

# CHEMICAL KINETICS

When one or more substance undergo a change which results in the formation of a new product, called chemical reaction.

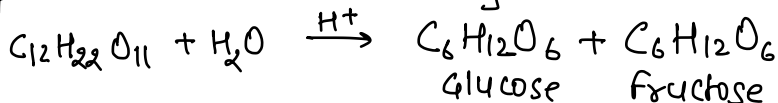
**CHEMICAL KINETICS**, is the branch of chemistry which deals with the study of rates of chemical reaction their mechanism and the conditions in which rates can be altered.

## ON THE BASIS OF SPEED

i) **VERY FAST REACTION**: Some reaction such as ionic reactions occur very fast e.g.  $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$

ii) **VERY SLOW REACTION**: Some reactions are months to years in completion very slow i.e. takes e.g. Rusting of iron in the presence of air and moisture  
• formation of coal and petroleum

iii) **MODERATE REACTION**: Those reactions which are neither very slow nor very fast but takes place at moderate speed.  
e.g. inversion of cane sugar



## ON THE BASIS OF NUMBER OF STEPS $\Rightarrow$

### ELEMENTARY REACTIONS

The reactions taking place in one step are called elementary reaction

### COMPLEX REACTIONS

when a sequence of elementary reactions gives us the product called complex reaction, each step in a complex reaction is called elementary rxn. slowest step is called rate determining step.

## RATE OF CHEMICAL REACTION:

It is the change in molar concentration of species taking part in the chemical reaction per unit time.

For the reaction  $A \rightarrow B$

Rate of disappearance of A

$$= \frac{\text{Decrease in conc. of A}}{\text{Time taken}} = -\frac{\Delta[A]}{\Delta t}$$

Rate of disappearance of B

$$= \frac{\text{Increase in conc. of B}}{\text{Time taken}} = +\frac{\Delta[B]}{\Delta t}$$

**NOTE**

The concentration of reactant decreases, so it represent by -ve sign, while the conc. of product increases so it represented by +ve sign.

## TYPES OF RATE OF REACTION:

### Average Rate

change in molar conc. of reactant and product at a given interval of time

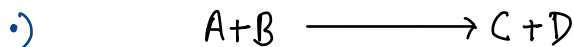
$$\text{Avg. Rate of Reaction} \quad R \longrightarrow P \quad -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

### Instantaneous Rate

change in molar conc. of reactant and product at a given instant of time.

$$\text{Inst. Rate of Reaction} \quad -\frac{d[R]}{dt} = +\frac{d[P]}{dt}$$

## RELATION BETWEEN RATE OF REACTION AND STOICHIOMETRY

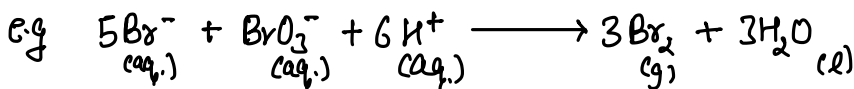


$$\text{Rate of Rxn} \quad -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

•)  $2A \longrightarrow C + D$  It is clear from stoichiometry of reaction that the rate of disappearance of A is twice the velocity of formation of C & D

So, rate of reaction can be given as below

$$\text{Rate of Rxn} \quad \frac{-1}{2} \frac{d[A]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt}$$

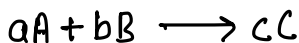


$$\text{Rate of Reaction} = \frac{-1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{-\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

## UNIT OF RATE OF REACTION

$$\frac{\Delta C}{\Delta t} = \frac{\text{Mol L}^{-1}}{\text{sec or min or hr}} \Rightarrow \text{Mol L}^{-1} \text{sec}^{-1} \text{ or Mol L}^{-1} \text{min}^{-1} \text{ or Mol L}^{-1} \text{hr}^{-1}$$

Consider a general reaction:



$$\text{Rate of reaction} \Rightarrow \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{+1}{c} \frac{d[C]}{dt}$$

$$\text{rate of disappearance of A} = -\frac{d[A]}{dt}$$

$$\text{rate of disappearance of B} = -\frac{d[B]}{dt}$$

$$\text{Rate of appearance of C} = \frac{+d[C]}{dt}$$

Q  $A + 2B \rightarrow 3C + 2D$ , the rate of disappearance of B is  $1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$  what will be

