

Chemical kinetics.

www.chemistryUP.in

1. Very fast reactions — This type consists of reactions which occur almost instantaneously.

The rates of such reactions (ionic-reactions) cannot be determined easily.

The obvious reason for a very fast rate of such reactions is that no chemical bonds are to be broken among the reactants.

exam— $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

2. Very slow reactions — Reactions which occur at a very slow rate. These reactions may require months or even years together for their completion.

3. Moderately slow reactions — This type refers to reactions in between the very fast and very slow reactions. These reactions proceed at moderate speed which can be easily measured.

exam— $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{10}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_5$.

$2(\text{C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} \rightarrow n\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

— Rate of chemical reaction — The rate of a chemical reaction is the speed or velocity with which a reaction take place. It can be expressed qualitatively as well as quantitatively.

(i) Qualitative rate — It is based on certain visual parameters like disappearance of reactants, colour change, effervescence etc. The rate expressed as such provides arbitrary conclusions about the rate of reaction.

(ii) Quantitative rate — The quantitative rate of a chemical reaction provided us with much better information about the rate-data and the accurate rate of a reaction.

— In quantitatively, the rate of chemical reaction may be expressed in two ways.

- (a) The rate of decrease in concentration of any one of the reactant
- (b) The rate of increase in concentration of any one of the product.

For a hypothetical reaction, Assuming that the volume of the system remains constant.



One mole of the Reactant (R) produce one mole of product (P) if R_1, P_1 are the concentrations of R and P at time t_1 , and R_2, P_2 are their concentration at time t_2 than.

$$\Delta t = t_2 - t_1,$$

$$\Delta R = R_2 - R_1,$$

$$\Delta P = P_2 - P_1$$

Rate of disappearance of R = $\frac{\text{Decrease in concentration of R}}{\text{Time taken}}$

$$= -\frac{\Delta R}{\Delta t}.$$

Rate of appearance of P = $\frac{\text{Increase in concentration of P}}{\text{Time taken}}$

$$= \frac{\Delta P}{\Delta t}.$$

In general for a hypothetical reaction.



$$\text{Rate of Reaction} = -\frac{1}{a} \frac{\Delta A}{\Delta t} = -\frac{1}{b} \frac{\Delta B}{\Delta t} = \frac{1}{c} \frac{\Delta C}{\Delta t} = \frac{1}{d} \frac{\Delta D}{\Delta t}.$$

Average rate and its Determination —

It is defined as the rate of change of Concentration per unit time. It is calculated by dividing the total change in Concentration of any one of the reactants or product by the total time taken to do so.

Average rate = $\frac{\text{Change in concentration in given time}}{\text{Time taken}}$

$$= -\frac{\Delta R}{\Delta t} = +\frac{\Delta P}{\Delta t}.$$

- Instantaneous rate and its determination -

The instantaneous rate of reaction is defined as the decrease in concentration of any one of the reactants or increase in concentration of any one of the product at a particular instant of time for a given temperature.

$$\text{r}_{\text{inst}} = - \frac{\Delta R}{\Delta t} = + \frac{\Delta P}{\Delta t}$$

$$\text{or } \text{r}_{\text{inst}} = - \frac{dR}{dt} = + \frac{dP}{dt}$$

It is important to mention that except concentration, all other factors which effect the rate are kept constant.

- Factors influencing rate of reaction -

- (1) Concentration of Reactants.
- (2) Temperature of reactants.
- (3) Nature of the reacting substances.
- (4) Presence of Catalyst
- (5) Exposure to radiations.

- Law of mass action - At a given temperature, the rate of a chemical reaction is directly proportional to the product of molar concentrations of reacting species with each concentration term raised to the power equal to numerical coefficient of that species in the chemical equation.

For any general according to law of mass



then rate of reaction according to law of mass action.

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

where k is rate constant. and it is defined as the rate of

- reaction when the concentration of each reactant is taken as unity.

- Characteristics of Rate Constant (K).
 - (1) The value of rate constant gives an idea about the speed of a reaction. Greater is the value of K, faster is the reaction.
 - (2) Each reaction has a definite value of the rate constant at a particular temperature.
 - (3) The value of K depends on the temperature. Change with change in temperature.
 - (4) The value of K is independent of the concentration of reacting species.
 - (5) The unit of rate constant depend on the order of reaction.

- Difference.

<u>Rate of reaction.</u>	<u>Rate Constant of reaction.</u>
1. It is the speed at which the reactants are converted into the products at any moment of time.	It is constant of proportionality in the rate law expression.
2. It depends upon the concentration of reactant species at that moment of time.	It refers to the rate of reaction at the specific point when concentration of every reacting species is unity.
3. It generally decreases with the progress of reaction.	It is constant and does not depend on the progress of the reaction.

