CHEMICAL KINETICS

→ Chemical kinetics is the branch of chemistry, which deals with the study of the reaction rates, the factors affecting the rate of reactions and the mechanism by which the reactions proceed. Rate of a chemical reaction can be defined as the change in concentration of reactants or products in unit time.

→ Rate of Disappearance and Rate of Appearance.

- Rate of a reaction can be expressed in terms of rate of disappearance of any of the reactant or rate of appearance of any of the product eg) for a reaction,

$$A + 2B \longrightarrow C$$

Rate of Disappearance of

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

Similarly, rate of appearance of

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

Where (-) indicates the decrease in conc. of reactant and (+) indicates the formation of product

- Unit of rate of a reaction is $mol\ l^{-1} s^{-1}$ or $atm\ s^{-1}$.

• Instantaneous Rate

It is defined as the rate of change in concentration of any one of the reactants or products at that particular instant of time.

It is equal to the small change in conc. of reactant or product in small interval of time.

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Instantaneous Rate,

$$r_{inst} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{d[C]}{dt}$$

NOTE: Rate of a reaction depends upon the experimental cond^n such as conc^n of reactants, temperature, and catalyst.
It also depends on Nature of reactants.

→ RATE LAW

It is the expression in which rate of reaction is given in terms of molar conc^n of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced equation.

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

The rate of expression for this reaction,

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

$$\text{or } -\frac{d[R]}{dt} = K[A^x]^x[B]^y \qquad K \text{ is constant.}$$

→ ORDER of a Reaction

- The sum of the powers of the concentration of the reactants in the law expression is called Order of that reaction.

$$aA + bB \rightarrow cC + dD$$

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

Order of reaction = $(x+y)$

- It is experimentally determined Quantity.
It may be zero, whole number, fractional or even Negative.

→ RATE CONSTANT.

Rate of reaction is expressed as rate constant, when conc^n of each of the reactant is unity.

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Reaction	Order	Units of rate constt.
Zero Order reaction	0	$mol\ L^{-1} s^{-1}$
First Order reaction	1	s^{-1}
Second Order reaction.	2	$mol^{-1} L s^{-1}$

- In case of gaseous reactions, conc. is expressed in terms of pressure. i.e., atmosphere (atm).
Rate constant increases with increase in temperature.

→ Complex and Elementary Reactions.
Reactions which proceed in two or more steps are known as complex reactions and each step of a complex reaction is elementary reaction.
- The rate of a complex reaction is given by the slowest step called Rate Determining step amongst these steps.

→ Molecularity
- It is the Number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction.
- It is a Theoretical concept. It is always a whole Number value.
- Its value can never be zero or Fractional.
- For a complex reaction, generally molecularity of the slowest step is same as the Order of overall reaction.
- Order is applicable to elementary as well as complex rxn. Whereas molecularity is applicable only for elementary reaction.

(2013)
eg For a reaction $A + B \rightarrow P$ the rate law is given $r = k[A]^{1/2}[B]^2$. what is the Order of reaction.

Ans 5/2

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Example) For a reaction : $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

Rate = k.

(i) Write the Order and molecularity of this reaction

→ Rate = k, Suggest that the reaction is of zero Order.

Molecularity is 2.

(ii) Write the unit of k

→ The unit of k for zero Order reaction is equal to rate of reaction which is mol $l^{-1}s^{-1}$.

→ Integrated Rate Equations.

→ The Differential rate equation is Integrated to get a relation b/w Directly measured experimental data i.e., Conc. at Diff. times and rate constant.

→ The Integrated rate equations are Different for the reaction of Different Orders.

→ ZERO Order Reaction.

- It means that the rate of the reaction is directly proportional to the zero power of the conc. of reactant R.