(i) Rate of Rxn (ii) Rate of change in conc. of A and C

Ans: Rate of disappearance B,  $-\frac{d[B]}{dt} = 1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\text{Rate of Rxn} = \frac{-1}{1} \frac{d[A]}{dt} = \frac{-1}{2} \frac{d[B]}{dt} = \frac{+1}{3} \frac{d[C]}{dt} = \frac{+1}{2} \frac{d[D]}{dt}$$

$$\therefore \text{Rate of Rxn} \quad \frac{-1}{2} \frac{d[B]}{dt} = \frac{1}{2} \times 1.0 \times 10^{-2} = 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii) Rate of change in conc. of A

$$-\frac{d[A]}{dt} = \text{R.O.R} \Rightarrow 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate of Change in conc. of C

$$\frac{d[C]}{dt} = 3 \times R.O.R \Rightarrow 3 \times 0.5 \times 10^{-2} \\ 1.5 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$$

## # FACTORS AFFECTING RATE OF REACTION

### • CONCENTRATION OF REACTANT:

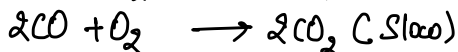
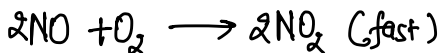
It is observed that rate of reaction decreases with time. We know that initially the conc. of reactant is maximum so the rate of change in conc. is also maximum. As the conc. of reactant decreases when the rate of reaction also decreases. It means that the rate of reaction is directly proportional to the conc. of reactant.

### • TEMPERATURE OF SYSTEM:

Generally, the rate of all reactions approximately increases on increasing temp. In other words, the rate of reaction also decreases on decreasing temp. Generally, the rate of reaction mixture increases two to three times on increasing temp. upto  $10^\circ\text{C}$

### • NATURE OF REACTANT:

In a chemical reaction old bonds are broken and new bonds are formed. So, the reactivity of substance depends on breaking and formation of specific bonds.



### • EFFECT OF CATALYST:

Catalyst increase the rate of reaction. are those substance which without undergoing any chemical change in them.

It is considered that presence of catalyst decrease the activation energy of reactant which increase the rate of rean.

## SURFACE AREA

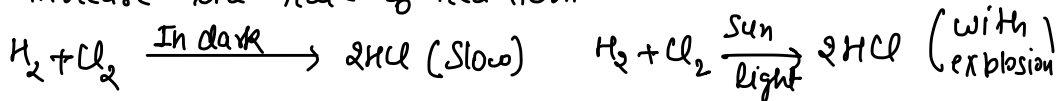
Greater the surface area of reactant, higher is the rate of reaction. It is observed that if reactant is a solid substance then rate of reaction depends upon the size of its particles.

e.g. A piece of wood burns slowly but it burns rapidly when cut into small pieces.

## EXPOSURE TO RADIATION:

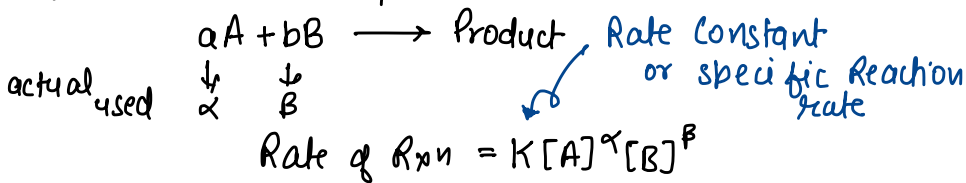
The rate of some reactions increases rapidly in presence of radiation (UV and visible).

Photons of UV and visible light having high energy dissociate chemical bonds of reactants rapidly which increase the rate of reaction.



## RATE LAW

Rate of Reaction is directly proportional to the product of molar concentration of reactant and each raise to the power their coefficient on which rate of reaction actually depends.



↳ Rate law for any reaction can not be predicted theoretically but must be determined experimentally.

## RATE CONSTANT:

Rate constant is equal to rate of reaction when concentration of each reactant becomes unity.

## ORDER:

It is the sum of powers acc. to rate law expression.

