Physical Chemistry

Chemical Kinetics and Catalysis

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Molecules, atoms and ions present in liquid or gaseous phase are in a state of random motion and are colliding with each other. Collision among these may result in physical or chemical change. **These reactions provoke** a **few questions in mind. How far do these reactions proceed? What factors govern these reactions? How fast are these reactions?**

An answer to first two questions can be obtained from a thermodynamic study. Knowledge of equilibrium constant 'K' gives an idea of the extent of reaction. A large value of 'K' indicates that most of the reactants have been converted into products whereas a small value of 'K' indicates that there are more reactant molecules than those of the product.

The study of factors affecting the reaction and hence the equilibrium constant can be carried out thermodynamically using Le-Chatelier Principle. According to this principle "When a system at equilibrium is subjected to change in temperature, pressure or concentration, the system reacts in such a way so as to undo the change."

But, an answer to the third question can not be obtained from thermodynamics. The branch of chemistry that deals with the study of speed of reactions is known as **"Chemical Kinetics".** The important characteristic features of Chemical kinetics are:-

(i) It predicts reaction time i.e. how fast or slow is the reaction.

(ii) It gives the knowledge of various factors such as temperature, pressure, concentration, catalyst affecting the rate of reaction

(iii) If gives an insight into the reaction mechanism.

Another, **question** that arises in the mind is **"Both thermodynamic and kinetic studies talk about the dependence of a reaction on temperature, pressure and concentration. How are these two studies different from each other"?**

An answer to this question is "Most of the reactions do not lead to the state of completion but to a state of equilibrium. How early does a system attain this equilibrium state by change in physical parameters is the domain of kinetic study. Once the system reaches the state of equilibrium the effect of change in physical parameters on the equilibrium state is the domain of thermodynamic study. (Fig. 1)

In Fig (1); Curve 'A' represents change in concentration of reactant P with time to Q'. This is the domain of kinetic study & beyond Q′ is the region of thermodynamic study. Curve 'B' is the change in concentration of product with time.

An insight into the **kinetics of a reaction plays a significant role** in the industrial synthesis of compounds. The thermodynamic equilibrium constant gives the maximum yield of a product obtainable at given temperature and pressure. But, if the reaction rate is very low, it is not economical to carry out the reaction. Therefore, the study of reaction rate is important in selecting optimum conditions for an industrial process so that it proceeds at a rate to give maximum yield. What happens to pollutants released to the atmosphere can be understood only by a kinetic analysis of atmospheric reactions.

Reaction rates are fundamental to the functioning of living organism by selective speeding up of certain reactions by enzymes that act as catalyst.

In summary, to predict and understand the behaviour of a chemical reaction, we must consider both thermodynamics and kinetics.

Types of reaction:

Broadly, all reactions can be classified into two categories :

(i) Homogeneous:- A reaction, where all reactants, products and catalyst (if employed) present in one phase, the reaction is referred to as homogeneous reaction.

$$H_2(g) + Cl_2(g) \quad 2HCl(g)$$

(ii) Heterogeneous:- A reaction, where all reactants, products and catalyst (if employed) are present in more than one phase, is a heterogeneous reaction.

$$H_2(g) + 1/2\, O_2(g) \quad H_2O(l)$$

$$\underset{(s)}{CaCO_3} \xrightarrow{\Delta} \underset{(S)}{CaO} + \underset{(g)}{CO_2}$$

On the basis of reaction time, various reactions can be divided into three categories:-

(a) Fast reaction
(b) slow reaction
(c) Moderate reaction

Fast reactions occur instantaneously. For example, a reaction between strong acid and strong base. Half life of a fast reaction may vary from a few milliseconds to a few femto seconds.

These reactions are too fast to be followed by classical methods. Depending upon the half life of a fast reaction, different techniques are employed for studying the kinetics of such reactions.

Reactions with half life of a few milliseconds are studied **spectrophotometrically.** A stopped-flow spectrophotometer is used for this purpose.

This assembly (Fig. 2) permits observation of the reaction velocity of two reactants, stored in reservoir syringes whose pistons are simultaneously driven by air-operated

plunger. The reactants are mixed in the mixing chamber in the observation cell. The observation is made by the photo cell of the spectrophetometer at desired wavelength. After leaving the observation cell, the mixed reactants advance the piston of a stopping syringe. Just prior to stopping, a switch is closed thereby supplying a 14 volt signal for triggering an oscilloscope. This converts the light signal into the electrical signal and is displayed on the oscilloscope.

For reactions having **half life of the order of few micro seconds, perturbation techniques are employed.** There are two perturbation techniques:-

(i) Temperature-Jump method:-

Initially the system is at equilibrium position and is perturbed from its equilibrium position by the sudden impulse of temperature. The subsequent relaxation is followed by monitoring any physical property for the system. Principally, this technique is applicable to system for which ΔH_m O (zero). This technique is useful for studying

(i) formation of a complex via outer sphere mechanism.

(ii) neutralization of a proton by hydroxyl ions $H_3O^+ + OH^- \rightarrow 2H_2O$.

(ii) Pressure-Jump Method:-

The system is perturbed from equilibrium position by suddenly changing the pressure and monitoring the subsequent relaxation by conductometric method.

This technique is applicable to the system where $\Delta V \neq 0$. Most of the ionic reactions are accompanied by the change in volume. Therefore, it is applicable to such systems.

For reactions having **half life of the order of a few nanoseconds**, large perturbation techniques are employed e.g. **Flash Photolysis, Nano flash photolysis, shock waves etc.** In aqueous solutions, the **fastest known second order elementary reaction** is between H^+ and $O\bar{H}$ ions to form water molecule. The rate constant for this reaction is 1.4×10^{11} $dm^3\ mol^{-1}\ s^{-1}$ at 25ºC.

Techniques have been developed to study even **reactions where the life time of the transition state is of the order of 10^{-15}s**.

Reactions like :

$$CH_3Cl + I^- \rightarrow CH_3I + Cl^-$$

The transition state involving stretching of C – Cl bond alongwith the formation of C – I bond have also been studied. Such studies are done under a different branch called **"Femtochemistry".** This is a current area of research in the field of kinetic study.

On the other extreme, **reactions are known which proceed at very slow speeds.** Half life of such reactions may vary from a few days to a few years. Rusting of iron is an example of a slow reaction. The rates of extremely slow reactions are measured by radioactively labeling a reactant, allowing the reaction to run for a few weeks, separating a radioactive product from reaction mixture and then measuring it radioactivity.

Between these two extremes, there are reactions which proceed at measurable speeds. Examples include hydrolysis of an ester, the reaction between persulphate and iodide ions. These reactions are known as **moderate reactions.** In this chapter we'll be concentrating on such reactions only.

Why do different reactions proceed at different speed?

We know that random collision among the molecules result in the formation of product. During collision, old bonds are broken and new bonds are formed. The amount of heat required for breaking up of different bonds is different for different reactions. Therefore, all reactions proceed at different rates.

Rate of Reaction:-

Consider a reaction $A \rightarrow B$

By the term rate of change of amount of a reactant or a product, we mean the disappearance of the amount of reactant 'A' or appearance of the amount of a product 'B' in a unit interval of time.

As the concentration of the reactant changes every moment, **the rate of reaction is not constant for a reaction but varies every instant**. Therefore, average rate of a reaction has no meaning. The rate at any particular instant has more practical application and importance. This rate is known as **Instantaneous rate** R_{ins} and is defined as

$$R_{inst} = \lim_{\Delta t \to o} \left\{ -\frac{\Delta n_A}{\Delta t} \right\} = \frac{-dn_A}{dt}$$

$$R_{inst} = \lim_{\Delta t \to o} \left\{ \frac{\Delta n_B}{\Delta t} \right\} = \frac{dn_B}{dt}$$

The instantaneous rate at a given time may be determined by finding out the slope of either reactant or product curve at that time. This is done by drawing a tangent at that instant. (Fig. 3)

$$R_{ins} == \left(\frac{-dn_A}{dt} \right) = -\left\{ \frac{n_{A_{(2)}} - n_{A_{(1)}}}{t_2 - t_1} \right\}$$

$$R_{ins} = -\left(\frac{dn_A}{dt}\right)$$

negative sign indicates that amount of reactant is decreasing with time.

$A \rightarrow 2B$

where 1 mol of A on disappearance forms 2 moles of B i.e. amount of B will increase twice as fast as the decrease in amount A. Hence, the quantity dn_B/dt is twice as large as ---dn_A/dt.

i.e. $-2\frac{dn_A}{dt} = \frac{dn_B}{dt}$

or $\boxed{-\frac{dn_A}{dt} = \frac{1}{2}\frac{dn_B}{dt}}$

In general, for a reaction.

a A + b B → c C + d D

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

Factors affecting the rate of reaction

The various factors affecting the rate of a reaction are:-

Concentration of reactants :- In general, rate of reaction is directly proportional to the concentration of reactants. Greater is the concentration, more is the rate of the reaction. Rate of reaction is maximum at the beginning and then decreases gradually, as with time the concentration of reactant decreases.

Nature of reactants :- Rate of a reaction depends upon the nature of reactants. For example, redox reaction between ferrous ions and permanganate ions can be studied at room temperature. But, the reaction between oxalic acid and permanganate ions doesn't occur readily at room temperature. Oxalic acid solution is heated to a temperature of 60-70°C (when it becomes unbearable to touch) before titrating against the solution of permanganate ions.

Catalyst:- A catalyst is a substance that accelerates the rate of a reaction without itself undergoing a net change. A catalyst provides an alternate pathway with lower activation energy (Fig.4). Since $\Delta G°$ is not changed, the equilibrium constant remains unchanged in the presence of a catalyst. Thus, the use of a catalyst helps in attaining

the equilibrium position rapidly and the relative proportion of products and reactants at equilibrium, remains same,

Temperature:- The dependence of rate constant on temperature is given by Arrhenius equation

$$\mathbf{k = A \exp(-E_a/RT)} \qquad (1)$$

where A = constant of proportionality called frequency factor

E_a = activation energy

R = gas constant

T = absolute temperature

This equation shows that only those colliding molecules end up forming the reaction product which have that extra energy called as energy of activation E_a. Each system has a characteristic value of E_a and can be computed using eq. (1).

Taking logarithm of both the side of eq. (1)

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

$$\text{or } \ln k = \ln A - \frac{E_a}{RT} \qquad (2)$$

At two temperatures T_1 & T_2, we can write the above equation as

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad (3)$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \qquad (4)$$

Subtracting eq. (3) from eq. (4)

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

$$\text{or } \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

$$= \frac{E_a}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

$$\text{or } \boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}} \qquad (5)$$

Thus, knowing the value of k_1 and k_2 at two temperatures T_1 and T_2, the value of activation energy for a particular reaction can be calculated.

eq. (2) is of the form y = mx +c , i.e. equation of a straight line. Therefore, a plot of ln k v/s $\frac{1}{T}$ should be a straight line with slope equal to $\frac{-E_a}{2.303k}$ (Fig.5). It has actually been found to be so. **This ascertains the validity of Arrhenius equation.**

The temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by 10K.

At 25°C, for many reactions Ea ~ 80 kJ/mol.