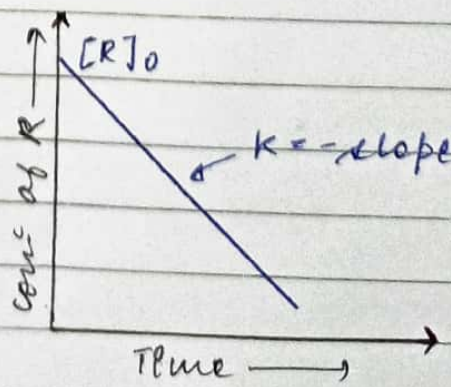
For the reaction, $R \longrightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0 = k \quad , \quad k = \frac{[R]_0 - [R]}{t}$$

where, $[R]_0$ is Initial conc. of reactant.

A plot of [R] with time, t is a straight line with slope = -k.

- The Thermal Decomposition of HI on gold surface and the decomposition of gaseous ammonia on a hot platinum surface are the examples of zero Order reaction.



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→ FIRST Order Reaction.

It means that the rate of the reactant is directly proportional to the first power of the conc. of the reactant, R.

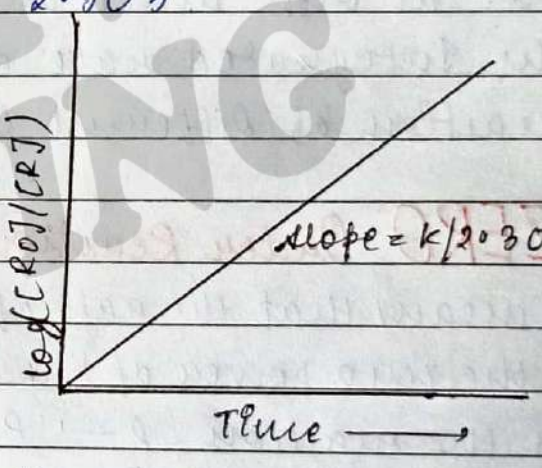
For the reaction $R \rightarrow P$.

$$\text{Rate} = -\frac{d[R]}{dt} = k[R], \quad k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

where, $[R]_0$ is the initial concentration and $[R]$ is the conc. of the reactant at time, t.

All Natural and artificial radioactive decay of unstable Nuclei takes place by First Order kinetics.

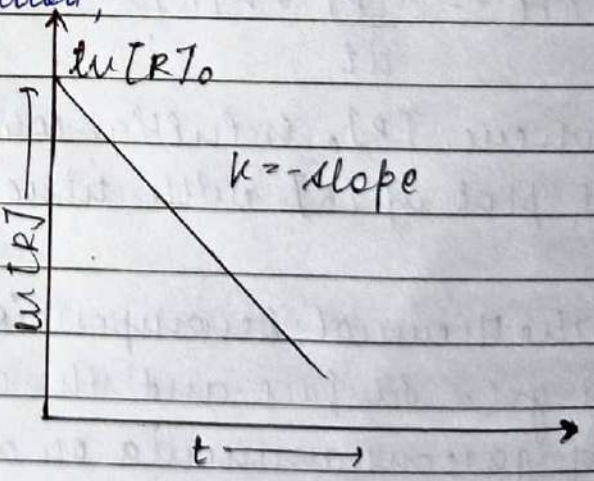
A plot of $\log [R_0]/[R]$ with time, t for a first order reaction is a straight line with slope = $\frac{k}{2.303}$



- Rate constant for first Order reaction is also given by

$$k = \frac{1}{t} \ln \frac{[R_0]}{[R]} \Rightarrow \ln [R] = \ln [R_0] - kt$$

Therefore, the variation in the conc. $\ln[R]$ vs time (t) plot is given below.



- For a typical First Order gas phase reaction,

$$A(g) \longrightarrow B(g) + C(g)$$

$$k = \frac{2.303}{t} \log \frac{P_i^\circ}{P_A} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{P_i^\circ}{(2P_i^\circ - P_i^\circ)}$$

→ Half-life [$t_{1/2}$] of a Reaction

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

For a zero Order reaction, $t_{1/2} = \frac{[R]_0}{2k}$

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and for first order reaction, $t_{1/2} = \frac{0.693}{k}$.

