(Reaction Kinetics:-)/(Chemical Kinetics)

⇒ formuls and units:-

- ⇒ Rate of reaction = $\frac{\text{Change in concentration of a substance}}{\text{Time taken for the change}}$ = $\boxed{\frac{\Delta C}{\Delta t}}$

Unit:

$= \frac{mol.dm^{-3}}{s}$

- Rate = $\boxed{mol.dm^{-3}.s^{-1}}$

Note:

In case of gases, concentration is taken in partial pressure.

- Rate = $\frac{atm}{s}$ = $\boxed{atms^{-1}}$ or $\boxed{mol\,L^{-1}.time^{-1}}$

e.g For a Reaction $A \longrightarrow P$

- Rate of disappearence of A = $-\frac{\Delta[A]}{\Delta T}$

(-ve sign means disappearence)

- Rate of Appearence of P = $+\frac{\Delta[P]}{\Delta T}$

⇒ $\boxed{\text{Instantaneous rate} = \frac{dx}{dt}}$

⇒ $\boxed{\text{Average rate} = \frac{\Delta x}{\Delta t}} = \frac{\text{change in conc. of one reactant or product}}{\text{Time taken for change}}$

⇒ **Units of K**

(i) In zero order $R_x = \boxed{mol . dm^{-3} \cdot s^{-1}}$ $\boxed{(Rate = K)}$

(ii) In 1^{st} order $R_x = \boxed{s^{-1}}$ $\boxed{K_1 = \left(\frac{Rate}{A}\right)}$

(iii) In 2^{nd} order $R_x = \boxed{mol^{-1}\ dm^{+3} \cdot s^{-1}}$ $\boxed{K_2 = \frac{Rate}{[A]^2}}$

(iv) In 3^{rd} order $R_x = \boxed{mol^{-2}\ dm^{+6} \cdot s^{-1}}$ $\boxed{K_3 = \frac{Rate}{[A]^3}}$

⇒ **Half life period.**

$$\boxed{[t_{1/2}]_n = \frac{1}{a^{n-1}}}$$

(i) $[t_{1/2}]_1$ for 1^{st} order $= \boxed{\frac{0.693}{K}}$

(ii) $[t_{1/2}]_2$ for 2^{nd} order $= \boxed{\frac{1}{Ka}}$

(iii) $[t^{1/2}]_3$ for 3^{rd} order $= \boxed{\frac{1.5}{Ka}}$.

⇒ half life method (formula for two different initial concentrations)

$$\boxed{n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}}}$$

⇒ **Arrhenius equation:**

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

→ help to determine "energy of Activation of a Reaction."

$$\boxed{K = Ae^{-\frac{E_a}{RT}}}$$

$$\boxed{\text{Slope} = \frac{-E_a}{2.303R}}$$

Note:- **modified arrhenius equation:**

$$\boxed{\frac{d\ln K}{dt} = \frac{E}{RT^2}}$$

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Chemical Kinetics:-

Branch of chemistry that deals with

- Rates of chemical Reactions
- factors effecting the rate of chem. Rx
- Mechanism of the Rx.

Rate of Reaction:

"Change in concentration of a reactant or a product divided by the time taken for the change"

- Rx with rapid rate → Many Aqeous solution Rxs.
  → ppt. of AgCl formed after addition of $AgNo_3$ sol. to NaCl sol.
- Rx with moderate rate → hydrolysis of an ester
- Rx with slow rate → Rusting of Iron
  → chemical weathering of stone work of buildings by acidic Gases in the Atmosphere.
  → fermentation of sugars

Note:-

$$2NO + O_2 \longrightarrow 2NO_2$$

The only reaction with negative temperature Cofficient.

The rate of reaction decreases with time.

→ **Instantaneous rate**	**Average rate**
• "The rate at any one instant during the interval"	• " The rate of reaction between two specific time intervals".
• At first instantaneous rate is higher than the average rate.	• At the end, average rate is higher than instaneous rate.