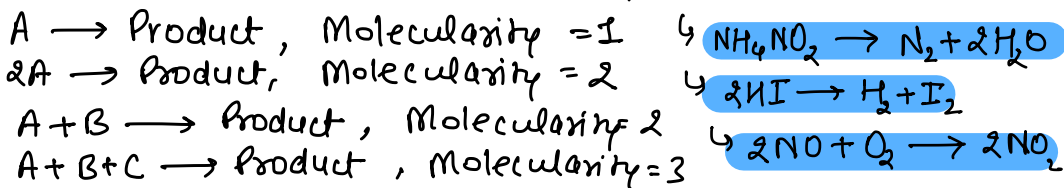
$$\text{Rate of Rxn} = K[A]^\alpha[B]^\beta \Rightarrow \text{order} = \alpha + \beta$$

## Characteristics of Rate Constant

- Indicates the speed of reaction, Greater the value of rate constant, faster is the reaction.
- Every reaction has a particular value of rate constant at a particular temperature.
- The rate constant for the same reaction differs with temperature.
- The value of rate constant for a reaction does not depend upon the concentration of reactant.
- The unit of rate constant is dependent on the order of reaction.

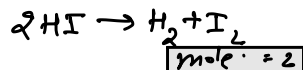
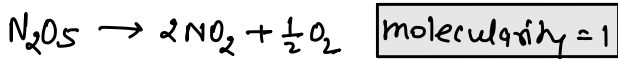
## MOLECULARITY OF REACTION

The total number of atoms, ions or molecules of the reactant which collide effectively to give product is termed as its molecularity.



## Characteristic of Molecularity:

- Molecularity of a reaction is always an integer.
- It can not have a fractional or zero values (a zero molecularity implies that no effective collisions b/w reactant molecule takes place i.e reaction doesn't occur at all).
- Molecularity can be judged by a balanced chemical <sup>Rxn</sup>
- For a complex reaction, molecularity has no significance



## ORDER OF REACTION

The order of a reaction is defined as the sum of powers to which the concentration terms are raised in rate law equation.



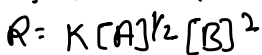
Rate law  $R = k[A]^m[B]^n$  (experimentally determined.)

order w.r.t A = m, order w.r.t B = n

Overall order of given reaction = m+n

Q. What is the order of reaction?

Ans. Rate law,

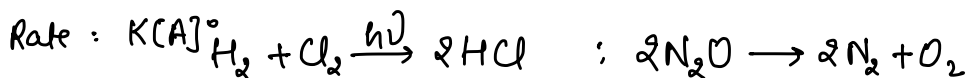


Order of reaction =  $2\frac{1}{2}$  or 2.5

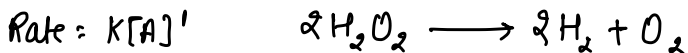
## Characteristics of Order of a Reaction:

- It represents the number of species whose concentration affects the rate of reaction directly.
- Reaction order can be obtained by adding all the exponents of the concentration terms in rate expression.
- The stoichiometric coefficients corresponding to each species in the balanced reaction have no effect on the order of the reaction.
- The reaction order of a chemical reaction is always defined with the help of reactant concentration and not with product concentration.
- For a complex reaction, the slowest step is rate determining step.

## Zero Order Reaction:

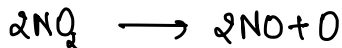
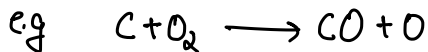


## First Order Reaction:



## Second Order Reaction

$$\text{Rate} = k[A]^2$$



## UNIT OF RATE CONSTANT

$$k = (\text{mol L}^{-1})^{1-n} \text{sec}^{-1} \quad k = (\text{atm})^{1-n} \text{sec}^{-1}$$

Zero order

$$n=0$$

$$k = (\text{mol L}^{-1})^{1-0} \text{sec}^{-1} \Rightarrow \text{mol L}^{-1} \text{sec}^{-1}$$

First order

$$n=1$$

$$k = (\text{mol L}^{-1})^{1-1} \text{sec}^{-1} \Rightarrow \text{sec}^{-1}$$

Second order

$$n=2$$

$$k = (\text{mol L}^{-1})^{1-2} \text{sec}^{-1} \Rightarrow \text{mol}^{-1} \text{L}^1 \text{sec}^{-1}$$

Half order

$$n = \frac{1}{2}$$

$$k = (\text{mol L}^{-1})^{1-\frac{1}{2}} \text{sec}^{-1} \Rightarrow \text{mol}^{\frac{1}{2}} \text{L}^{\frac{1}{2}} \text{sec}^{-1}$$

Q. Identify the reaction order

(i)  $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1} \rightarrow \text{Order} = 2$

(ii)  $k = 3 \times 10^{-4} \text{ s}^{-1} \rightarrow \text{Order} = 1$

Q. The conversion of molecules X to Y follows second order kinetics, if concentration of X is increased to three times how will it affect the rate of formation of Y?