The half-life of a reaction with n^{th} order is

$$t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$$

Therefore, for zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.
For second order reaction $t_{1/2} \propto \frac{1}{[R]_0}$ and so on.

In General (for a first order reaction only).

$N = N_0\left(\frac{1}{2}\right)^n$ where, N_0 = initial amt. of reactant
N = amt. of reactant left after time t.
$n = \frac{\text{Total time } (t)}{\text{Half-life } (t_{1/2})}$

→ Pseudo First Order Reactions.

- Pseudo first order reactions are not truly first order but show first order kinetics under certain conditions

eg) Inversion of cane sugar and alkic hydrolysis of an ester.

These reactions are bimolecular but have order one.
- In other words, we can say that when a reaction is first order wrt each of the two reactants then, it becomes pseudo first order, when one of the reactants is taken in excess.

eg) $CH_3COOC_2H_5 + H_2O$ (excess) $\xrightarrow{H^+}$ $CH_3COOH + C_2H_5OH$.

Note the relation between half-life period of a reactant and its initial concentration for a reaction of n^{th} order is $t_{1/2} = \frac{1}{k[R_0]^{n-1}}$.

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→ Temperature Dependence of the Rate.

The Rate of reaction is dependent on temperature.
This is expressed in terms of temperature coefficient. Most of the chemical reaction are accelerated by increase in temp.

→ ARRHENIUS EQUATION.

- The temp. dependence of rate of a chemical reaction is expressed by Arrhenius equation.

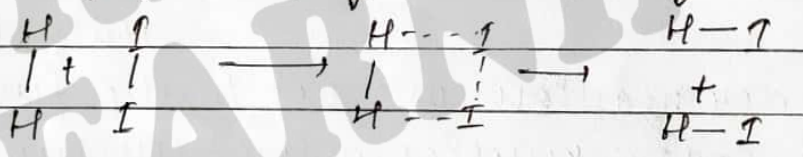
$$k = A \cdot e^{-E_a/RT}$$

A = Frequency Factor
Ea = activation energy (in J/mol)
R = gas constant
T = temperature.

→ Arrhenius Theory.

Arrhenius theory state that product are formed through the intermediates or activated complex.

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$



→ Activation Energy (Ea)

- It is given by the energy diff. b/w activated complex and the reactant molecules.
- It is the energy needed to form the intermediates called activated complex. or It is the extra energy contained by the reactant molecules that result into effective collision between them to form the products.

→ Threshold Energy.

It is the minimum energy which the colliding molecules must have for effective collisions i.e., those collisions which lead to the formation of product molecules.

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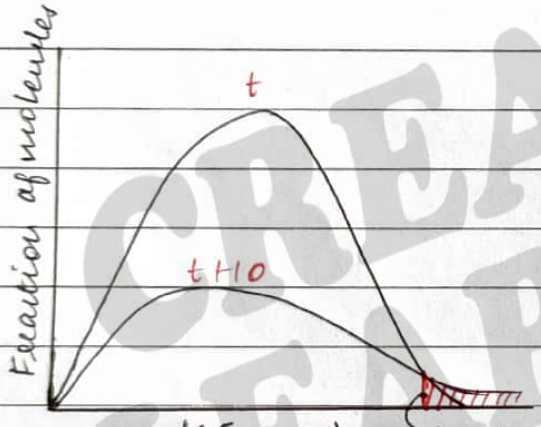
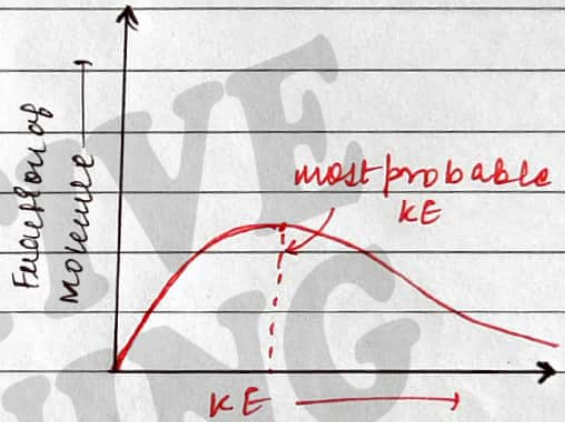
→ MAXWELL-BOLTZMAN Distribution curve.