Factors affecting rate of reaction:-

Reactions involving cleavage of strong bond in reactant molecules are slower when compared to reactions involving weak bond in reactants molecules.

$$2NO + O_2 \rightarrow 2NO_2 \quad \text{— (i)}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O \quad \text{— (ii)}$$

Reaction (ii) is faster than reaction (i)

i- Concentration of reactants.

$$\boxed{\text{conc. of reactants} \propto \text{rate of reaction}}$$

Because increase in conc. brings more effective collisions between reactant molecules, which results in faster chemical change.

ii- Surface area of the reactants:-

$$\boxed{\text{Surface area} \propto \text{Rate of Rx}}$$

large surface area, greater will be rate of Rx.

iii) Catalyst: presence of catalyst increase as well as decrease rate depending upon its nature.

iv. Temperature:

Reaction rates are normally favoured by increasing temperature.

→ When the temperature of the reaction gases is raised by 10K, the fraction of molecule with energy more than Ea roughly doubles. So the reaction rate also doubles.

v- Pressure:- $\boxed{\frac{dx}{dt} \propto (\text{pressure})}$ (as "p" $\propto$ "conc.") → For gaseous Rxs.

vi Radiation: $\boxed{\frac{dx}{dt} \propto \text{Intensity of radiation}}$ → In photochemical Rx

Rate constant of the reaction:

→ The rate constant or velocity constant or specific rate of a Rx is generally equal to the rate of Rx when the conc. of each of reactant is unity.

Note:- Rate constant doesnot depends upon concentration, pressure and volume.

Rate of Reaction	Rate constant
• It is the speed at which the reactants are converted into products.	• It is the constant of proportionality in rate law expression.
• It decreases with the progress of reaction generally.	• It is constant and doesnot depend on the progress of the reaction.
• It depends upon the conc. of reactant species at that moment.	• It refers to rate of Rx at specific point when the conc. of every reacting species is unity.

Order of Rx:-

The sum of all the exponents to which the conc. in the

Reaction	Order	Rate Equation	Expression	Unit of K
$A \rightarrow P$	zero	Rate = $K(A)^0$ Rate = K	$K = \frac{1}{t}[A_0 - A]$	mol. lit^{-1} time^{-1}
$A \rightarrow P$	first	Rate = $K[A]^1$	$K = \frac{2.303}{t} \log_{10} \frac{[A_0]}{[A]}$	Time^{-1}
$2A \rightarrow P$	Second	Rate = $K[A]^2$	$K = \frac{1}{t}\left(\frac{1}{A} - \frac{1}{A_0}\right)$	Lit mol^{-1} time^{-1}
$A + B \rightarrow P$	second	Rate = $K[A][B]$	$K = \frac{2.303}{t(a-b)} \log \frac{b[A]}{a[B]}$	Lit^{-2} mol^{-2} time^{-1}
$3A \rightarrow P$	Third	Rate = $K[A]^3$	$K = \frac{1}{2t}\left(\frac{1}{(A)^2} - \frac{1}{(A_0)^2}\right)$	Mol^{-2} time^{-1}

rate equation are raised"

$$aA + bB \longrightarrow cC + dD$$

Reactants Products

order = a+b

rate of Rx = $K[A]^a[B]^b$

→ Order may be any number, integral or fraction including zero.

→ Order of Rx is experimentally determined quantity, cannot be determined simply by looking at the Rx equation.