- Molecularity - According to Collision theory, a chemical reaction takes place due to collisions between the particles of the reactants. The number of reacting species which must collide simultaneously in order to bring about the chemical reaction is called molecularity of the reaction. The molecularity of the reaction can be 1, 2, 3

Molecularity is simply the sum of molecules of the different reactants as represented by the balanced chemical equation. Such reactions are known as elementary reactions.

- Chemical reactions which proceed through more than one steps are termed as complex reactions.

The detailed description of various steps of the complex chemical reactions is called mechanism of the reaction.

- Rate law - A mathematical expression that gives the true rate of a reaction in term of concentration of the reactants, which actually influence the rate. It is called rate law.

For a general reaction:



Where, a, b, c, d are the stoichiometric coefficients of reactants and products. The rate of this reaction is:

$$\text{Rate} \propto [A]^x [B]^y.$$

Where x and y may or may not be equal to a and b .

The above reaction can also be written in differential form.

$$\frac{-dR}{dt} = k [A]^x [B]^y.$$

- Rate Controlling Step - The slowest step of the complex reaction is called the rate controlling step or rate determining step.

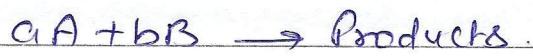
- Difference between rate law and Law of mass action -

The rate law gives the mathematical expression which gives the actual rate of a reaction whereas the law of mass action give the rate on the basis of stoichiometry of the balance equation.

- Order of reaction - It may be defined as the sum of powers or

exponents to which the concentration terms are raised in the rate law expression.

For a hypothetical reaction.



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

The order of the above reaction is equal to $[x+y]$. These powers x and y have no relation to the a and b . If sum of the power is equal to one then the reaction is called first order reaction. If the sum of the powers is two or three, the reaction is second order or third order. The order of a reaction also be zero or fractional.

- Units of rate constant for reactions of different orders-

1. For zero order reaction.

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

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k \cdot 1 \quad \text{or} \quad k = \frac{\text{mol L}^{-1}}{\text{sec}}$$

2. For First order reaction.

$$\text{Rate} = k [A].$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k \cdot \text{mol L}^{-1} \quad \text{or} \quad k = \text{sec}^{-1}$$

3. For Second order reaction.

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

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k \cdot (\text{mol L}^{-1})^2 \quad \text{or} \quad k = \text{L mol}^{-1} \text{ s}^{-1}$$

4. For three order reaction.

$$\text{Rate} = k [A]^3.$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k [\text{mol L}^{-1}]^3 \quad \text{or} \quad k = \text{L}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

- In general, for a reaction of n th order.

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

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k [\text{mol L}^{-1}]^n \quad \text{or} \quad k = \text{L}^{n-1} \text{ mol}^{1-n} \text{ sec}^{-1}$$

Difference.Molecularity.

	order.
1. It is the number of reacting species undergoing simultaneous collision in the reaction.	It is sum of the powers of the concentration terms in the rate law expression.
2. It is a theoretical concept.	It is determined experimentally.
3. It can have integral values only.	It can have fractional values only.
4. It can be zero.	It can be zero.
5. It does not tell us anything about the mechanism of the reaction.	It tells us about the slowest step in the mechanism and hence gives some clue about the mechanism of the reaction.
6. It does not change with change in temperature and pressure.	It changes with change in temperature and pressure.

— zero order reactions — A reaction is zero order if its rate is independent of the concentration of reactants or a zero order reaction means that the rate of reaction is proportional to zero power of the concentration of reactants.
For a zero order reaction of the form.



The rate of reaction Rate = $-\frac{d[R]}{dt} = k[R]_0$

$$= -\frac{d[R]}{dt} = k \cdot x 1.$$

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

Integrating both sides.

$$[R] = -kt + I.$$

where I is the constant of integration.

At $t = 0$, $[R] = [R]_0$, where $[R]_0$ is initial concentration of reactants.

$$[R] = -kt + [R_0].$$

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

- First order reaction - let a simple hypothetical first order reaction is. $R \rightarrow P$.

If the initial concentration of R is $[R_0]$, k is the rate constant and $[R]$ is concentration at time t then the differential form of this first order reaction is.

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

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

Integrating both side

$$-\ln[R] = kt + I.$$

$$\text{At } t=0$$

$$-\ln[R] = kx_0 + I$$

$$\text{so } I = -\ln[R_0]$$

$$\text{then } -\ln[R] = kt - \ln[R_0].$$

$$kt = \ln[R_0] - \ln[R] = \ln \frac{[R_0]}{[R]}$$

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

- In general for the reactions of n order $nA \rightarrow \text{Product}$.

$$\text{the rate of equation } k_n = \frac{1}{t(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

where a = initial Concentration of Reactant.

x = Concentration which convert in Product.

- Half Life of a reaction - It is defined as the time during which the Concentration of reactants is reduced to half of the initial Concentration or it is the time required for the completion of half of the reaction. It is denoted by $t_{1/2}$.