Ans: The reaction is  $X \longrightarrow Y$

Acc. to rate law

$$\text{rate} = k[X]^2$$

If [X] is increased to 3 times, then

$$\text{rate}' = k[3X]^2$$

$$\text{rate}' = 9k[X]^2$$

$$\Rightarrow 9 \times \text{rate}$$

Thus, rate of reaction becomes 9 times and hence rate of formation of increases 9-times.

# Integrated Rate Equation

## First Order

Those reaction whose rate depends upon one concentration term of reactant.



Rate of Reaction  $\propto [R]^1$

$$-\frac{d[R]}{dt} = k[R]$$

$$-\frac{d[R]}{[R]} = k \cdot dt$$

I.B.S (Integrating both sides)

$$-\int \frac{d[R]}{[R]} = \int k \cdot dt$$

$$-\ln R = kt + I$$

Integration constant

to get the value of I  
 $t = 0, R = R_0$   
 $-\ln R_0 = I$

Put value of I in eq (1)

$$-\ln R = kt + I$$

$$-\ln R = kt - \ln R_0$$

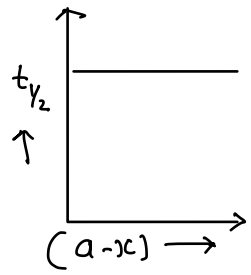
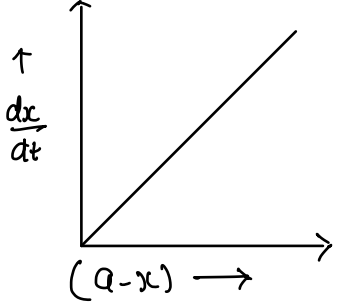
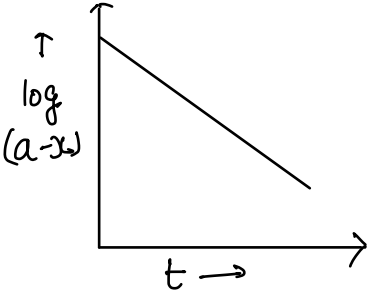
$$\ln R_0 - \ln R = kt$$

$$\ln \frac{R_0}{R} = kt$$

$$t = \frac{2.303 \log \frac{R_0}{R}}{k}$$

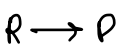
UNIT = mol L<sup>-1</sup> s<sup>-1</sup>

$$t = \frac{2.303 \log \frac{a}{a-x}}{k}$$



## Zero Order Reaction

Those reaction whose rate depends upon zero concentration terms of reactant.



Rate of Reaction  $\propto [R]^0$

$$-\frac{d[R]}{dt} = k$$

$$-d[R] = k \cdot dt$$

∴ B.S.C (Integrating both sides)

$$-\int d[R] = k \int dt$$

$$-R = kt + I$$

← Integration constant

to get the value of I

$$t=0, R=R_0$$

$$-R_0 = I$$

Put I in equation 1

### Half life of a Reaction:

The time in which the concentration of a reactant is reduced to one half of its initial conc.

It is represented by  $t_{1/2}$ .

$$t = \frac{2.303}{k} \log \frac{R_0}{R}$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{R_0}{R_0/2} \times 2$$

$$t = \frac{R_0 - R}{k}$$

$$t = t_{1/2}, R = R_0/2$$

$$t_{1/2} = \frac{R_0 - R_0/2}{k} \Rightarrow \frac{R_0}{2k}$$

Q write general expression for half life period of a reaction of nth order

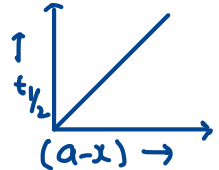
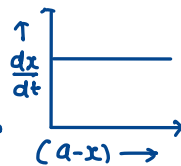
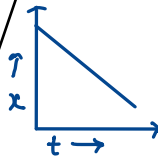
Ans - 
$$t_{1/2} = \frac{1}{[R_0]^{n-1}}$$

$$-R = kt + I$$

$$-R = kt - R_0$$

$$R_0 - R = kt$$

$$\frac{R_0 - R}{t} = k$$





Q. A first order is found to have a rate constant  $k = 5.5 \times 10^{-14} \text{ sec}^{-1}$ . Find half life of the reaction.

