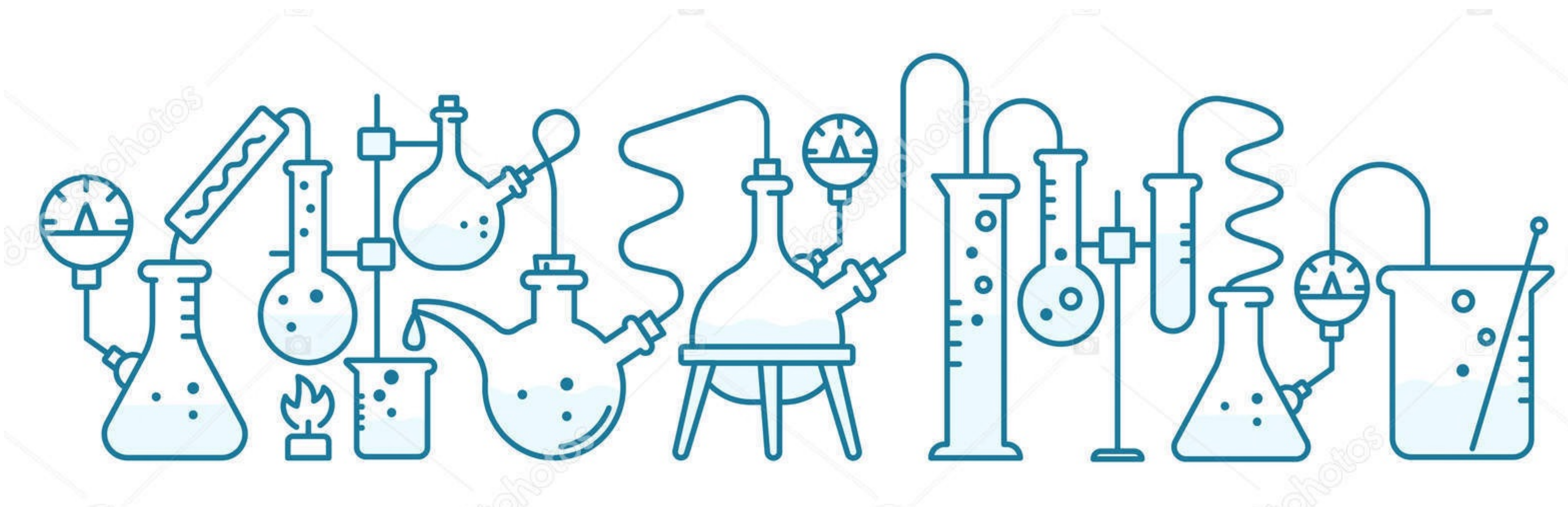
CLASS - 12th

2022-23

HANDWRITTEN NOTES

Chemical Kinetics



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4. 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 $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

ii) **VERY SLOW REACTION:** Some reactions are very slow i.e takes months to years in combletion

e.g. Rusting of iron in the bresence of air and moisture

- Formation of coal and petrolium

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

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

ON THE BASIS OF NUMBER OF STEPS ⇒

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 concenteration of species taking part in the chemical reaction per unit time.

For the reaction $A \longrightarrow B$

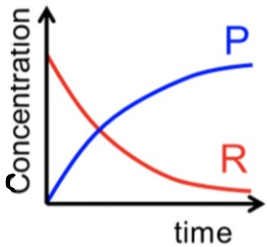
Rate of disappearance of A

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

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

Instantaneous Rate

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

$$R \longrightarrow P$$

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

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

RELATION BETWEEN RATE OF REACTION AND STOICHIOMETRY

•) $A + B \longrightarrow C + D$

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

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

e.g. $5Br^-_{(aq.)} + BrO_3^-{}_{(aq.)} + 6H^+_{(aq.)} \longrightarrow 3Br_2{}_{(g)} + 3H_2O_{(l)}$

Rate of Reaction $= -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$

UNIT OF RATE OF REACTION

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

Consider a general reaction:

$aA + bB \longrightarrow cC$

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

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

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

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

Q $A + 2B \longrightarrow 3C + 2D$, the rate of disappearance of B is $1\times10^{-2}\ mol\ L^{-1}\ s^{-1}$ what will be

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

Ans: Rate of disappearance B, $-\frac{d[B]}{dt} = 1\times10^{-2}\ mol\ L^{-1}\ s^{-1}$

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

∴ Rate of Rxn $-\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{2}\times1.0\times10^{-2} = 0.5\times10^{-2}\ mol\ L^{-1}s^{-1}$

(ii) Rate of change in conc. of A $-\frac{d[A]}{dt} = R.O.R \Rightarrow 0.5\times10^{-2}\ mol\ L^{-1}s^{-1}$