Thus at 25°C, temperature coefficient of many reaction has a value.

$$\frac{k_{T+10}}{k_T} = \exp\left\{ \frac{10 \times 80,000}{8.314 \times 300 \times 310} \right\} \; \square \; e^{1.03} \approx 2.8 \qquad (6)$$

The rate constant for the given value of E_a increases about 2.8 times for every ten degree rise in temperature. For most reactions, the observed value lies between 2 and 3.

At lower temperatures, increase in temperature causes more change in the value of k than at higher temperatures as T appears in the denominator of Arrhenius equation. These observations are found to be true for simple reactions.

In many complex reactions, the observed rate constant is found to decrease with increase in temperature.

e.g. The reaction between NO and O_2 to form NO_2. This behaviour is explained on the basis of proposed mechanism.

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2\ NO_2 \qquad \text{(slow)}$$

The observed rate constant ‘k’ is given by

$$k = k_2 \left(\frac{k_1}{k_{-1}} \right) = k_2 K_{eq} \qquad (7)$$

Since the reaction is exothermic, the decrease in K_{eq} with increase in temperature more than compensates the increase in k_2 and **thus k decreases with increase in temperature.**

Light:- Rate of certain reactions are found to become extremely high when exposed to sunlight**.**

e.g.

$H_2(g) + Cl_2(g) \xrightarrow{\text{dark}} 2HCl(g)$ (slow)

$H_2(g) + Cl_2(g) \xrightarrow{\text{sunlight}} 2HCl(g)$ (fast)

Reactions induced by the absorption of light do not follow normal kinetic equation. Therefore, these reactions are studied under a separate branch called **"Photochemistry"**.

Solvent:- The reactions which take place both in gas-phase and in solutions are not much influenced by the solvent. The solvent only provides a physical environment. For example, thermal decomposition of N_2O_5. The value of rate constant in gas phase and different solvents is almost the same.

Table 1:- Comparison of kinetics of N_2O_5 decomposition in Gas phase and in selected solvents at 20°C

Phase	Rate Constant (k)	k_{soln}/k_{gas}
Gas–phase	$4.5 \times 10^{13}. e^{-24500/RT}$	1.00
solvent		
CCl_4	$2.8 \times 10^{13}. e^{-24100/RT}$	1.24
$CHCl_3$	$6.4 \times 10^{13}. e^{-24600/RT}$	1.45
Br_2	$2.5 \times 10^{13}. e^{-24000/RT}$	1.14

These results show that rate differs by a factor 1.00 to 2.00. The equality between rate of a reaction in gas-phase and solution phase is applicable for **ideal solutions only.**

The kinetic study of reactions in solution phase is very complicated and is governed by many factors:-

(a) The movement of ions in solution depends upon the **viscosity of the solvent**. Therefore, the rate constants of reactions vary with nature of solvent. The rate of reaction between oppositely charged ions is expected to be higher than that for a reaction involving an ion and a neutral molecule or two neutral molecules.

(b) Extent of solvation:- The degree of solvation of any reacting species affects the rate of the reaction. The reaction rate will be larger in solvents which have least solvation tendency for the reactants. e.g. rate of formation of quaternary ammonium salts is faster in nitrobenzene than in benzene.

(c) Nature of reacting species:- The reaction is faster in that solvent in which the activated complex is more stable. If the activated complex is polar, the reaction would be faster in polar solvent. If the activated complex is non-polar, the reaction would be fast in non-polar solvent.

Ionic strength :- In ionic reactions, due to electrostatic interactions between the reacting ions, the rate of the reaction is influenced by the charges of reacting ions and also ionic strength in solution (Fig. 6). These effects are generally known as salt effects and are of two types:-

(a) Primary salt effect:- It is observed in non-catalytic reactions where the added salt doesn't have any ion common with the ions of the reacting species. But it's addition changes the ionic strength of the solution, as a result of which the degree of dissociation of substances change.

A simple and satisfactory treatment of Primary salt effect was made by Bjerrum. He proposed that reacting molecules first form an activated complex which is in equilibrium with the reactants. The activated complex decomposes to yield the products.

$$A^{z_A} + B^{z_B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[AB^{z_A+z_B}\right]^{\#} \xrightarrow{k_3} \text{Products}$$

where z_A and z_B = charges on the reacting species

$(z_A + z_B)$ = charge on the activated complex

k_1, k_2, k_3 = rate constants of respective steps

According to Bronsted-Bjerrum equation for the same

$$\log k = \log k_o + 1.018\, z_A\, z_B \sqrt{\mu} \quad - \qquad (8)$$

where μ = ionic strength of dilute solution.

$k_0 = k_3 K^{\#}$ = constant

$K^{\#}$ = equilibrium constant = $\frac{k_1}{k_2}$

(i) The eq. (8) shows that variation of rate constant k with ionic strength (μ) depends upon the charges on the reacting ions.

(ii) The plot of log (k/k_0) versus $\sqrt{\mu}$ would be linear passing through origin. The slope of the line would be 1.018 z_A z_B (Fig. 6).

(iii) Three special cases are possible.

Case (i)- When $z_A . z_B = 0$ i.e. one of the reactant is uncharged (i.e. non-electrolyte) then

log k = iog k_o = constant

i,e. rate constant is independent of ionic strength (μ).

e.g:- $CH_2ICOOH + CNS^- \rightarrow CH_2(CNS)COOH + I^-$ $\quad z_A z_B = 0$

Case (ii): When $z_A z_B$ = (+)ve i.e. z_A and z_B are of same sign then

$\log (k/k_o) = + 1.018 Z_A Z_B \sqrt{\mu}$.

i.e., rate constant k would increase with $\sqrt{\mu}$.

e.g.:- $S_2O_8^{2-} + 2\ \bar{I} \rightarrow I_2 + 2\ SO_4^{2-}$ $\quad z_A . z_B = +2$

Case (iii): When $z_A . z_B$ = (-) ve i.e. z_A and z_B are of opposite sign, the rate constant would decrease with increase in $\sqrt{\mu}$

e.g :- $H_2O_2 + 2\ Br^- + 2H^+ \rightarrow 2H_2O + Br_2$ $\quad z_A . z_B = -1$

Secondary salt effect : It refers to the actual change in the concentration of reacting ions by addition of electrolyte in catalytic reactions. Arrhenius discovered when a salt of the acid catalyzing a reaction is added to it, the catalytic effect is enhanced. Because this addition increases the concentration of anion and undissociated acid (due to common ion effect). This indicates that both undissociated acid and it's anion have catalytic

activity. Thus, the reaction rate indirectly depends upon the amount of salt added in the catalytic reactions. This is called **Secondary salt effect.**

The addition of a salt having no common ion with the acid catalyzing a reaction can also sometimes lead to an increase in catalytic action of acid. It is called as **Primary Salt effect**. e.g. :- The rate of inversion of cane sugar in presence of acetic acid increases by 30 % when 10 % of NaCl is added .

The secondary salt effect can either increase or decrease the rate constant. It can be either larger or smaller than a primary salt effect. For uncharged reactants (neutral molecules), the rate constant is independent of ionic strength.

The existence of salt effects indicate the necessity of adequate control of ionic strength in a kinetic investigation. Either the ionic strength must be kept low so that the effects are small or a series of measurements must be made and extrapolated to zero ionic concentration. Another method is to add small quantities of electrolytes in the reaction which may involve ions, and study the influence of ionic strength. If salt effects are observed, they must be interpreted with care in terms of mechanism because of many possible sources of these effects.

Pressure:- Generally, the reaction rates of gaseous reactions are determined at constant volume and of reactions in solution at constant pressure. At normal pressure, the rate of reaction doesn't depend upon it. But at high pressures, changes in reaction rates have been observed.

The dependence of rate constant on volume is given by the following eq. (9) derived from transition state theory (see theories of reaction rate for detail)

$$\left(\frac{\partial \ln(k_2 / k_2^0}{\partial P}\right)_T = -\frac{\Delta V^{\#}}{RT} \qquad (9)$$

where $\Delta V^{\#}$ = Volume change due to the formation of activated complex.

$k_2^0 = k_2$ at $P = 0$

Case (i) $\Delta V^{\#}$ = (–) ve.

The rate of the reaction increases linearly with increase in pressure

Case (ii) $\Delta V^{\#}$ = (+) ve.

The rate constant decrease with increase in pressure

Case (iii) $\Delta V^{\#}$ = negligibly small

the rate constant is almost independent of pressure.

Methods for monitoring rate of reaction:-

Rate of any reaction can be determined if we know how does the concentration of reactants or products vary during the course of reaction. Depending upon the type of reaction, different methods can be employed for the same.

Volumetric analysis:- To determine the concentration of a particular species at different time interval, a known volume of reaction mixture is withdrawn and the reaction is stopped either by lowering the temperature significantly or by eliminating the catalyst if possible. This reaction mixture is then titrated against a solution of known strength using a suitable indicator. The volume of titrant used is directly related to the concentration of species present in the reaction mixture. The reaction is completed by heating a known volume of a reaction mixture to temperature ($60 - 70^0$ C). It is assumed at this temperature most of the reactants are converted to product and the reaction is complete.

Example :- During saponification of ethyl acetate.

$$CH_3\ COOC_2H_{5(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(Aq)} + C_2H_5OH_{(aq)}$$

The concentration of NaOH in the reaction mixture can be easily estimated by carrying out its reaction with an acid solution (say HCl) using phenolphthalein as an indicator. The volume of acid used is directly proportional to the concentration of NaOH solution in the reaction mixture at different time intervals. Let V_o, V_t and V_∞ be the volume of acid used at the start, at time t and at the and of reaction.

The volume of acid used at the start of the reaction refers to the initial concentration of the reactant i.e.,

$V_0 = [NaOH]_0 = a$

The volume of acid used at any time 't' refers to the amount of the reactant left unreacted

i.e., $V_t = [NaOH]_t$

Then, the amount of the product formed at any time 't' is

$x = [NaOH]_0 - [NaOH]_t = V_0 - V_t$

Measuring the change in Volume or Pressure

If a reaction occurs in a gaseous phase, then the concentration of various species at various time intervals can be determined from the change in pressure of a constant

volume reaction vessel or the change in volume of a constant pressure reaction vessel. These changes are measured instantaneously and therefore are fast method.

Monitoring the change in electrical conductance:- If in a reaction ions are produced or consumed, the concentration of reaction species at different time intervals can be determined conductometrically.

Example:- In the saponification of ethyl acetate

$$CH_3COO\,C_2H_5 + Na^+ + OH^- \rightarrow CH_3\,COO^-Na^+ + C_2H_5OH$$

The fast conducting OH^- ions are replaced by slow moving acetate ions. The change in conductivity will be directly proportional to the amount of OH^- ions consumed or acetate ions formed.

Let κ_0, κ_t and κ_∞ be the conductivities of the reaction mixture at the start of the reaction, after time t and at the end of the reaction respectively, then

$$[OH^-]_o \alpha \quad \kappa_0 - \kappa_\infty$$

$$[OH^-]_t \alpha \kappa_t - \kappa_\infty$$

and $x \alpha \kappa_0 - \kappa_t$

where x is the concentration of product.

Monitoring the rotation of the plane of polarised light : Some species if present in the reaction mixture can change the plane of polarized light falling on it. The concentration of species in the reaction mixture can be determined by noting the change in angle of rotation.