Ans. Half life for a first order reaction is

NCERT

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}} = 1.26 \times 10^{13} \text{ s}$$

Q. The half life for radioactive decay of  $^{14}\text{C}$  is 5730 yr. An archaeological artifact contained wood that had only 80% of the  $^{14}\text{C}$  found in living tree. Estimate age of the sample

NCERT

Ans. Radioactive decay follows first order kinetics

$$\text{Decay } [k] = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$$

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]} = \frac{2.303 \times 5730 \times 0.0969}{0.693} = 1845 \text{ years.}$$

Q. A first order reaction takes 20 minutes for 20% decomposition. Calculate  $t_{1/2}$ . ( $\log \frac{100}{80} = 0.0969$ )

Ans.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$
$$= \frac{2.303}{20} \log \frac{100}{80} = \frac{2.303}{20} \times 0.0969$$
$$= 0.011158 = 11.158 \times 10^{-3}$$
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{11.158 \times 10^{-3}} = 62.1 \text{ min.}$$

All the Best 😊

## → Effect of Temperature on rate of reaction:-

The rate of reaction increases with increase in temperature  
 Arrhenius proposed an equation that related temperature and rate constant for a reaction quantitatively

### Acc. to Arrhenius Equation

$$k = A e^{-E_a/RT}$$

Where

$k$  = rate constant of the Rxn

$A$  = Arrhenius factor / frequency factors / pre exponential factor

$E_a$  = Activation Energy

$R$  = Universal Gas Constant

$T$  = Temp. in Kelvin (absolute scale)

Taking ln both sides

$$\ln k = \ln A e^{-E_a/RT}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

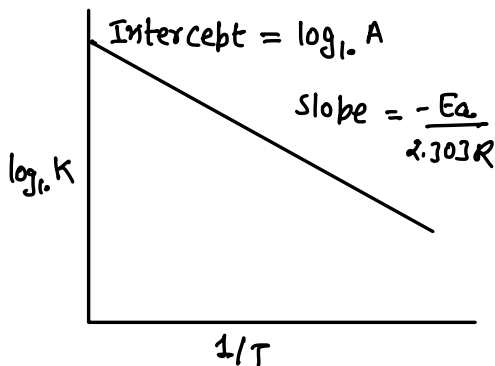
↳ At temp  $T_1$ ,

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{--- (1)}$$

↳ At temp  $T_2$ ,

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{--- (2)}$$

operating (2) - (1)



$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_2} - \frac{E_a}{RT_1}$$

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

$$2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_2 T_1} \right)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{T_1 - T_2}{T_2 T_1} \right)$$

where

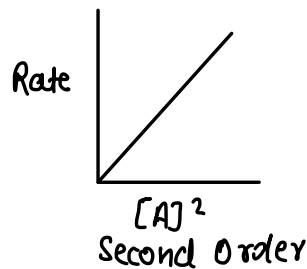
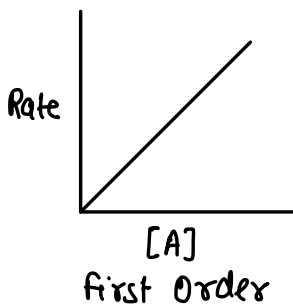
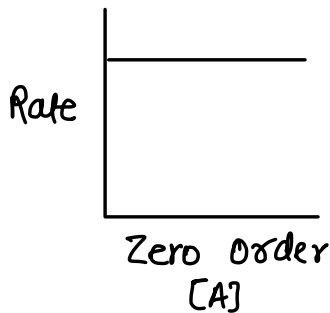
$E_a$  → Activation Energy

