*

# Factors affecting rate

- ◆ Nature of reactants
- ◆ Concentrations of reactants
- ◆ Temperature
- ◆ Catalyst
- ◆ Radiation

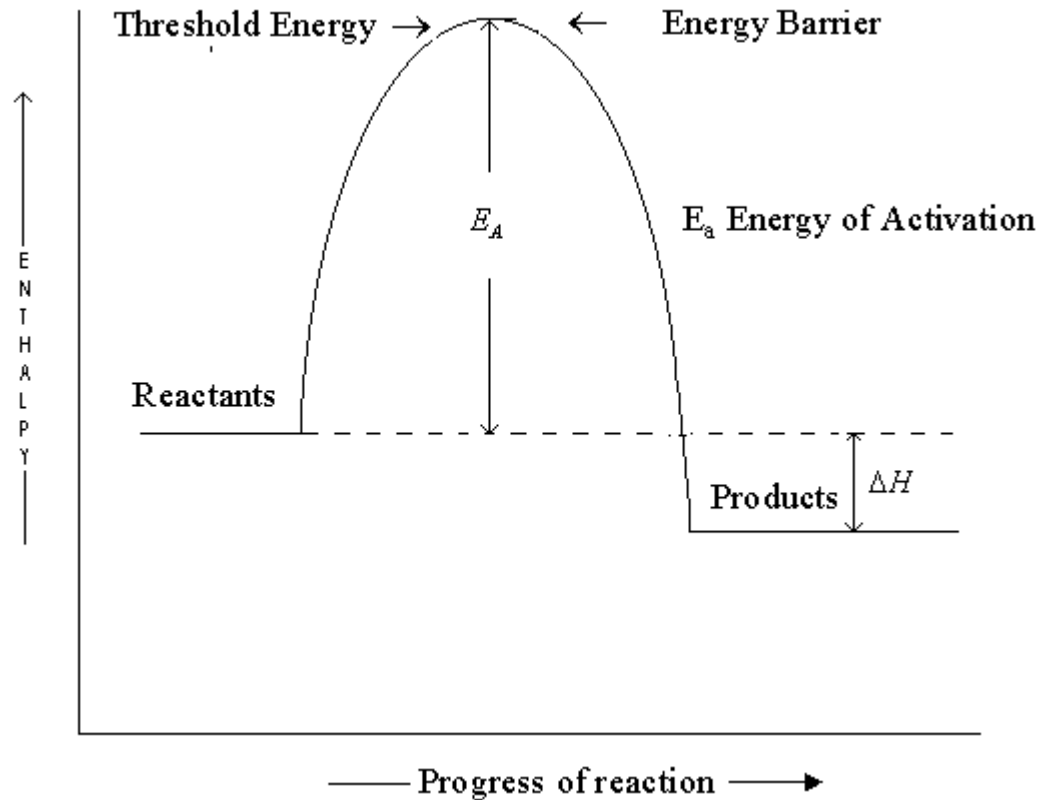
# Nature of reactants

- ◆ Physical state of reactants
  - Gases
  - Liquid
  - Solid
- ◆ Particle size of reactants
  - Larger the surface area the greater is the rate of reaction. Powdered substances reacts faster.
- ◆ Chemical nature of reactants

# Concentration of reactants

- ◆ The rate of the reaction decreases with decrease in concentration.
- ◆ This is obvious from the law of mass action.
- ◆ When the concentration is large the chance of reactants coming in contact with each other is greater.
- ◆ Hence the rate of the reaction will increase

# Effect of temperature



# Temperature

- ◆ As a rule generally speaking a rise in temperature increases the rate of reaction (whether endothermic or exothermic)
- ◆ This is because all reactions occur only if the reactants molecules possess *Threshold Energy*



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# Threshold energy

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- ◆ It may be defined as the minimum amount of energy which the colliding molecules must possess in order that the collisions may become effective.