Rate of Change in conc. of C

$$+\frac{d[C]}{dt} = 3 \times R.O.R \Rightarrow 3 \times 0.5 \times 10^{-2}$$

$$1.5 \times 10^{-2} mol\, L^{-1} s^{-1}$$

FACTORS AFFECTING RATE OF REACTION

• CONCENTERATION 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°C

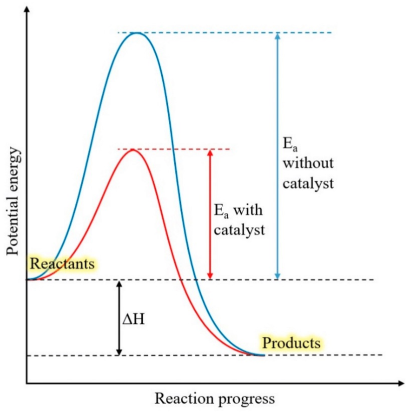
• NATURE OF REACTANT: In a chemical reaction old bonds are broken and new bonds are formed. So, the reactivity of substance depends on breaking and formation of specific bonds.

$$2NO + O_2 \longrightarrow 2NO_2 \text{ (fast)}$$

$$2CO + O_2 \longrightarrow 2CO_2 \text{ (Slow)}$$

• 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 rxn.



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 dissociates chemical bonds of reactants rapidly which increase the rate of reaction.

$H_2 + Cl_2 \xrightarrow{\text{In dark}} 2HCl$ (Slow) $H_2 + Cl_2 \xrightarrow[\text{light}]{\text{Sun}} 2HCl$ (with explosion)

RATE LAW

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

$$aA + bB \longrightarrow \text{Product}$$

actual used α β

Rate Constant or specific Reaction rate

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

↳ 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 concenteration of each reactant becomes unity.

ORDER :

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

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

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.

$A \longrightarrow$ Product, Molecularity $=1$ ↳ $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$2A \longrightarrow$ Product, Molecularity $=2$ ↳ $2HI \longrightarrow H_2 + I_2$

$A+B \longrightarrow$ Product, Molecularity $=2$ ↳ $2NO + O_2 \longrightarrow 2NO_2$

$A+B+C \longrightarrow$ Product, Molecularity $=3$

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 Rxn
- For a complex reaction, molecularity has no significance

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ $\boxed{\text{molecularity} = 1}$ $2HI \longrightarrow H_2 + I_2$ $\boxed{\text{mole.} = 2}$

ORDER OF REACTION

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

$$A + 2B \longrightarrow C + D$$

Rate law $\quad R = K[A]^m[B]^n$ (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, $\quad R = K[A]^{1/2}[B]^2$

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

Characteristics of Order of a Reaction :

- It represents the number of species whose concenteration affects the rate of reaction directly.
- Reaction order can be obtained by adding all the exponents of the concenteration 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 concenteration and not with product concenteration.
- For a complex reaction, the slowest step is rate determining step.

Zero Order Reaction:

Rate : $K[A]^0$ $\quad H_2 + Cl_2 \xrightarrow{h\nu} 2HCl \quad ; \quad 2N_2O \longrightarrow 2N_2 + O_2$

First Order Reaction:

Rate $= K[A]^1 \qquad 2H_2O_2 \longrightarrow 2H_2 + O_2$

Second Order Reaction

Rate $= K[A]^2$

e.g. $C + O_2 \longrightarrow CO + O$

$2NO_2 \longrightarrow 2NO + O$

UNIT OF RATE CONSTANT

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

Zero order $\boxed{n=0}$ $\quad K = (mol\ L^{-1})^{1-0}\ sec^{-1} \Rightarrow mol\ L^{-1}\ sec^{-1}$

First order $\boxed{n=1}$ $\quad K = (mol\ L^{-1})^{1-1}\ sec^{-1} \Rightarrow sec^{-1}$

Second order $\boxed{n=2}$ $\quad K = (mol\ L^{-1})^{1-2}\ sec^{-1} \Rightarrow mol^{-1}\ L^{1}\ sec^{-1}$

Half order $\boxed{n=1/2}$ $\quad K = (mol\ L^{-1})^{1-\frac{1}{2}}\ sec^{-1} \Rightarrow mol^{1/2}\ L^{-1/2}\ sec^{-1}$

Q. Identify the reaction order

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

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

Q. The conversion of molecules X to Y follows second order kinetics, if concenteration 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

rate $= K[X]^2$

If [X] is increased to 3 times, then

rate$' = K[3X]^2$

rate$' = 9K[X]^2$

$\Rightarrow 9 \times$ rate

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

Integrated Rate Equation

First Order

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

$R \longrightarrow P$

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

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

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

I.B.S (Integerating both Sides)