Zero order Rx: Rx entirely independent of the conc. of reactant molecules

e.g

- $H_2 + Cl_2 \xrightarrow{\text{(darkness)}}$ no reaction

  $H_2 + Cl_2 \xrightarrow{\text{(sunlight)}} 2HCl$
- photochemical Rxs
- $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$

1st order Rx: Rx in which molar conc. of only one molecule alters as a result of chemical change

e.g. • $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

• $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

• $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

e.g:- • $\underbrace{2N_2O_5} \longrightarrow 2N_2O_4 + O_2$

order of Rx = 1 ⇒ Rate ⇒ $K[N_2O_5]^1$

$N_2O_5 \xrightarrow{Slow} N_2O_4 + [O]$

$N_2O_5 + [O] \xrightarrow{Fast} N_2O_4 + O_2$

2nd order Rx:

Rx in which molal conc. of two reactants alters as a result of chemical change.

e.g $\underbrace{H_2} + \underbrace{I_2} \longrightarrow 2HI$

order of Rx = 1+1 = 2

3rd Order Rx: "The Rx in which molal conc of three reactant molecules alters as a result of chemical change".

e.g

$2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$

order of Rx = 1+2 = 3

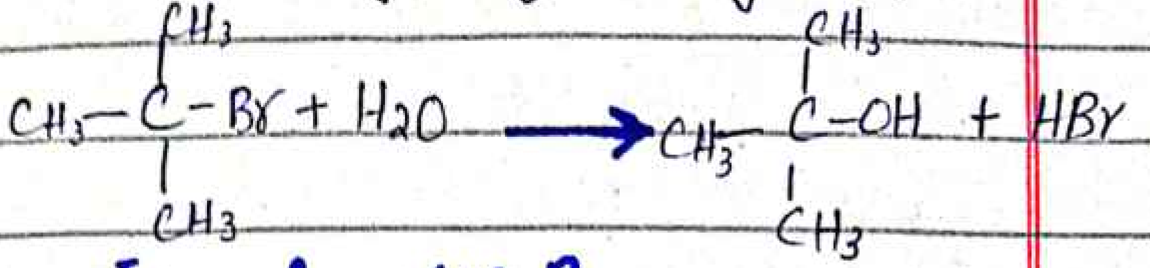
Rate = $K[FeCl_3]^1[KI]^2$

Pseudo first order:-

The Rx in which rate Rx remains effectively independ of the

conc. of H_2O because being a solvent"
⇒ It is present in large excess.

e.g • Hydrolysis of ethyl acetate
• Hydrolysis of tertiary butyl bromide.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + H_2O \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + HBr$$

fractional order Rx:

The order of a Rx is usually positive integal or a zero but can also be a fraction or can have a negative value.

e.g

formation of CCl_4 from $CHCl_3$.

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

order $= 1 + \frac{1}{2} = 1.5$

Note Rate constant and order for various species is an experimental finding and cannot be predicted directly from the stiochiometry of the balanced Rx.

Molecularity:- It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction or elementary reaction.

- → It is a theoretical value.
- → It is always a whole number.
- → It does not determine rate of Rx.
- → It does not depend upon external factors like temperature, pressure etc.

→ The overall molecularity of a complex Rx. is equal to the molecularity of slowest step (Rate determining step)

Note:- → Molecularity cannot be more than three as there is no chance for more than three molecules to undergo an effective collision at a time.

⇒ If molecularity is one reaction is called Unimolecular.

e.g $PCl_5 \longrightarrow PCl_3 + Cl_2$

⇒ Bimolecular Rx.

e.g $C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{Glucose}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6}$

- termolecular Rx:(molecularity is three)

eg $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

Half life period:-

"The time which is required to convert 50% of the reactants into products".