The instrument that is used for studying such reactions is known as **polarimeter**. Example:- Hydrolysis of cane sugar.

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

Sucrose glucose fructose.

(Dextro) (Levo)

cane sugar (sucrose) is dextro rotatory i.e. It rotates the plane of polarised light towards right. On hydrolyses, it yields glucose and fructose. Fructose is levo rotatory i.e. it moves the plane of polarised light towards left. Thus, during the course of reaction, the plane of polarized light changes its direction. The concentration of reacting species at different

time intervals is directly proportional to the change in angle of rotation at that time. Because of its characteristic feature, this reaction is commonly known as **Inversion of cane sugar.**

Let α_o, α_t and α_∞ be the angle of rotation of polarized light at the start, at time t and at the end of reaction respectively.

$$\left[C_{12}H_{22}O_{11}\right]_O = \alpha_o - \alpha_\infty$$

$$\left[C_{12}H_{22}O_{11}\right]_t = \alpha_t - \alpha_\infty$$

and [product] = $\alpha_o - \alpha_t$

[net change in angle should be positive. That's why we do not write $\alpha_\infty - \alpha_o$ as α_∞ is negative because at the end of the reaction, solution becomes levo rotatory]

Monitoring the colour change using colorimetry or spectrophotometry :- The concentration of reacting mixture can be determined using these methods provided the solution is coloured. If a solution itself is not coloured, a reagent may be added with which it forms a coloured complex. Such solutions have been found to follow **Lambert-Beer's Law.** According to this law, **"Decrease in the intensity of the incident light with the thickness of the absorbing medium is directly proportional to the intensity of the incident light and concentration of the solution"**

Mathematically,

$$\log \frac{I_o}{I_t} = A = \in Cl \qquad (10)$$

I_t/I_o = Fraction of light transmitted and is known as Transmittance 'T',

– log T = absorbance 'A'

$\in$= molar absorptivity coefficient and is a function of wavelength and nature of absorbing material.

C= Concentration of the solution

l = thickness of the medium.

Greater the concentration of the solution, more would be the absorption of the incident light and lesser would be the transmittance.

Thus, the dependence of concentration on time can be easily monitored by plotting a graph of log (I_o/ I_t) v/s time.

Potentiometeric Method :- The value of electrode potential for any electrode depends on the concentration of involved electrolyte. A quantitative dependence is given by the Nernst equation

$$E= E^0 - \frac{RT}{nF} \ln \frac{[Products]}{[Reactants]} \text{ where } E^0 = E^0_{Cathode} - E^0_{anode} \qquad (11)$$

During the reaction, as the concentration of reactant/product varies, potential of cell also changes. Knowledge of emf of cell at different time intervals can help us in studying the kinetics of the reaction.

Rate of reaction and rate constant

Consider a reaction

$A+B \rightarrow C+D$

Rate α [A] [B]

$$\text{or Rate} = k [A] [B] \Rightarrow k = \frac{\text{Rate}}{[A][B]} \qquad (1)$$

" k" is known as constant of proportionality or simply rate constant.

Comparison between Rate and Rate Constant

Rate of Reaction	**Rate constant**
(1) Rate of reaction is defined as change in the amount of reactants or product with time.	Rate of reaction when the concentration of each reactant is taken to be unity.
(2) Rate of reaction is a function of concentration.	Rate constant is independent of of concentration.
(3) The S.I. unit of rate of reaction is moles/L /s.	The S.I. unit of rate constant depends upon the order of

reaction. For zero order; unit

:- moles/L/s first order, unit :- s^{-1}

Rate constant becomes equal to rate of reaction for a zero order reaction.

Characteristic feature of rate and rate constant

The expression of rate 'r' in terms of change of concentration of a reactant or product depend on the way the chemical equation is formulated. For example, the combination of H_2 and I_2 is experimentally found to be a second order reaction. Hence, for two ways of writing the chemical equations

½ H_2 + ½ I_2 $\rightarrow$ HI

$$r = -\frac{1}{2}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[I_2]}{dt} = k[H_2][I_2] \qquad (2)$$

$H_2 + I_2 \rightarrow 2HI$

$$r' = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = k'[H_2][I_2] \qquad (3)$$

Since the rate at which a reactant is consumed doesn't depend upon the way the chemical equation is formulated.

Therefore, $2r = r'$ and $2k = k'$

Rate law and order of reaction

Consider a general reaction

$aA + bB \rightarrow cC + dD$

According to the law of mass action, rate of forward reaction is

Rate $\alpha [A]^a [B]^b$

According to the kinetic study, rate of such reaction is expressed as:-

$$\text{Rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \alpha [A]^{\alpha} [B]^{\beta}$$

or $\boxed{\text{Rate} = k[A]^{\alpha}[B]^{\beta}}$ (4)

where exponents may or may not be equal to the respective stoichiometric coefficient. Constant α, β may have an integer or fractional value.

The above expression for rate 'r' as a function of concentration at a fixed temperature is called **Rate Law**.

Characteristic features of rate law are:-

(i) It may not bear a simple relationship to the stoichiometric equation and always refer to the overall reaction.

(ii) It may not depend upon concentration of every reactant.

(iii) It may depend upon the concentration of species (Catalyst) which do not appear in the equation for the overall reaction.

(iv) Rate law cannot be predicted from the form of the stoichiometric equation for the overall reaction.

Hence, it must be determined experimentally.

Order of reaction

The constant 'α' is known as order of the reaction with respect to A, 'β' as order w.r.t B. as so on. The exponents α, β,… are also called partial orders. The sum of $\alpha+\beta$ is known as overall order of a reaction.

It is defined as **"The sum of the powers to which concentration terms are raised in the final rate equation is termed as the order of reaction."** It is an experimentally determined quantity.

If $\alpha + \beta = 1$: the reaction is said to be first order

$\alpha + \beta = 2$: the reaction is said to be second order.

The dependence of reaction rate on concentration helps in proposing the mechanism of reaction.

But, in certain cases order of reaction is meaningless. For example:-

(i) Consider reaction between H_2 and Br_2

$H_2 + Br_2 \rightarrow 2\,HBr$

The rate law for this reaction is found to be

$$\text{Rate} = \frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k^1[HBr][Br_2]} \qquad (5)$$

The order of reaction w.r.t. H_2 is 1 but it is not possible to assign order w.r.t. Br_2 and HBr.

(ii) reaction between $OC\ell^-$ and I^- ions in the presence of OH^- ions.

$$OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^- \qquad (6)$$

$$\text{Rate} = \frac{d[Cl^-]}{dt} = \frac{k[OCl^-][I^-]}{[OH^-]} \qquad (7)$$

Though OH^- doesn't appear in the overall reaction yet it appears in the denominator of rate law indicating that OH^- acts as inhibitor.

(iii) Iodination of acetone in the presence of H^+ ions

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI \qquad (8)$$

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]\,[H^+] \qquad (9)$$

This reaction doesn't involve H^+ ions in the overall reaction but it appears in the numerator of rate law indicating that H^+ ions act as catalyst and take part in the mechanism of the reaction. The order of reaction w.r.t. iodine is found to be zero.

Elementary Reaction and Molecularity

Most chemical reactions proceed through a series of elementary reactions. An **elementary reaction is the one which takes place in single step.**

The number of atoms, ions or molecules that are colliding with each other in an elementary step is referred to as the molecularity of that step. It is defined for elementary reactions and should not be used to describe overall reactions that consist of more than one elementary step. If a reaction involves three steps, each step will have different molecularity. e.g decomposition of N_2O_5 is a first order reaction but it proceeds through the following elementary steps.

		Molecularity
N_2O_5 ⇌	$NO_2 + NO_3$	1
$NO_2 + NO_3 \rightarrow$	$NO + NO_2 + O_2$	2
$NO + NO_3 \rightarrow$	$2NO_2$	2

How is molecularіy different from order of reaction?

Order of reaction	**Molecularіy**
(1) It is defined as sum of the powers to which concentration terms are raised in the final rate equation.	It refers to number of atoms or ions involved in each elementary step.
(2) It is an experimentally determined quantity.	It is a theoretically determined quantity.
(3) Partial order of reaction may be an integer or a fraction. But the overall order of reaction is either a whole number or a fraction.	Molecularity is always a whole number.
(4) Order of a reaction refers to overall reaction	Molecularity is defined only for elementary reaction.
(5) Order of a reaction can be changed by changing the physical parameters For eg:- decomposition of HI is a second order reaction but when this reaction is studied on the surface	Molecularity of a step cannot be changed as it refers to the mechanism of a reaction.

of gold it becomes a zero order reaction.

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

(Homogeneous reaction) (2^{nd} order)

$2HI(g) \xrightarrow{Au(s)} H_2(g) + I_2(g)$

(Heterogeneous reaction) (zero order)

(6) For complex reactions, slowest step is the rate determining step. As the overall rate of the reaction, cannot be faster than this step. Therefore number of molecules involved in this step is referred to as Order of reaction.

Molecularity of slowest step has no meaning.

The knowledge of order of reaction helps in proposing the mechanism of a reaction. For an **elementary reaction (i.e. reactions completed in single step) molecularity and order of reaction has the same value.**

For example:- decomposition of HI is an elementary reaction. Here both molecularity and order is 2.

Integrated Rate law:-

The variation of concentration of reactant with time can be determined by carrying out the integration of the differential rate law. We'll be deriving integrated rate equation for zero first and second order reactions.

Zero-Order reaction : Reactions in which rate of reaction is found to be independent of the concentration of reactant is termed as zero order reaction.

A zero order reaction is represented as:

$A \rightarrow B$

Rate of this reaction is:

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]^0$$

Let the initial concentration of reactant be 'a'. After time 't', the amount of product formed is 'x'. Rate of the reaction is given as

$$\text{Rate} = -\frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a)^0 = k \qquad (10)$$

$$\text{or } \frac{dx}{dt} = k \qquad (11)$$

$$\text{or } dx = kdt \qquad (12)$$

Integration of this equation within the limits

$$\int_{x=0}^{x} dx = \int_{t=0}^{t} kdt$$

(limit is always first assigned to independent variable and then the corresponding limit to dependent variable. Here, time is an independent parameter. At t = 0, amount of product formed, x = 0)

$$\boxed{x = kt} \qquad \text{or} \qquad \boxed{k = \frac{x}{t}} \qquad (13)$$

Equation (13) is known as integrated rate equation of zero order reaction.

The S.I. unit of k is moles/dm^3/s.

Characteristics of zero order reaction :-

1. Plot of x v/s t is a straight line passing through origin. Slope of the line gives the value of rate constant 'k' for a zero for a reaction (Fig.7)

2. **Half life of a zero order reaction:-** Half life of a reaction is the time at which initial concentration of reactant is reduced to half i.e. concentration of product is half the initial concentration of reactant.

$$\text{i.e. } x = \frac{a}{2} \qquad (14)$$

Putting eq. (14) in (13) we get

$$t_{½} = \frac{a}{2k} \qquad (15)$$

An interesting characteristic of a zero order reaction is that its half life is a function of initial concentration.

Examples of Zero Order Reaction

1. **Heterogeneous reactions:-** Reactions involving more than one phase are termed as heterogeneous reactions. All such reactions are found to be of zero order.

e.g. decomposition of HI on the surface of gold is found to be a zero order reaction.