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

$$\boxed{-\ln R = Kt + I} \quad \text{(1)}$$

integeration constant

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

Put value of I in eq (1)

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

$$-\ln R = Kt - \ln R_0$$

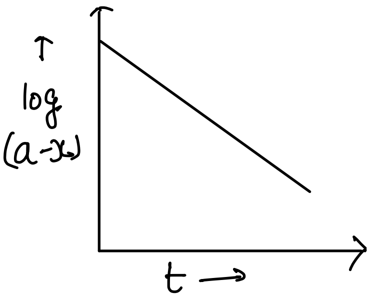
$$\ln R_0 - \ln R = Kt$$

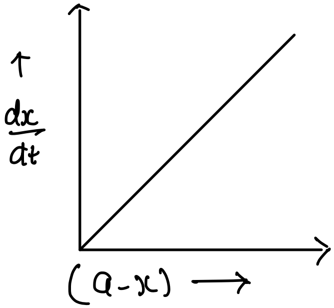
$$\ln \frac{R_0}{R} = Kt$$

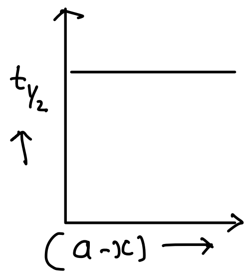
$$\frac{2.303}{K} \log \frac{R_0}{R} = t$$

UNIT = $mol\ L^{-1} s^{-1}$

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







Zero Order Reaction

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

$R \longrightarrow P$

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

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

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

I.B.S (Integerating both sides)

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

$$-R = Kt + I \leftarrow I \text{ Integeration constant}$$

$\boxed{\text{to get the value of } I}$

$t = 0, \quad R = R_0$

$$-R_0 = I$$

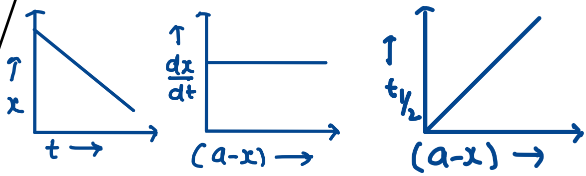
Put I in equation 1

$$-R = Kt + I$$

$$-R = Kt - R_0$$

$$R_0 - R = Kt$$

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



Half life of a Reaction:

The time in which the concenteration of a reactant is reduced to one half of its initial conc. It is represented by $t_{1/2}$.

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

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

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

$$t_{1/2} = \frac{0.693}{K}$$

first Order

$$t = \frac{R_0 - R}{K} \qquad t = t_{1/2}, R = R_0/2$$

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

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

Ans.

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

PSEUDO FIRST ORDER REACTION

Reaction which are not truely of the first order but under certain conditions become reactions of first order are called pseudo first order Reactions.

eg Acid catalysed inversion of cane sugar

$$C_{12}H_{22}O_{11} + \underset{\text{(excess)}}{H_2O} \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = K[C_{12}H_{22}O_{11}]$$

Acid catalysed hydrolysis of ethyl acetate.

$$CH_3COOC_2H_5 + \underset{\text{(excess)}}{H_2O} \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\text{Rate} = K[CH_3COOC_2H_5]$$

Both of the above reactions are biomolecular but are found to be the first order because water is present in such a large excess that its concenteration remains almost constant during the reaction.

P.Y.Q

Q. A reaction is second order w.r.t a reactant. How is the rate of reaction affected if the concenteration of reactant is NCERT (2009, 2012, 2014)

(i) doubled (ii) reduced to half

Ans: Rate $= K[A]^2$

$[A] = 2a$, rate $= K(2a)^2 = 4Ka^2$
$= 4$ times

$[A] = \frac{1}{2}a$, rate $= K\left[\frac{a}{2}\right]^2 = \frac{1}{4}Ka^2 = \frac{1}{4}$th

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

Ans: Half life for a first order Reaction is NCERT

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

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

NCERT

Ans: Radioactive decay follows first order Kinetics

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

$$t = \frac{2.303}{K} \log \frac{[A_0]}{[A]} = \frac{2.303 \times 5730}{0.693} \times 0.0969$$

$= 1845$ year.