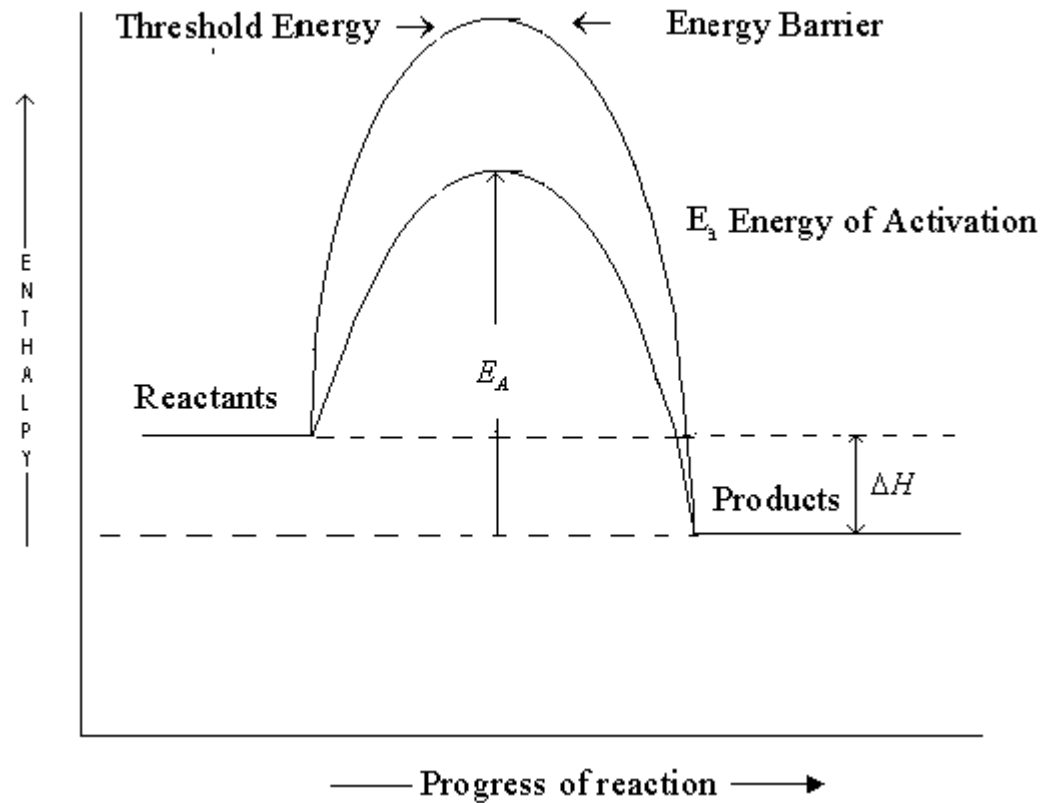
# Energy of Activation

- ◆ The extra amount of energy which the molecules of the reactants have to absorb so that their energy becomes equal to the threshold energy is called *Activation Energy*. (Refer graph)
- ◆  $\text{Activation Energy} = \text{Threshold Energy} - \text{Energy possessed by the reactant molecules.}$
- ◆ *Fast reactions have low activation energy*
- ◆ *Slow reactions have high activation energy*

# Catalyst

- ◆ A catalyst is a substance that increases the speed of a reaction without itself undergoing any chemical change.
- ◆ A catalyst provides an alternate path with lower energy barrier. It decreases the *energy of activation* of the reaction.

# Catalyst



# Radiation

- ◆ Photochemical reactions: Reactions which take place in the presence of light.
- ◆ Reaction between  $\text{H}_2$  and  $\text{Cl}_2$
- ◆ Steps involved in photochemical reactions

# Examples

- ◆ Photography
- ◆ Photosynthesis
- ◆ Blue Printing
- ◆ Reaction between  $\text{H}_2$  and  $\text{Cl}_2$  in the formation of  $\text{HCl}$



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# Photochemical reactions

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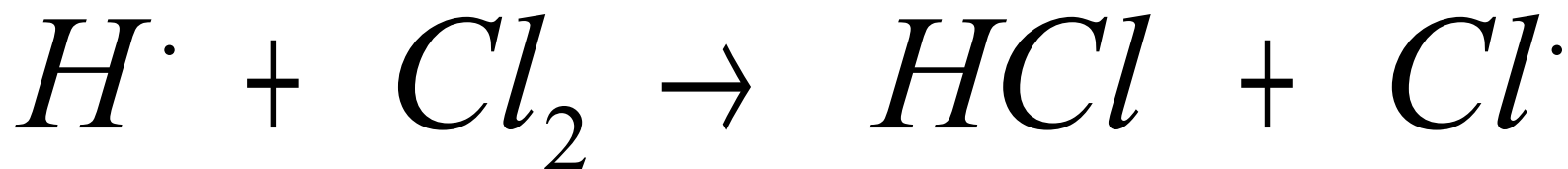
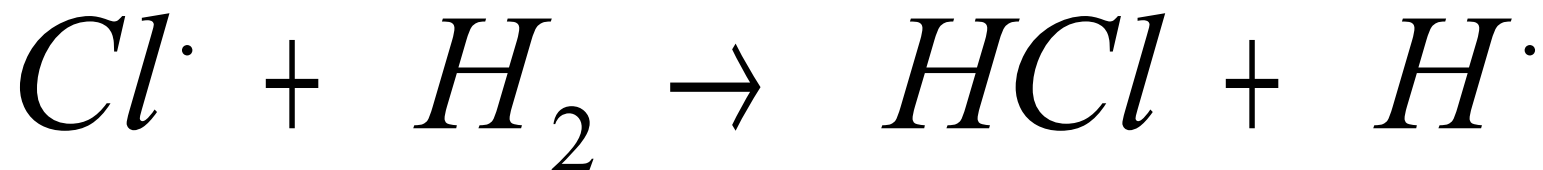


- ◆ Chain initiation
- ◆ Chain propagation
- ◆ Chain termination

# Chain initiation



# Chain propagation



# Chain termination