$R$  → Gas Constant

# Methods to Determine Order of Reaction

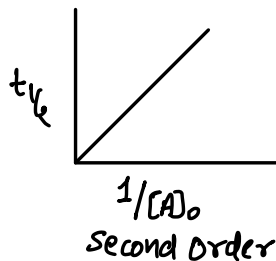
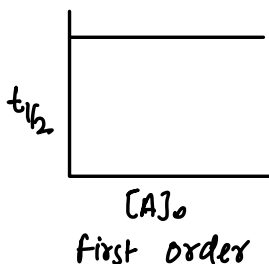
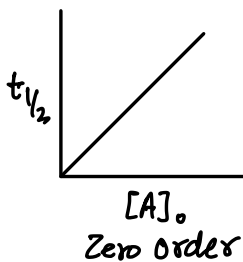
## i) Graphical Method

In this method, rate of reaction is plotted against the concentration.



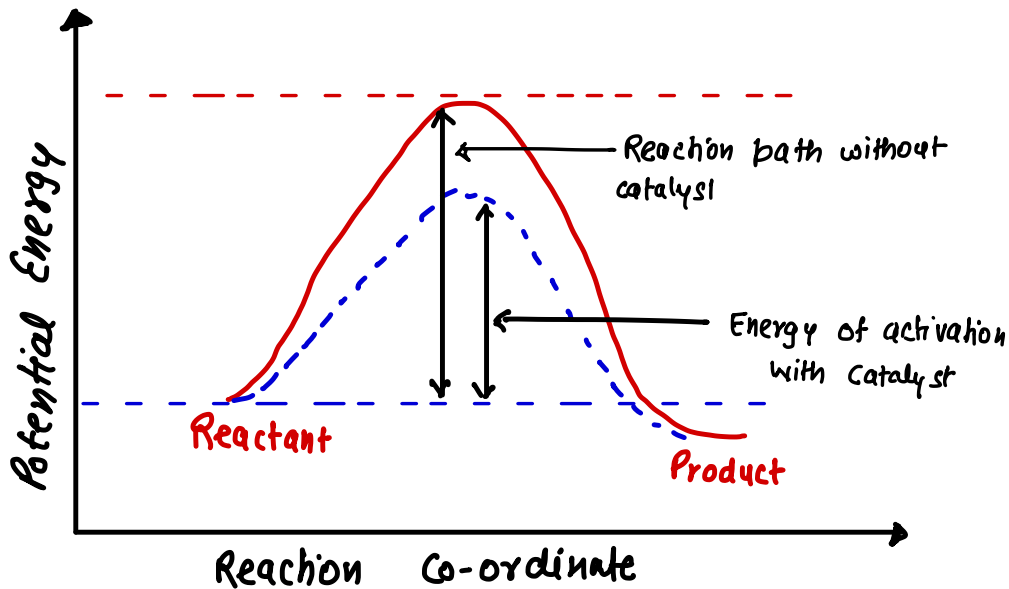
## ii) Half life Method

In general half life period of  $(t_{1/2})$  of a reaction of  $n$ th order is related to initial concentration of reactant



## Rate of Catalyst in a Chemical Reaction -

A catalyst is a chemical substance which alters the rate of a reaction without itself undergoing any permanent chemical change



Catalyst provide an alternate path by reducing the activation energy between reactants and products and hence, lowering the potential energy.

## → Collision Theory of chemical reactions

- ↳ Reaction occur due to collision of molecules
- ↳ All collisions are not effective
- ↳ Effective collisions are those collisions in which molecules collide with sufficient kinetic energy (called threshold energy which is equal to activation energy + energy possessed by reacting species) and proper orientation.

## Collision Frequency

no. of collisions per second per unit volume of reacting mixture. It is generally denoted by  $Z$

Consider the bimolecular reaction



Acc. to Collision Theory...

$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

where

$Z_{AB}$  = Collision frequency of reactant A & B

$E_a$  = Activation Energy

$R$  = Universal Gas Constant

$T$  = Temperature in absolute scale.

## CONDITIONS FOR EFFECTIVE COLLISIONS -

- Molecules must collide with sufficient energy called threshold energy
- Molecules must be oriented properly in order to break old bonds and form new bonds
- another factor,  $P$  called the probability or steric factor is introduced to explain effective collisions

$$\text{So, rate} = P Z_{AB} e^{-E_a/RT}$$