$2HI(g) \xrightarrow{Au(s)} H_{2(g)} + I_{2(g)}$

2. **Photochemical reaction:-** All reactions induced by absorption of light have also been found to be of zero order.

e.g. $H_2 + Cl_2 \xrightarrow[\text{sunlight}]{h\upsilon} 2HCl$.

3. There are many reactions where order with respect to one of the reactants is zero.

e.g. enzyme catalysed reaction.

$\text{substrate} \xrightarrow{\text{enzyme}} \text{Product}$

$\text{Rate} = k\,[\text{enzyme}]^1\,[\text{substrate}]^0$

Such reactions are found to of first order with respect to enzyme and zero order w.r.t substrate.

First Order reactions.

Reactions for which rate is linearly proportional to the concentration of reactant are termed as first order reaction.

In general, a first order reaction is expressed as $A \rightarrow B$

Let the initial concentration of 'A' at time t = 0 be 'a'. After time 't' let the amount of product formed be 'x'. Therefore, the amount of A at time 't' is equal to 'a-x'.

Rate of this reaction is expressed as:-

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} \alpha [A]^1$$

$$\text{or Rate} = -\frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a-x)^1 \qquad (15)$$

Equation (15) is known as **differential rate equation of first order reaction.**

Equating last two terms of this equation

$$\frac{dx}{dt} = k(a-x) \qquad (16)$$

It can be rewritten as

$$\frac{dx}{(a-x)} = k\,dt \qquad (17)$$

Integrating the above equation within the limits

$$\int_{x=0}^{x=x} \frac{dx}{(a-x)} = \int_{t=0}^{t} k\,dt$$

we get

$$-\ln(a-x)\Big|_0^x = kt\Big|_0^t$$

$$\text{or } -\{\ln(a-x) - \ln a\} = kt$$

$$\text{or } \ln\frac{a}{(a-x)} = kt \qquad (18)$$

$$\text{or } \boxed{k = \frac{2.303}{t}\log\frac{a}{(a-x)}} \qquad (19)$$

Equation (19) is known as Integrated rate equation of first order reaction. The S.I unit of first order rate constant is s^{-1}.

Characteristics of first Order reactions

1. Plot of $\log\frac{a}{a-x}$ v/s t is a straight line passing through origin. Slope of this line gives the value of first order rate constant. (Fig.8)

2. When the initial concentration of reactant is not known, but its concentration at different time intervals is known. A graph of log $\frac{1}{(a-x)}$ v/s time is plotted (Fig.9) Slope of the graph gives the value of first order rate constant.

Intercept of the plot gives the value of log (1/a). **Knowing this value, initial concentration of reactant can be determined.**

3. When concentration of reactant at two time intervals is known. The value of rate constant can be obtained by integrating eq (17) within the limits as:

$$\int_{x=x_1}^{x=x_2} \frac{dx}{a-x} = \int_{t=t_1}^{t=t_2} k\,dt \qquad (20)$$

$$-\ln (a-x) \Big|_{x_1}^{x_2} = kt \Big|_{t_1}^{t_2}$$

$$\text{or } -\{\ln(a-x_2) - \ln(a-x_1)\} = k\,(t_2 - t_1)$$

$$\text{or } \ln \frac{(a-x_1)}{(a-x_2)} = k\,(t_2 - t_1)$$

$$\text{or } \boxed{k = \frac{2.303}{t_2 - t_1} \log \frac{(a-x_1)}{(a-x_2)}} \qquad (21)$$

where,

$a - x_1$ = Concentration of reactant at time $t_1 = C_1$

$a - x_2$ = Concentration of reactant at time $t_2 = C_2$

then,

$$\boxed{k = \frac{2.303}{t_2 - t_1} \log \frac{C_1}{C_2}} \qquad (22)$$

If the concentration at time 't' is known for a reaction with a given value of 'k' the concentration of reactant at any other time can also be determined by using this equation.

Half life of a first Order reaction.

Using eq. (19)

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

At $t = t_{½}$, $x = a/2$

Putting these values in eq. (19) we get

$$k = \frac{2.303}{t_{1/2}}\log\frac{a}{a-\frac{a}{2}}$$

$$\text{or } k = \frac{2.303}{t_{1/2}}\log 2$$

$$\text{or } \boxed{t_{½} = \frac{0.693}{k}} \qquad (23)$$

Half life of a first order reaction is independent of the concentration of reactant or product.

Examples of first Order reactions:-

A large number of reactions exhibiting first order kinetics are known.

e.g.:- **(i) All radioactive decay**

The decay of a radioactive isotope follows first order kinetics. Each nucleus of a particular radioactive isotope has a certain probability of breaking down in unit time. The number of nuclei (– dN) that decay in a unit time is directly proportional to the number of radioactive nuclei present in the system (Fig. 10).

$$\text{i.e. } -\frac{dN}{dt} \alpha N$$

$$\text{or } -\frac{dN}{dt} = \lambda N$$

where λ = proportionality constant called decay constant

$$\text{or } -\frac{dN}{N} = \lambda\, dt \qquad (24)$$

Equation (24) is a first order law and can be integrated to the form

$$\boxed{N = N_O e^{-\lambda t}} \qquad (25)$$

where N_0 = number of nuclei present at t = 0

N = number of nuclei at any time t.

Since the kinetics is a first order, the isotope's half life is given by eq. (23)

$$t_{½} = \frac{0.693}{\lambda}$$

In contrast to the rate constant of a chemical reaction the decay constant λ is completely independent of any external influence such as temperature or pressure. Some half lives and decay modes are given in Table (2)

Table 2 : Half life and decay mode

	n	^{12}N	^{14}C	^{238}U
Half life	15 min	0.01s	5730 yr	4.5×10^{9}yr
Decay mode	β^-	β^+	β^-	α

(ii) Decomposition of dinitrogen pentoxide

$$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

The reaction is studied by collecting volume of Oxygen at regular intervals of time.

Volume of gas collected $\propto$ Amount of N_2O_5 decomposed

i.e. $x \propto V_t$

Volume of gas collected at infinite time (V_∞) $\propto$ Amount of N_2O_5 initially taken

(which is done by heating the reaction vessel)

i.e. $a \propto V_\infty$

Substituting these values in the first order equation

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

$$\boxed{k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}} \qquad (26)$$

(iii) Acid hydrolysis of an ester

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

In this reaction, acetic acid is one of the product whose concentration can be determined by carrying out titration with NaOH solution. Since this is an acid catalysed reaction, the volume of NaOH solution is also used in the neutralization of the same.

Volume of NaOH used in the beginning $\propto$ Amount of acid present only as catalyst

i.e. at zero time (V_0) as no CH_3COOH is produced at t = 0

Volume of NaOH used at time t (V_t) $\propto$ Amount of acid present as catalyst + amount of CH_3COOH produced

$\Rightarrow$ Amount of acetic acid produced at any instant (x) $\propto$ $V_t - V_0$

Initial concentration of ester (a) $\propto$ Maximum amount of acetic acid produced

i.e. $a \propto V_\infty - V_0$

Substituting the value of ‘a ‘ and ‘ x ‘ in first order equation, we get.

$$\boxed{k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}} \qquad (27)$$

(iv) Inversion of cane sugar

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

Cane sugar glucose Fructose

The first order rate constant is determined by using equation

$$\boxed{k = \frac{2.303}{t}\log\frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}} \qquad (28)$$

where α_0, α_t and α_∞ are angle of rotation at the beginning, at time t and at the end of reaction respectively.

Second Order Reactions

In second order reactions, the rate of the reaction depends on two concentration terms. These concentration terms may refer to either the same species or two different species. Thus, two cases are possible :-

Case 1:- Rate law involves one type of species.

Such a reaction is represented as :-

$$\nu A \rightarrow B$$

rate law for above reaction is represented as :

$$\text{Rate} = \frac{-1}{\nu}\frac{d[A]}{dt} = \frac{d[B]}{dt} \alpha[A]^2 \qquad (29)$$

Let the initial concentration of reactant be 'a'. After time 't' let the amount of product formed be 'x' such that the amount of reactant left is 'a-x'.

Putting these values in eq (29), we get

$$\text{Rate} = \frac{-1}{\nu}\frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a-x)^2 \qquad (30)$$

Equation (30) is known as differential rate equation of a second order reaction.
Comparing last two terms of this equation, we get

$$\frac{dx}{dt} = k(a-x)^2$$

$$\text{or } \frac{dx}{(a-x)^2} = kdt \qquad (31)$$

Integrating eq(31) within the limits

$$\int_{X=0}^{X=X} \frac{dx}{(a-x)^2} = \int_{t=0}^{t} kdt$$

or $\frac{(a-x)^{-2+1}}{(-2+1)} \times (-1) \Big|_0^x = kt\Big|_0^t$

or $\frac{1}{(a-x)}\Big|_0^x = kt$

or $\frac{1}{(a-x)} - \frac{1}{a} = kt$

or $\frac{a-(a-x)}{a(a-x)} = kt$

or $\boxed{k = \frac{1}{t}\frac{x}{a(a-x)}}$ (32)

Equation (32) is known as Integrated rate equation for a second order reaction involving one type of species.

Case 2:- Rate law involves two different species.

Such a reaction is represented as :-

$\nu_1 A + \nu_2 B \rightarrow$ Products (P)

Rate law for above reaction is represented as :-

$$\text{Rate} = \frac{-1}{\nu_1}\frac{d[A]}{dt} = \frac{-1}{\nu_2}\frac{d[B]}{dt} = \frac{d[P]}{dt} \alpha [A]^1 [B]^1$$

Let the initial concentration of reactants 'a' and 'b' be a and b respectively. Let after time 't' the concentration of product formed be 'x' such that the concentration of reactants left is 'a–x' and 'b–x' respectively.

Putting these values in eq (33), we get.

$$\text{Rate} = \frac{-1}{\nu_1}\frac{d(a-x)}{dt} = \frac{-1}{\nu_2}\frac{d(b-x)}{dt} = \frac{dx}{dt} = k(a-x)(b-x) \quad (34)$$

This equation is known as differential rate equation for a second order reaction involving two different species.

Comparing last two terms of this equation, we get

$$\frac{dx}{dt} = k(a-x)(b-x)$$

$$\text{or } \frac{dx}{(a-x)(b-x)} = kdt \qquad (35)$$

Integrating the above equation within the limit we get

$$\int_{x=0}^{x} \frac{dx}{(a-x)(b-x)} = \int_{t=0}^{t} kdt$$

$$\text{or } \int_{x=0}^{x} \frac{1}{(a-b)}\left\{\frac{1}{(b-x)} - \frac{1}{(a-x)}\right\}dx = \int_{t=0}^{t} kdt$$

$$\text{or } \frac{\mathbf{1}}{(a-b)}\int_{\mathbf{0}}^{x} \frac{\mathbf{1}}{(b-x)}dx - \frac{\mathbf{1}}{(a-b)}\int_{\mathbf{0}}^{x} \frac{dx}{(a-x)} = \int_{\mathbf{0}}^{t} kdt$$

$$\text{or } \frac{(-)\mathbf{1}}{(a-b)}\ln(b-x)\Big|_{\mathbf{0}}^{x} + \frac{\mathbf{1}}{(a-b)}\ln(a-x)\Big|_{\mathbf{0}}^{x} = kt\Big|_{\mathbf{0}}^{t}$$

$$\frac{\mathbf{1}}{(a-b)}\left\{\ln(a-x) - \ln(b-x)\right\}_{\mathbf{0}}^{x} \Big| = kt\Big|_{\mathbf{0}}^{t}$$

$$\text{or } \frac{\mathbf{1}}{(a-b)}\ln\frac{(a-x)}{(b-x)}\Big|_{\mathbf{0}}^{x} = kt$$

$$\text{or } \frac{\mathbf{1}}{(a-b)}\left\{\ln\frac{(a-x)}{(b-x)} - \ln\frac{a}{b}\right\} = kt$$

$$\text{or } \frac{\mathbf{1}}{(a-b)}\ln\frac{b(a-x)}{a(b-x)} = kt$$

$$\text{or } \boxed{k = \frac{\mathbf{2.303}}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}} \qquad (36)$$

The equation (36) is known as **integrated rate equation of a second order reaction involving two different species. The unit of second order rate constant is L mol $^{-1}$ s^{-1}.**

Characteristics of a second order reaction:-

(i)The plot of $\frac{\mathbf{1}}{(a-x)}$ v/s t will be a straight line with slope equal to k (eq.32) (Fig. 11).