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 quantitavely

Acc. to Arrhenius Equation

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

where

K = rate constant of the Rx^n

A = Arrhenius factor / Frequency factor / pre exponential factor

E_a = Activation Energy

R = Universal Gas Constant

T = Temp. in Kelvin (absolute scale)

Taking ln both sides

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

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

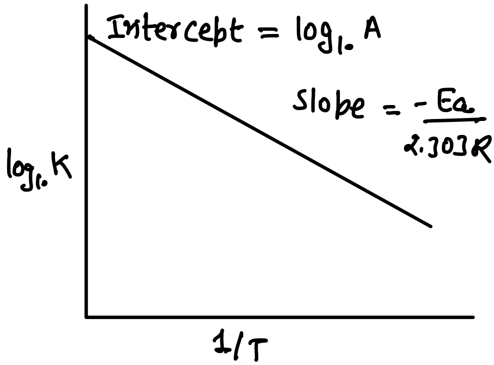
↳ At temp T_1,

$$\ln K_1 = \ln A - \frac{E_1}{RT_1} \quad \text{—— (1)}$$

↳ At temp T_2,

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \quad \text{—— (2)}$$

Operating (2) − (1)



$$\ln K_2 - \ln K_1 = \frac{E_a}{RT_2} - \frac{E_a}{RT_1}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)$$

$$2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)$$

where

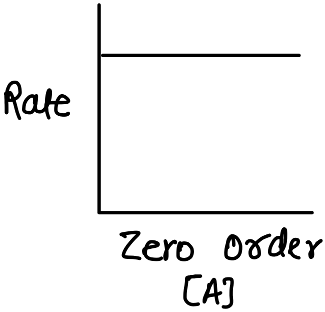
E_a → Activation Energy

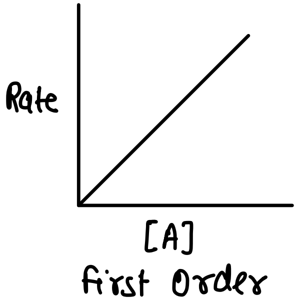
R → Gas Constant

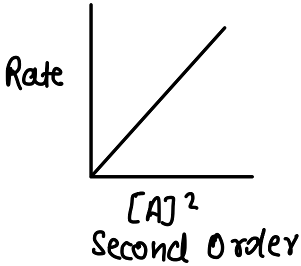
Methods to Determine Order of Reaction

i) Graphical Method

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

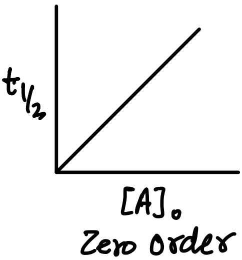


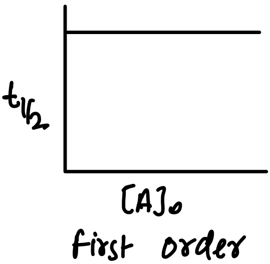


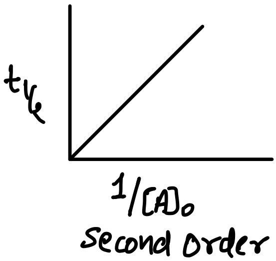


ii.) Half life Method

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

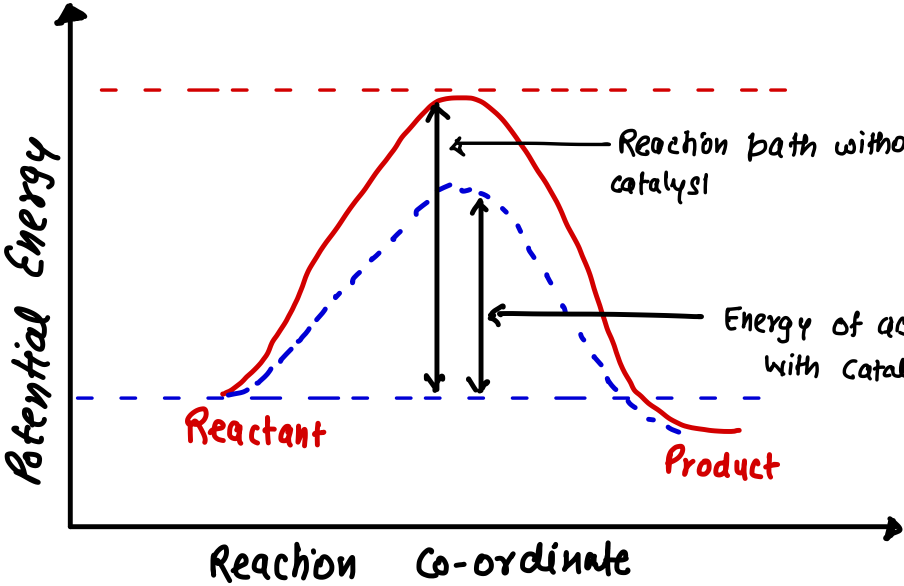






Rate of Catalyst in a Chemical Reaction –

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 biomolecular reaction

$$A + B \longrightarrow \text{Product}$$

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 EFFECTVE 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

So,

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