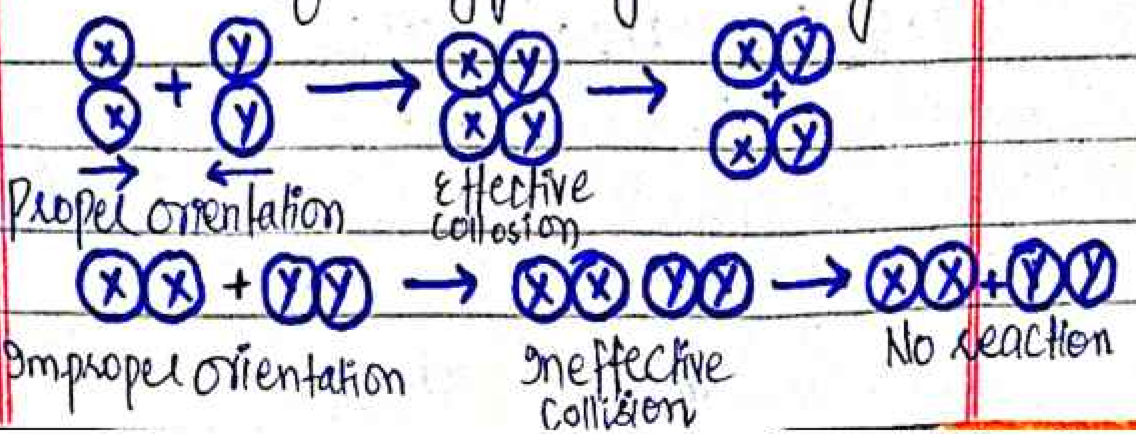
⇒ The Radioactive decay is always a 1st order Rx because only one reactant is involved.

Collision Theory:-

Chemical Rx occurs as a result of effective collosions between reacting molecules, for which posses the

① proper orientation of reacting molecules.

② possesion of certain minimum amount of energy by reacting molecules.



Threshold energy:- "The minimum amount of energy possessed by the reacting molecules to have effective collosions, resulting in the formation of product"

Activation energy:- "The excess energy over and above the average potential energy possessed by reacting molecules to have effective collosions resulting in the formation of product."

Activation energy = threshold energy - Average energy of reactants

$$\boxed{\text{Rate of Reaction} \propto \frac{1}{E_a}}$$

Collosion frequency:- "The number of collosions which occur among the reactant molecules per second per unit volume"

$$\boxed{Z = \sqrt{2}\,\pi\bar{v}\sigma^2 n^2}$$

$\bar{v}$ = average velocity

σ = moleculae diameter in cm

n = number of molecules per cc.

Determination of Activation energy:-

→ Larger the value of Ea of a reaction, smaller is K.

→ Larger the value of Ea of a reaction, greater will be the influence of change in temperature on rate constant.

Arrehius Equation:

It is used to evaluate energy of activation and to show the effect of temperature on rate constant.

→ Both "Ea" and "A" are independent from temperature.

→ Arrhenius equation cannot be used for nuclear reactions.

In Exothermic Rxs:- ● ΔH is negative

As, potential energy of Reactant > potential energy of product

In Endothermic Rxs:-

- ΔH is positive

As, potential energy of product > potential energy of Reactants

Ea of forward Reaction > Ea of backward Reaction

Catalyst:-

"Substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of the Rx."

Homogenous catalysis	**Heterogeneous catalysis**
● catalysis in which both the catalyst and reacting substance are in same physical state/phase.	● ″ ″ ″ substance are in different phases
● catalyst is uniformly distributed	● No uniform distribution of catalyst

• Mostly liquid or gaseous catalyst are used	• Catalyst is solid and reacting substances are either liquids or gases.
e.g $SO_{2(g)} + O_{2(g)} \overset{NO_{(g)}}{\rightleftharpoons} 2SO_{3(g)}$	**e.g** $4NH_{3(g)} + 5O_{2(g)} \overset{Pt_{(s)}}{\rightleftharpoons} 4NO_{(g)} + 6H_2O_{(g)}$

Auto calatysis:

"The substance which is formed during the course of Reaction Sometimes act as catalyst."

e.g. $CH_3COOC_2H_5 + H_2O \rightleftharpoons \underbrace{CH_3COOH}_{Autocatalyst} + C_2H_5OH$

Catalytic poisoning:-

The presence of some amount of foreign substances which render them ineffective.

- Poisoning may be temporary or permanent.

Activation of catalyst:-

Substance which promotes the activity of a catalyst (promoter/Activator).

Negative calatysis: Rate of Reaction is retarded by adding a substance called Inhibitor/Negative catalysis