For reactions involving two different species, plot of ln{(a–x)/(b–x)} v/s t will be a straight line with slope giving the value of k (Fig. 12)

(ii) Half life of the reaction

when t = $t_{1/2}$ x = a/2,

$$t_{½} = \frac{\mathbf{1}}{k}\frac{a}{\mathbf{2}a\left(a-\frac{a}{\mathbf{2}}\right)} = \frac{\mathbf{1}}{k}\frac{\mathbf{2}a}{\mathbf{2}a^{2}}$$

or $$\boxed{t_{1/2} = \frac{1}{ka}} \qquad (37)$$

For the second order reactions involving one species or two species with $[A]=[B]$ and $v_1 = v_2 = 1$, half life is inversely proportional to the initial concentration.

(iii) **Condition under which a second order reaction behaves like a first order reaction.**

When one of reactant say 'A' is present in excess.

i.e. $[A] \square [B]$

or $a \square b$

then $a - b \approx a$

The concentration of product formed can not be more than the concentration of reactant present in smaller quantity. Therefore, when $a \square b$ it is also applicable that $a >> x$

Putting these approximations in eq (36). we get

$$k = \frac{\mathbf{2.303}}{ta}\log\frac{b.a}{a(b-x)}$$

Since 'A' is present in excess therefore its concentration 'a' practically remains constant during the reaction. Hence, the product of rate constant and concentration of 'A' is a constant i.e.

$$\boxed{k.a = k' = \frac{\mathbf{2.303}}{t}\log\frac{b}{(b-x)}} \qquad (38)$$

This expression is same as that of a first order reaction (eq 19).

Thus, whenever either of the reactant is present in excess, a second order reaction behaves like a first order reaction, such reactions are known as pseudo-first-order reactions.

Example of Pseudo- first-order reaction

Hydrolysis of an ester. Reaction involves two reacting species-an ester and water. But, the concentration of water (55.55 M) is very large in comparison to the concentration of an ester (~1M). This reaction is found to follow first order kinetics (eq 27).

Examples of second order reactions

(1) Saponification of an ester.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

(2) Reaction between persulphate and Iodide ions

$$S_2O_8^{2-} + \mathbf{2}I^- \rightarrow \mathbf{2}SO_4^{2-} + I_2$$

(3) Thermal dissociation of acetaldehyde follows second order kinetics over a certain range of temperature

$$\mathbf{2}CH_3CHO \rightarrow \mathbf{2}CH_4 + \mathbf{2}CO$$

Third Order Reactions:-

A few third order reactions are known, which can be represented as :-

$$\mathbf{2}A + B \rightarrow \text{products}$$

The differential rate law can be represented as:

$$\frac{-\mathbf{1}}{\mathbf{2}}\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[P]}{dt} = k[A]^2[B] \qquad (65)$$

Examples:-

Only 5 homogeneous gas reactions of third order are known in which one of the reactant is nitric oxide.

(i) $\mathbf{2}NO + Cl_2 \rightarrow \mathbf{2}NOCl$

(ii) $\mathbf{2}NO + Br_2 \rightarrow \mathbf{2}NOBr$

(iii) $\mathbf{2}NO + O_2 \rightarrow \mathbf{2}NO_2$

(iv) $\mathbf{2}NO + D_2 \rightarrow N_2O + D_2O$

(v) $2NO + H_2 \rightarrow N_2O + H_2O$

In aqueous solutions

(1) Oxidation of $FeSO_4$

(2) Reaction between Iodide and ferric ions.

$\mathbf{2}I^- + Fe^{3+} \rightarrow Products$

(3) Reduction of $FeCl_3$ with $SnCl_2$

$\mathbf{2}FeCl_3 + SnCl_2 \rightarrow \mathbf{2}FeCl_2 + SnCl_4$

The Question that arises in mind is " Why reactions having order higher than 2 are rare in nature?" We know that molecules in liquid/ gaseous phase are in a state of random motion. Collision among the molecules result in the formation of products. For elementary reactions with order 3 or more than that, the probability of 3 or more molecules with certain minimum energy colliding with each other with proper orientation is very less. For complex reaction, the slowest step is the rate determining step. For order of reaction to be 3 or more these molecules must approach and collide with each other with proper orientation. The probability of such a collision is very less. **Thus, these reactions are rare in nature.**

Expression for nth order reaction.

Consider a reaction

$$\nu A \rightarrow Products$$

The differential rate law of such a reaction is given as :-

$$\text{Rate} = \frac{-1}{\nu}\frac{d[A]}{dt} = \frac{d[P]}{dt} \alpha [A]^n \qquad (40)$$

Let the initial concentration of reactant be 'a'. Let after time 't', the concentration of product be 'x' such that the concentration of reactant left is 'a–x'. Then,

$$\text{Rate} = \frac{-1}{\nu}\frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a-x)^n \qquad (41)$$

Equating last two terms, we get,

$$\frac{dx}{dt} = k(a-x)^n$$

or $$\frac{dx}{(a-x)^n} = kdt$$

Integrating above equation within the limits

$$\int_{x=0}^{x} \frac{dx}{(a-x)^n} = \int_{t=0}^{t} kdt$$

or $$\int_{x=0}^{x} (a-x)^{-n}\, dx = \int_{0}^{t} kdt$$

or $$-\frac{(a-x)^{-n+1}}{(-n+1)} \Big|_0^x = kt \Big|_0^t$$

or $$\boxed{\frac{1}{(n-1)}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} = kt} \qquad (42)$$

This is a general expression of integrated rate law of a reaction involving one concentration term. This equation is not applicable for n = 1 i.e. reaction of first order.

Half life of nth Order reaction:-

At $t = t_{½}$; $x = a/2$

Putting this value of 'x' in eq (42), we get

$$kt_{1/2} = \frac{1}{(n-1)}\left\{\frac{1}{\left(a-\frac{a}{2}\right)^{n-1}} - \frac{1}{(a)^{n-1}}\right\}$$

$$= \frac{1}{(n-1)}\left\{\frac{1}{(a/2)^{n-1}} - \frac{1}{(a)^{n-1}}\right\}$$

$$= \frac{1}{(n-1)}\left\{\frac{2^{n-1}-1}{a^{n-1}}\right\}$$

$$\text{or } \boxed{t_{1/2} = \frac{1}{k(n-1)}\left\{\frac{2^{n-1}-1}{a^{n-1}}\right\}} \qquad (43)$$

Fractional Order reaction:-

It is observed when order of reaction with respect to one of the reactant is non-integral. **Examples:-** (i) The conversion of para hydrogen to ortho hydrogen at high temperature

$$\text{Rate} = \frac{dx}{dt} = k\left(P_{H_2}\right)^{3/2}$$

(ii) Thermal decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO$$

$$\text{Rate} = \frac{-d[CH_3CHO]}{dt} = k[CH_3CHO]^{3/2}$$

Negative Order reaction:-

Sometimes the rate of reaction decreases as the concentration of one of the constituents is increased. It is generally observed when the reaction involves complicated reaction mechanism. For such reactions, **the partial order becomes negative. But overall order of reaction has positive integral value.**

Example:- During transformation of Ozone into oxygen

$$2O_3 \rightarrow 3O_2$$

$$\frac{-1}{2}\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]} = k[O_3]^2[O_2]^{-1}$$

Order of reaction w.r.t. O_3 is 2

Order of reaction w.r.t. O_2 is –1

Determination of Order of reaction :-

If the data on variation in concentration with time is available, then any one of the following methods can be employed for the determination of order of reaction and its rate constant.

Integration method :- In this method, the data is substituted into various integrated rate equations. The equation which gives almost a constant value of rate constant refers to the order of the reaction. (Table 3)

Table-3 Order of fitting Integrated Rate Equations.

Kinetics	Equations to be fitted
(i) Zero Order	$k = \frac{x}{t}$
(ii) First Order	$k = \frac{2.303}{t} \log\frac{a}{a(a-x)}$
(iii) Second Order with equal concentration of reactants	$k = \frac{1}{t}\frac{x}{a(a-x)}$
(iv) Second Order with unequal concentration of reactants	$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$
(v) Third Order with equal concentration of reactants	$k = \frac{1}{2t}\left\{\frac{x(2a-x)}{a^2(a-x)^2}\right\}$
(vi) Third order with equal concentration of two of the reactants	

$$= \frac{1}{t(2b-a)^2}\left\{\frac{2x(2b-a)}{a\ (a-2x)} + \ln\left\{\frac{b(a-2x)}{a(b-x)}\right\}\right\}$$

Graphical method :- In this method, data points are plotted according to the different integrated rate equations. The equation which gives a straight line plot refers to the order of the reaction. The slope of the plot gives the value of rate constant. (Table 4)

Table 4: Order of Plotting the Straight-Line Plot

Kinetics	Straight line Plot.	slope of the plot
(1) Zero Order	x v/s t	k
(2) First Order	ln 1/(a–x) v/s t	k/2.303
(3) Second order with equal concentration reactants.	$\frac{1}{a-x}$ v/s t	k
(4) Second Order with unequal concentration of reactants	$\log\frac{(a-x)}{(b-x)}$ v/s t	$\frac{k(a-b)}{2.303}$

The value of 'n' can also be determined graphically using eq(43) for half life of nth order reaction. Taking logarithm on both sides, we get

$$\log\left(\frac{t_{1/2}}{s}\right) = \log\left(\frac{2^{n-1}-1}{k'n(n-1)}\right) + (1-n)\log\left(\frac{a}{mol\,dm^{-3}}\right) \qquad (44)$$

A plot of $\log t_{1/2}/s$ v/s $\log a/mol\,dm^{-3}$ will have a slope of (1–n) from where the value of 'n' can be determined.

In equation (43) we can not take the logarithm of dimension. Therefore, term within the logarithm should be dimensionless. Thus, the value of ' $t_{½}$' and 'a' is determined w.r.t. some standard state. As a result, the value of rate constant also changes from k to k′.

It is not necessary to determine fractional time with different initial concentration. In single run, the concentration at the end of one time interval becomes initial concentration for the next time interval and so on.