Half life

1 Half time of zero order reaction -

$$[R] = [R_0] - kt.$$

$$\text{Now at } t_{1/2}, \quad [R] = \frac{[R_0]}{2}.$$

$$\therefore \frac{[R_0]}{2} = [R_0] - kt. \quad \text{or} \quad kt = [R_0] - \frac{[R_0]}{2}.$$

$$t = \frac{[R_0]}{2k}.$$

Half time of a zero order reaction is directly proportional to initial concentration.

$$t_{1/2} \propto [A]_0$$

2 Half life of first order reaction -

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}.$$

$$\text{When } t = t_{1/2}, \text{ then } [A] = \frac{[A]_0}{2}.$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{k} \log 2.$$

$$t_{1/2} = \frac{0.693}{k}.$$

Half life Period or half change time for first order reaction does not depend upon initial Concentration of the reactants.

The time required to reduce the concentration of the reactant to any fraction of the initial concentration for the first order reaction is also independent of the initial concentration.

In general, for the reaction of n th order.

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

In general, the time required to complete n th fraction of a first order reaction is -

$$t_{vn} = \frac{2.303}{k} \log \frac{n}{n-1}$$

- Amount of substance after N half-lives -

The amount of a substance which is left in a reaction after n half-lives.

$$\text{Initial Concentration} = [R]_0$$

$$\text{Conc. after 1st half life} = \frac{[R]_0}{2}$$

$$\text{Conc. after 2nd half life} = \frac{[R_0]/2}{2} = \frac{[R_0]}{2^2}$$

$$\text{Conc. after } n\text{th half life} = \frac{[R_0]}{2^n}$$

- Activation energy - The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and products is called activation energy.

Activation energy = Threshold energy - Average energy of reactants.

For fast reaction - activation energy is low.

for slow reaction - activation energy is high.

- Activated complex or transition state - The arrangement of atoms corresponding to energy maxima (threshold energy) is called transition state or activated complex.

In transition state the system has partial reactant character and partial product character.

The difference between energy of the transition state and energy of the reactants is equal to activation energy.

$$\text{Activation} = E_{\text{transition}}^{10} - E_{\text{reactant}}$$

Increase in the rate of reaction with increase in temperature is mainly due to increase in number of collision which are energetically effective.

- Effect of temperature on the rate constant of reaction -

The rate constant of reaction increases with increase of temperature. This increase is generally two-fold to five-fold for 10K rise in temperature. This is explain on the basis of Collision theory. The main points of collision theory are.

- (i) For a reaction to occur, there must be collision between the reacting species.
- (ii) Only a certain fraction of total collisions are effective in forming the products.
- (iii) For effective collisions, the molecule must possess the sufficient energy (equal or greater than threshold energy) as well as proper orientation.

on the basis of above conclusion, rate of reaction is

$$\text{Rate} = f \times z$$

where f is the effective collision and z is total number of collisions per unit volume per second.

- Quantitatively - The effect of temperature on the rate of a reaction and hence on the rate constant k was proposed by Arrhenius. The equation is called Arrhenius equation.

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

where A is a constant called frequency factor (because it gives the frequency of binary collision of the reacting molecules per second per liter). E_a is the energy of activation, R is gas constant and T is the absolute temperature. The factor $e^{-\frac{E_a}{RT}}$ gives the fraction of molecules having energy equal to or greater than the activation energy E_a .

The energy of activation (E_a) is an important quantity as it is characteristic of the reaction.

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

Taking Log both side.

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

If the value of the rate constant at temperature T_1 and T_2 are K_1 and K_2 .

then.

$$\ln K_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2}$$

$$\text{then. } \ln K_2 - \ln K_1 = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

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

- Effect of Catalyst on rate of reaction -

- (i) A catalyst speeds up a reaction but it must be involved chemically however temporarily in some way and is continually changed and reformed as the reaction proceeds.
- (ii) Catalysts work by providing an alternative reaction pathway of lower activation energy.

Characteristics of the Catalyst.

- (i) A catalyst is highly specific in its action. This means that a catalyst may increase the rate of one reaction but may be completely ineffective in another reaction.

- (IV) A Catalyst may undergo intermediate physical change and may even form temporary chemical bonds with the reactants but is recovered unchanged in mass and composition at the end of the reaction.
- (V) A Catalyst never starts a reaction which has no tendency to proceed.
- (VI) Since Catalyst does not alter the individual energies of reactants and products therefore ΔH or ΔU of the reaction remains unaltered.

- Collision frequency (Z) - The number of collisions per second per unit volume of the reaction mixture is known as Collision frequency.
- Postulates of Collision theory -
 - (I) A reaction occurs on collision of two molecules only if they possess a certain minimum amount of energy in excess of the normal energy of molecules.
 - (II) The minimum energy which molecules must possess before collision should be equal to or greater than the activation energy.
 - Temperature Coefficient - It is ratio of rate constant at 308 K. and 298 K.