→ According to Ludwig Boltzman and James clerk Maxwell, the Distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E) V/S KE, where N_E is the Number of molecules with energy E and N_T is the total No. of molecules this is called, Maxwell's Distribution of energies.

- when the temp is raised, the max. of the curve moves to higher energy value and the curve broadens out.





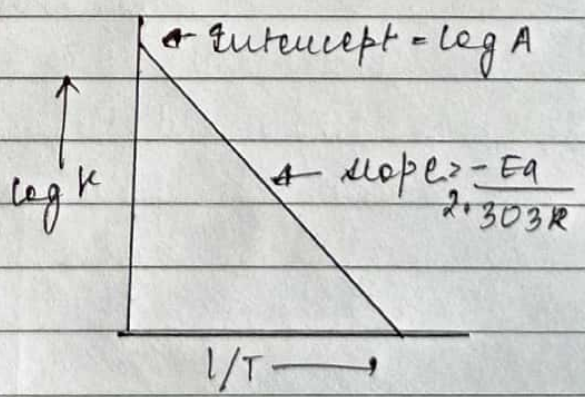
this area of shows fraction of molecules reacting at t.

- Taking logarithm of both sides, Arrhenius eqⁿ becomes

$$-\log k = \log A - \frac{E_a}{2.303RT}$$

A plot of log k with 1/T gives a st. line with slope = $\frac{-E_a}{2.303R}$

Intercept = log A



at Temp T_1 and T_2,

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

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- The rate of a chemical reaction alters by the presence of a catalyst.
- It alters the rate by providing alternative path of lower activation energy to the reactants.

Ⓚ A catalyst does not change enthalpy (ΔrH), Gibb's energy, equilibrium constant.

- It only helps in attaining equilibrium faster

COLLISION THEORY

- According to the collision theory, rate of reaction depends on the collision frequency and effective collisions.

The No. of collision per sec per unit volume is called collision Frequency (Z).

- For a Bimolecular elementary reaction,

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

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

Here $e^{-Ea/RT}$ represent the fraction of molecules having energy equal to or Greater than Ea.

→ The proper Orientation of reactant molecules lead to bond formation whereas Improper orientation makes them simply bounce back and no products are formed.

→ A collision of correctly Oriented particles will be effective if the KE of collision ≥ Ea.

→ According to collision theory, another factor P called Steric Factor which refers to the orientation of molecules which collide is important and contributes to effective collision.

$$\text{Rate} = PZ_{AB} e^{-Ea/RT}$$

- Thus in a collision theory both activation energy and proper

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Orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical Reaction.

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eg) What is the effect of catalyst on

(i) Activation energy (E_a)

(ii) Gibb's energy (ΔG)

→ catalyst :

(i) Lowers the activation energy and changes the path of Reaction

(ii) Doesn't affect ΔG.

eg) The activation energy for the reaction

$2HI(g) \longrightarrow H_2(g) + I_2(g)$ is 209.5 KJmol^{-1}. at 581 K

Calculate the fraction of molecules having energy equal to or greater than activation energy. ($R = 8.31\ JK^{-1}mol^{-1}$) (2010)

→ Given, $E_a = 209.5\ KJmol^{-1} = 209 \times 10^3$.

$R = 8.314$ and $T = 581\ K$.

Fraction of molecules 'x'

$$\log x = \frac{-E_a}{2.303RT} \Rightarrow \log x = \frac{-209500}{2.303 \times 8.314 \times 581}$$

$$\log x = -18.83$$

$$\boxed{x = 1.471 \times 10^{-19}}$$

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