The equation derived above is equally applicable for fraction other than half.

i.e. $t_{1/y} \propto \frac{1}{a^{n-1}}$

(3) Half life method :- This method is applicable to those reactions where rate law depends upon the concentration of one reactant only.

According to general expression for half life of nth order reaction

$$t_{1/2} = \frac{1}{k(n-1)} \frac{2^{n-1}-1}{a^{n-1}} \qquad (71)$$

If the reaction is studied with two different concentrations. then

$$(t_{½})_1 \ \alpha \frac{\mathbf{1}}{a_{\mathbf{1}}^{\mathbf{n-1}}}$$

$$(t_{½})_2 \ \alpha \frac{\mathbf{1}}{a_{\mathbf{2}}^{\mathbf{n-1}}}$$

or $$\frac{(t½)_{\mathbf{1}}}{(t½)_{\mathbf{2}}} = \left(\frac{a_{\mathbf{2}}}{a_{\mathbf{1}}}\right)^{\mathbf{n-1}}$$

Taking logarithm on both side of eq^n we get

$$\log \frac{(t_{½})_1}{(t_{½})_2} = (n-1)\log \frac{a_2}{a_1}$$

or $$\boxed{n = \frac{\log(t_{1/2})_2 + \log(t_{1/2})_2}{\log a_2 - \log a_1} + 1} \qquad (45)$$

Differential method :- This method is also known as Van't Hoff method. It is based upon the fact that the rate of a reaction of the nth order is proportional to the nth power of its concentration (C)

Rate of reaction $$\left(-\frac{dC}{dt}\right) \propto C^n$$

$$r = -\frac{dC}{dt} = kC^n$$

where C is the concentration at the instant of time 't' when the rate is 'r'.

For two different concentrations

$r_1 = kC_1^n$

$r_2 = kC_2^n$

$$\therefore \frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n$$

Taking logarithm on both sides

$$\log \frac{r_1}{r_2} = n \log \frac{C_1}{C_2}$$

or $$n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2}$$

$\therefore$ To calculate the value of n, we need to know the rates r_1 and r_2 or $\left(\frac{-dC_1}{dt} \text{ and } \frac{-dC_2}{dt}\right)$ at two different concentration C_1 and C_2 respectively.

This may be determined by either of the two methods :-

(i) The change in concentration (ΔC) in an appreciable interval of time (Δt) is measured. The value $\Delta C/\Delta t$ is approximated to dC/dt at the mean value of C in the interval considered. At two different intervals during the course of reaction the values of $(-dC_1/dt)$ and $(-dC_2/dt)$ are computed at concentrations C_1 and C_2 respectively (Fig. 13).

(ii) The concentration of reactant is plotted against time. Rate at any concentration can be determined from the slope of the tangent drawn at that concentration.

Ostwald Isolation method: This method can be used for the determination of order of those reactions which involve two or more reactants. It is based upon the fact that the order of reaction is independent of that reactant which is present in excess. The kinetic study is carried out by taking all reactant except one in excess and the order with respect to species present in small amount is determined. Let it be α. Subsequently the order w.r.t. each reactant species is determined and is represented as β, γ, δ …. and so on. The overall order of the reaction is the sum of the order found with respect to the different reactant one by one by isolation.

For a reaction involving three reactant A, B and C, let the order w.r.t. each be α, β and γ respectively. Then the overall order of reaction $n = \alpha + \beta + \gamma$

Complicating Factors in Reaction Kinetics

Only a few reactions are simple or straight i.e. purely first, second or third order reactions. In actual practice, complications arise quite often because of certain reactions which occur simultaneously along with the main reaction. These reactions are:-

(i) Reversible or opposing reactions

(ii) Consecutive reactions

(iii) Parallel or side reactions

(iv) Surface reactions

Reversible reactions:- The reactions in which products of the chemical change combine together to give back the original reactants are called **reversible or opposed reactions.** At the start, the rate of forward reaction is very large and it decreases as the concentration of reactants decrease with time. On the other hand, initially the rate of backward reaction is small and it increases as the concentration of products increases with time. A stage is reached where the rate of forward reaction becomes equal to the backward reaction and no net change is observed. This state of the system is known as **equilibrium state. Thus. a reversible reaction can never attain the state of completion.**

A reversible reaction can be classified on the basis of order of forward and backward reaction :-

(a) First Order Opposed by First Order

Such a reaction is represented as:-

(1)

where k_f and k_b are the reaction rates of forward and backward reactions respectively.

If the rate constant for the backward reaction (k_b) is very small as compared to that of forward reaction (k_f), the former (k_b) can be neglected in comparison to the latter. However, if forward and backward reactions take place at comparable rates, the rate equation has to be modified.

Let ‘a’ be the initial concentration of A and ‘x’ be the decrease in the concentration of A in time ‘t’ then.

[A] = a–x

[B] = x

Rate of forward reaction = $k_f(a–x)$

Rate of backward reaction = $k_b x$

$\therefore$ Net rate of reaction in forward direction

$$\frac{dx}{dt} = k_f(a–x) – k_b x \qquad (2)$$

At equilibrium, rate of forward reaction is equal to the backward reaction

$$k_f(a–x_e) = k_b x_e \qquad (3)$$

where x_e = concentration of product formed at equilibrium.

Substituting the value of k_b from eq (3) in eq(2) we get,

$$\frac{dx}{dt} = k_f(a–x) – \frac{k_f\left(a – x_e\right)x}{x_e}$$

$$= k_f\left\{\frac{ax_e – ax}{x_e}\right\}$$

$$= \frac{k_f a\left(x_e – x\right)}{x_e}$$

$$\text{or } \frac{x_e}{\left(x_e – x\right)}dx = k_f\, a\, dt \qquad (4)$$

Integrating this equation, we get

$$–x_e \ln (x_e–x) = k_f\, at + I \qquad (5)$$

where I = constant of integration

when t = 0, x = O

$$\therefore I = –x_e \ln x_e \qquad (6)$$

Substituting this value of I in eq (5), we get

$$– x_e \ln (x_e–x) = k_f\, at – x_e \ln x_e$$

On rearrangement we have

$$\boxed{k_f = \frac{2.303 x_e}{at} \log \frac{x_e}{x_e - x}} \qquad (7)$$

Thus, knowing the value of a and x_e, the rate constant k_f for the forward reaction can be evaluated.

From eq (3)

$k_f a - k_f x_e = k_b x_e$

or $k_f a = x_e(k_b + k_f)$

$$\therefore\ k_b + k_f = \frac{k_f a}{x_e}$$

$$\boxed{k_f + k_b = \frac{2.303}{t} \log \frac{x_e}{x_e - x}} \qquad (8)$$

Thus, knowing k_f, x_e, x and t, k_b can be calculated.

similarly, expression can be obtained when

(i) A first order is opposed by a reaction of the second order.

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B + C$$

(ii) A second order reaction is opposed by a reaction of first order.

$$\mathbf{A + B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$$

(iii) A second order reaction is opposed by a reaction of second order.

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

Examples of Reversible reactions:-

(i) **Conversion of ammonium thiocyanate into urea**

$$NH_4CNO \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CO(NH_2)_2$$

(ii) **Hydrolysis of ethyl acetate**

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

(iii) **Formation of ammonia**

$$N_2 + 3H_2 \rightarrow 2NH_3$$

(iv) **Formation of Hydrogen Iodide**

$$H_2 + I_2 \rightarrow 2HI$$

Consecutive Reactions:- The reactions which proceed from reactants to final product through one or more intermediates stages. The overall reaction is a result of several consecutive steps. In such reactions the products obtained in one step react with each other or with original reactants to from new products. This reaction may be represented as:-

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Each step has a characteristic rate constant and the slowest step is the rate determining step. But, when two reactions have comparable rate the overall reaction rate becomes complicated. The overall rate of the reaction depends upon the magnitude of the two rate constants $k_1$and k_2.

The differential rate expression is given as:-

$$-\frac{d[A]}{dt} = k_1[A]$$

$$-\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

The variation in concentration of different species during the course of reaction is shown in Fig.14. The concentration of reactant A decreases and that of C increases during the reaction. The concentration of B initially increases but when its concentration becomes appreciable it gets converted into product ‘C’. Therefore, concentration of B starts decreasing.

Example:-

(1) **Reduction of NO by H_2.**

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

It has been found to be a third order reaction. It proceeds through stages.

$$2NO + H_2 \rightarrow N_2 + H_2O_2 \text{ (slow)}$$

$$H_2O_2 + H_2 \rightarrow 2H_2O \text{ (fast)}$$

slowest step is the rate determining step

$$\therefore \frac{dx}{dt} = k\,[NO]^2\,[H_2]$$

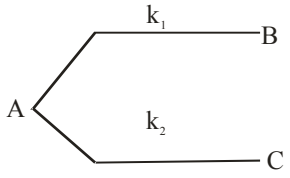
(ii) Decomposition of ethylene oxide:-

$$(CH_2)_2\,O \xrightarrow{k_1} CH_3CHO$$

$$CH_3CHO \xrightarrow{k_2} CH_4 + CO$$

(3) Parallel or competing or side reactions:-

The reactions in which a substance reacts or decomposes in more than one way are called Parallel reactions. Such reactions give rise to more than one independent product; The reaction giving large amount of product is called **main reaction** while the other giving smaller amount of the product is called **side reaction** or **parallel reaction.**



If in the above reaction $k_1 >> k_2$ then

$A \rightarrow B$ is main reaction

$A \rightarrow C$ side reaction

Let both the reactions be of first order and concentration of A is [A] at time 't'

$$r_1 = \frac{-d[A]}{dt} = k_1 [A]$$

$$r_2 = \frac{-d[A]}{dt} = k_2 [A]$$

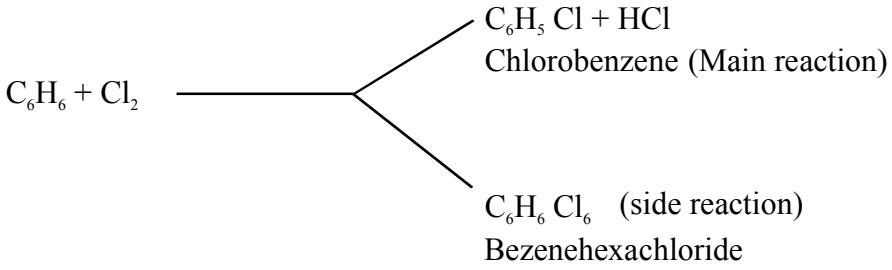
Total rate = $r_1 + r_2$

$= k_1 [A] + k_2 [A]$

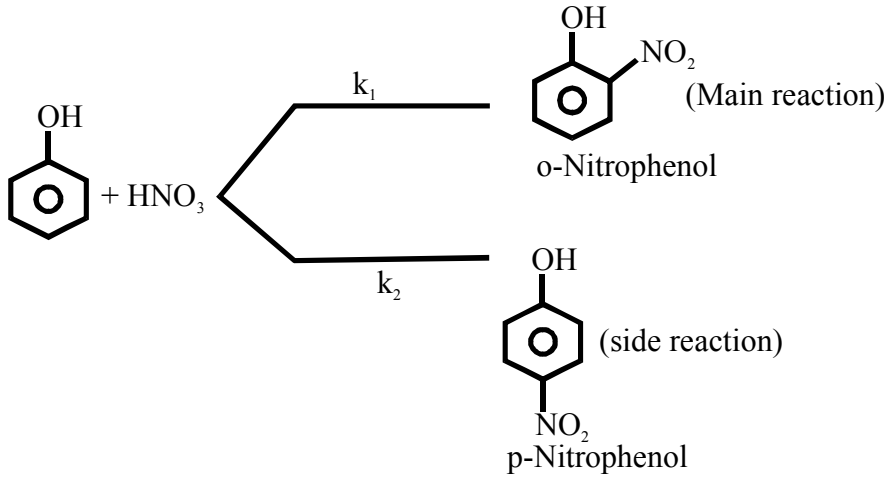
$= (k_1 + k_2) [A]$

Examples:-

(i) Chlorination of benzene



(ii) Nitration of phenol



If alcoholic KOH is used, ethylene is the main product, and if aq. KOH is used ethyl alcohol is main product

(4) Surface reactions:-

Gaseous reactions which occur on the walls of the container which acts as a solid surface are called surface reactions. When the surface is sparsely covered then at high temperature, the rate of reaction depends upon the number of molecules colliding per unit time i.e. on the pressure of the gas. It can written as

$$\frac{dx}{dt} = kP$$

This is the equation of first order and hence all such reactions are of first order.

Example: Decomposition of phosphine on the surface of glass.

But when the surface is fully covered, the rate of reaction is independent of pressure and follows zero order kinetics.

Stationary state:-

When a reaction is studied under the conditions of constant temperature and volume in a closed reaction vessel, it is said to be a **static system;** The various rate equations that have been derived so far refer to such systems only.

But, in large number of industrial reactions, reactants are continuously supplied in and products are withdrawn. Therefore, a state of equilibrium cannot be attained. Such systems are called **flow system.** If the inflow of reactants is continued at a constant rate then after some time the concentration of different components become constant with time. The system is then said to be in **steady state.** This state depends upon the flow rate and the rate constant of the system. **When a steady state is attained the system is not in an equilibrium state but is said to be in a Stationary state.**

Steady state approximation:-

For a reaction involving an intermediate during the conversion of reactants into products. the concentration of intermediate practically remains constant. This is known as steady state approximation. (S.S.A.)

Example:- Consider a reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

'B' is an intermediate during conversion of reactant 'A' into product 'C'

Here $\frac{d[B]}{dt} = k_1 [A] - k_2 [B]$

According to S.S.A

$$\frac{d[B]}{dt} = 0$$

$$\Rightarrow k_1[A] - k_2[B] = 0$$

The use of this approximation helps in simplifying the kinetics of a reaction and in deriving the differential rate expression from the proposed reaction mechanism of a given reaction.

Simple Reaction Mechanism:-

Most of the reactions fall into the following, four categories of simple reaction mechanism:-

Type 1 :- First step is rate determining slow step and is followed by rapid subsequent reaction.

Type 2:- First step is rapid equilibrium which produces an intermediate which reacts slowly in rate determining step.

Type 3:- Reaction involving more than two elementary steps with at least one slow step.

Type 4:- Reactions involving more than one step with comparable rate constants (whether the steps are slow or fast is not known).

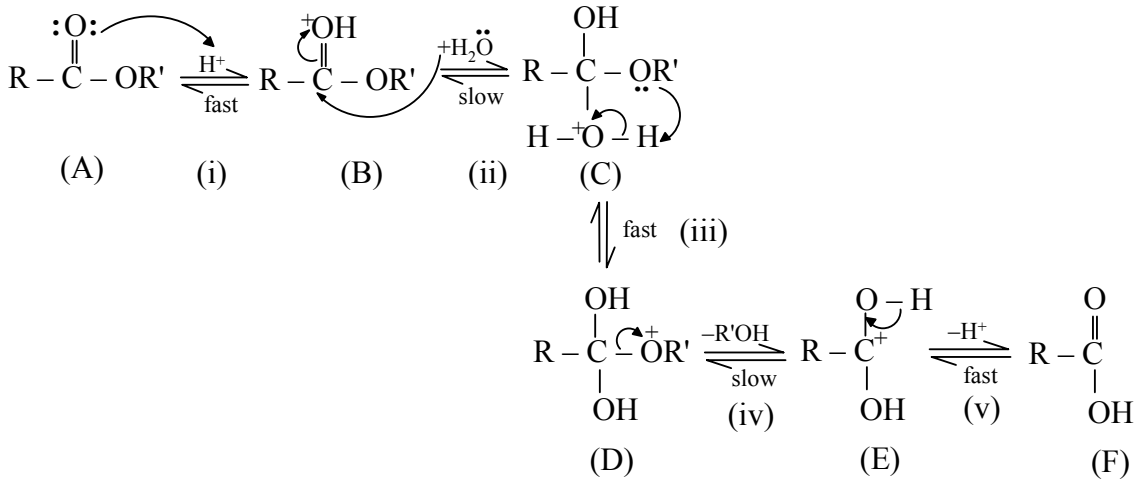
Example:- I Acid Hydrolysis of an ester

$$R - \overset{O}{\overset{\|}{C}} - OR' + H_2O \xrightarrow{H^+} R' - \overset{O}{\overset{\|}{C}} - OH + R'OH$$

The reaction is experimentally found to be a first order reaction depending upon the concentration of ester only. The differential rate equation is written as

$$\frac{d\left[R - \overset{O}{\overset{\|}{C}} - OH\right]}{dt} = k\left[R - \overset{O}{\overset{\|}{C}} - OR'\right] \qquad (1)$$

The proposed mechanism is



Step (ii) and (iv) are slow steps as these involve making and breaking of bond. Step (iv) is slower than step (ii) that involves proton transfer

$\therefore$ rate = k_4 [D] = k_4 (K_3 [C]) = k_4 K_3 (K_2 [B] [H_2O]) (2)

= k_4 K_3 K_2 (K_1 [A] [H^+] [H_2O])

i.e. rate = k′ [A] [H^+] [H_2O]

or r = k′ [ester] [H^+] [H_2O] (3)

where, K_1, K_2 and K_3 are equilibrium constant of step (i) (ii) & (iii) respectively

and k_4 K_3 K_2 K_1 = constant = k′

Since [H_2O] is present in excess and [H^+] remains constant throughout the reaction therefore,

$\boxed{r = k[ester]}$ (4)

where k = k′ [H^+] [H_2O]

Equation (1) and (4) are similar indicating that the proposed mechanism satisfies the observed rate law. **This doesn't mean that the reaction follows this mechanism only. Instead this is the most probable path. The reaction may proceed via any other path as well. This mechanism is of Type 3.**

Example II : Decomposition of gaseous N_2O_5

The reaction is

$2N_2O_5 \rightarrow 4NO_2 + O_2$

The rate law is found to be

$$\frac{d[O_2]}{dt} = k\,[N_2O_5] \qquad (5)$$

The proposed mechanism is :-

(i) $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

(ii) $NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$

(iii) $NO_3 + NO \xrightarrow{k_3} 2\,NO_2$

From step (ii), rate of formation of O_2 is

$$\frac{d[O_2]}{dt} = k_2\,[NO_3]\,[NO_2] \qquad (6)$$

NO and NO_3 are intermediates formed during the reaction. Therefore, we can apply steady state approximation to these species.

$$\frac{d[NO]}{dt} = 0 = k_2\,[NO_3]\,[NO_2] - k_3[NO_3]\,[NO] \qquad (7)$$

$$\frac{d[NO_3]}{dt} = 0 = k_1\,[N_2O_5] - k_{-1}\,[NO_2]\,[NO_3]$$

$$-k_2\,[NO_3]\,[NO_2] - k_3\,[NO_3]\,[NO] \qquad (8)$$

Eq (7) gives,

$$[NO] = \frac{k_2}{k_3}\,[NO_2]$$

From eq. (8) we have,

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_3[NO]} \qquad (9)$$

Substituting [NO] in eq. (9) get

$$[NO_3] = \frac{k_1[N_2O_5]}{(k_{-1} + 2k_2)[NO_2]} \qquad (10)$$

Putting eq.(10) in (6) we get

$$\frac{d[O_2]}{dt} = k_2 \left(\frac{k_1[N_2O_5]}{(k_{-1} + 2k_2)[NO_2]} \right) [NO_2]$$

$$= \frac{k_2 k_1}{k_{-1} + 2k_2} [N_2O_5]$$

$$\text{or } \boxed{\frac{d[O_2]}{dt} = k[N_2O_5]} \qquad (11)$$

which is the desired rate law Eq.(11) is same as eq.(5). The reaction mechanism is of Type 4.

If the theoretical value of rate constant is found to be in agreement with the observed data, the reaction is supposed to be following the proposed mechanism. This doesn't mean that the reaction can proceed through this path only. There can be some other mechanism as well with which the experimental rate constant is in agreement with.

Theories of Reaction Rates:-

The two important theories to explain the rates of different reactions are:-

(i) Collision Theory

(ii) Transition state theory/ absolute reaction rate theory.

Collision Theory:-

This theory is based upon kinetic theory of gases. Molecules are continuously moving and hence colliding with each other. The reaction can be unimolecular or bimolecular. Two different hypothesis have been proposed for these reactions. Unimolecular reactions are studied using **Lindemann Hypothesis.**

Collision Theory for Unimolecular Reactions (Lindemann time lag theory):-

According to this theory, the molecules acquire activation energy through collision with other molecules, as a result some molecules are activated. The activated molecules do not

decompose into products immediately but remain in activated form for a finite period i.e. there exist a time lag between activation and reaction.

It can be represented as:-

(i) Activation of the molecules of the reactant through bimolecular collision

$$A + A \xrightarrow{k_1} A^* + A$$

where A = Normal ordinary molecules

A^* = activated molecule which possess sufficient energy to pass into products.

(ii) Deactivation of some of the activated complex through collision with ordinary molecule during time lag.

$$A^* \xrightarrow{k_2} A + A$$

The decomposition of remaining activated molecules into products.

$$A^* \xrightarrow{k_3} \text{Products}$$

Using steady state approximation, rate of such a reaction is given as :

$$\frac{-d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} \qquad (1)$$

Case (i) When concentration of A is very high

$$k_2[A] >> k_3$$

Then,
$$\frac{-d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2 [A]}$$

$$= \frac{k_1 k_3}{k_2} [A]$$

$$= k\,[A]$$

where $k = \frac{k_1 k_3}{k_2}$

This rate equation indicates that the reaction follows first order kinetics.

Case (ii) When concentration of A is very low.

$$k_2[A] << k_3$$

then $$\frac{-d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_3} = k_1 [A]^2$$

i.e. the reaction follows second order kinetics.

Collision Theory for Bimolecular Reactions:-

A chemical reaction takes place only by collision between the reacting molecules. But not all collisions are effective. In actual practice, rate of the reaction is much smaller than the number of collisions between the reactant molecules. In order to overcome this discrepancy it is assumed that molecules are activated and only those molecules possessing energy greater than or equal to the threshold energy are able to form the product.

The reaction rate constant (k) depends upon the number of effective collisions per cc per second.

i.e. $k = zf$ (2)

where z = number of molecules per cc taking part in the collision

f = fraction of molecules that are activated

According to Kinetic theory of gases, fraction of molecules possessing energy greater than a particular value is given as

$$f = \frac{\Delta N}{N} = e^{-Ea/RT} \quad (3)$$

Using (1) & (2), we have

$$\boxed{k = Ze^{-E_a/RT}} \quad (4)$$

Using this equation, rate constants of various gaseous bimolecular reactions were calculated. For simple elementary reactions like decomposition of HI, the theoretical and experimental values were found to be in good agreement. For other reactions, the theoretical value was found to greater than the observed value. **To account for relatively smaller value of rate constants, collision theory was modified.**

According to modified theory, the essential requirements for a reaction to occur are :

(i) collision between the reactant molecules

(ii) activation of molecules i.e. must possess sufficient kinetic energy to cause a reaction.

(iii) proper orientation at the time of collision i.e. direct contact between the atom involved in the forming and breaking of bonds.

For a reaction,

$A + B \rightarrow C + D$

$k = f\, p\, z$ (5)

where p = probable fraction of collision with proper orientation. **This probability factor is a measure of discrepancy between simple collision theory and experimental results.**

Using eq. (3) & (4) we have,

$$\boxed{k = z\, p\, \bar{e}^{E_a/RT}} \quad (6)$$

Value of p varies between 1 to 10^{-9}

when p = 1, reaction obeys collision theory.

Limitations of collision theory:- Though it is logical and correct but still

(i) is applicable to simple gaseous reactions only.

(ii) For complex reactions, the experimental rate constants are quite different from the calculated value.

(iii) It is supposed that only the kinetic energy of the colliding molecules contribute to the energy required for passing the energy barrier. There is no justification for ignoring other forms of energy associated with moving molecules i.e rotational and vibrational energies.

(iv) It doesn't talk about how a simple collision result in the breaking up of old bonds and formation of new bonds resulting in the product formation.

Transition State Theory:-

This theory proposed by Henry Erying 1935 is also known as **absolute reaction rate theory because with its help, it is possible to obtain the absolute value of rate**

constant The drawbacks of earlier theory do not appear in this modern theory. It has made an attempt to treat the reaction rates from thermodynamic considerations.

According to this theory, "A simple collision between reactant molecules doesn't cause a reaction. During the collision, reactant molecules form an activated complex which decomposes to give product. This activated complex inspite of its transitory existence is treated as a molecule. It always exist in equilibrium with the reactants such that laws of thermodynamics can be applied to it.

The transition theory can be summarized as:-

(a) The fast approaching reactant molecules are slowed down due to repulsion between their electronic clouds. In the process kinetic energy gets converted into potential energy.

(b) As the molecules come close, interpenetration of their electronic clouds occur which allows the rearrangement of valence electrons.

(c) A partial bond is formed between reactant molecules leading to the formation of an activated complex. The energy of activated complex is higher than that of reactants or products.

(d) An activated complex decomposes to form product.

(e) The rate of reaction depends upon

(i) the concentration of activated complex formed

(ii) the rate at which activated complex decomposes.

For reaction,

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AB]^{\#} \xrightarrow{k_2} \text{Products}$$

activated complex.

Rate of reaction = (concentration of activated complex) × (frequency of decomposition of activated complex).

$$\text{i.e Rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = [AB^{\#}]\, \nu = K^{\#}_{eq.}\, [A]\, [B]\, \nu \qquad (7)$$

Also,

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{-d[B]}{dt} = k_2\,[A]\,[B] \qquad (8)$$

$\Rightarrow k_2\,[A]\,[B] = K_{eq}^{\#}\,[A]\,[B]\,\nu.$

$$\text{or } k_2 = K_{eq}^{\#}\,\nu \qquad (9)$$

where $K_{eq}^{\#}$ is the equilibrium constant for the formation of activated complex. Since activated complex is an unstable species and is held together by loose bonds, the vibration of low frequency will decompose the activated complex. The average energy of such a vibrational degree of freedom is given by kT.

According to Planck's equation, energy of vibration is given as:-

$E = h\nu$

$$\text{or } \nu = \frac{E}{h} = \frac{kT}{h}\left(\text{but } k = \frac{R}{N}\right) \therefore \nu = \frac{RT}{Nh} \qquad (10)$$

where R = Gas constant, T = Absolute temperature, N = Avogadro Number, h = Planck's constant

Using eq. (8) and (9) we get

$$\boxed{k_2 = \frac{RT}{Nh}K_{eq}^{\circ\#}} \qquad (11)$$

Equation (10) is known as Mathematical statement of transition state theory

We know $\Delta \overset{o}{G}^{\#} = -RT \ln K_{eq}^{0\#}$

$$\Rightarrow K_{eq}^{0\#} = e^{-\Delta G^{o\#}/RT} \qquad (13)$$

Where $\Delta \overset{o}{G}^{\#}$ = Change in standard free energy in going from reactants to activated complex

Also $\Delta \overset{o}{G}^{\#} = \Delta \overset{o}{H}^{\#} - T\,\Delta \overset{o}{S}^{\#}$

$$\Rightarrow K_{eq}^{0\#} = e^{(-\Delta H^{o\#} - T\Delta S^{o\#})/RT} \qquad (12)$$

The constants $K_{eq}^{\#}$ and $K_{eq}^{0\#}$ are related to each other through the expression.

$$K_{eq}^{0\#} = K_{eq}^{\#} c^0$$

Where c^0 = unit concentration i.e. 1 mol / dm^3

Using eq.(10) and (12) we get

$$\boxed{k_2 = \frac{RT}{c^0 Nh} e^{-\Delta H^{\#}/RT} e^{\Delta S^{\#}/R}} \qquad (14)$$

These equations indicate that at a particular temperature, greater is the value of free energy of activation for a reaction, the slower will be the reaction.

Advantages of Transition State Theory:

(1) It is not restricted to bimolecular processes. It is also applicable to unimolecular and trimolecular reaction.

(2) It can be applied to reactions in solution as well.

From first law of thermodynamic

$$\Delta H^{\neq} = \Delta U^{\#} + P\Delta V^{\#} \qquad (15)$$

where $\Delta U^{\#}$ = change in internal energy when the reactants pass from initial state to activated state.

Using Arrhenius equation and transition state theory

$$E_a = RT + \Delta U^{\#} \qquad (16)$$

From eq. (15) and (16)

$$E_a = \Delta H^{\#} + RT - P\Delta V^{\#} \qquad (17)$$

For Ideal gas, $P\Delta V^{\#} = \Delta n^{\#} RT$ (18)

$$\therefore E_a = \Delta H^{\#} + RT - \Delta n^{\#} RT \qquad (19)$$

where $\Delta V^{\#}$ = Change in volume when the reactants pass from initial state to activated state. $\Delta n^{\#}$ = Change in the number of moles in passing from initial state to activated state.

For Unimolecular reactions:- There is no change in number of moles (or molecules) as the activated complex is formed

$\therefore \Delta n^{\#} = 0 \; ; \Delta V^{\#} = 0$

Eq.(19) becomes

$E_a = \Delta H^{\#} + RT$

or $\Delta H^{\#} = E_a - RT$ (20)

Using eq.(14) and (20) we get

$$k = \frac{RT}{c^{\circ} Nh} e^{-Ea/RT} e^{1} e^{\Delta S/R}$$

For a bimolecular reaction

$\Delta n^{\#} = -1$

$\therefore E_a = \Delta H^{\#} + 2RT$ (21)

$$\Rightarrow k = \frac{RT}{c^{0} Nh} e^{-(Ea - 2RT)/RT} e^{\Delta S^{\#}/R}$$

$$\boxed{k = \frac{RT}{c^{0} Nh} e^{2} e^{-E_a/RT} e^{\Delta S^{\#}/R}} \quad (22)$$

It has been found that the difference between $\Delta H^{\#}$ and E_a is small. For unimolecular reactions in gaseous phase and reactions in solution

$\Delta H^{\#} = E_a$

In other cases involving gases, an additional term $\Delta n^{\#} RT$ has been included.

For most system, eq(13) can also be written as

$$k = \frac{RT}{c^{0} Nh} e^{-Ea/RT} e^{\Delta S^{\#}/R} \quad (23)$$

Comparison with Arrhenius equation

Equation (23) resembles the Arrhenius equation which is

$k = A\, e^{-Ea/RT}$

Comparison between the two shows that

$$A = \frac{RT}{Nhc^0} e^{\Delta S^{\#}/R}$$

i.e. A is a function of entropy of activation. The value of $\Delta S^{\#}$ may by positive or negative.

The concept of entropy of activation is very useful for qualitative purposes. A positive value of $\Delta S^{\#}$ indicates that the entropy of activated complex is more than that of reactants:

A negative value of $\Delta S^{\#}$ indicates the entropy of activated complex is less than that of reactants i.e. activated complex is more ordered than the reactants. Generally the formation of activated complex is associated with a decrease in entropy.

Comparison with Collision Theory:-

From Collision theory

$$k = pz\, e^{-Ea/RT} \qquad (5)$$

From transition state theory

$$k = \frac{RT}{c^0 Nh}\; e^{-\Delta H^{\#}/RT}\; e^{\Delta S^{\#}/R}$$

$$\text{or } k = \frac{RT}{c^0 Nh}\; e^{-E_a/RT}\; e^{\Delta S^{\#}/R} \qquad (20)$$

Comparing both equations, we have

$$p\, Z\, e^{-E_a/RT} = \frac{RT}{c^0 Nh}\; e^{-E_a/RT}\; e^{\Delta S\#/R}$$

$$\Rightarrow \boxed{p = \frac{RT}{c^0 NhZ} e^{\Delta S\#/R}} \qquad (24)$$

$\Rightarrow$ Steric factor 'p' is related to entropy of activation $\Delta S^{\#}$.

In Collision theory, the correction term 'p' was introduced arbitrarily whereas in the transition state theory its inclusion has been justified in terms of entropy of activation.

The concept of formation of activated complex seems to be more appropriate than assuming that the molecules first collide together and change into products. **The transition state theory is more logical and convincing.**

Catalysis

The substances that can enhance the rate of the reaction without itself undergoing any net chemical change are known as catalyst and the process is known as catalysis. A catalysed reaction can be represented as:-

$$R_1 + R_2 \xrightarrow{C} I \longrightarrow P_1 + P_2 \qquad (1)$$

where C = catalyst

R_1 and R_2 = reactants

I = Intermediate

P_1 and P_2 = Products

Type of Catalysis

There are two main types of catalysis:-

(a) Homogeneous Catalysis:- The catalyst is present in the same phase as the reactants and products are i.e **This catalysed reaction occurs in one phase.**

Examples:- (i) Homogeneous catalysis in gaseous phase :

Decomposition of acetaldehyde in the presence of iodine vapours as catalyst

$CH_3\,CHO + I_2 \rightarrow CH_4 + CO$

Vapour Vapour gas gas.

(ii) Homogeneous catalysis in solution phase :

Hydrolysis of ester in the presence of an acid as catalyst

$CH_3\,COOR + H_2O \xrightarrow{H^+} CH_3COOH + ROH$

(b) Heterogeneous Catalysis:- The catalyst is present in a different phase than the reactants. The catalysis occurs at the interface of two phases.

Example:- Decomposition of of HI on the surface of gold

$$2HI \xrightarrow{Au(s)} H_2 + I_2$$

(v)

The role of a catalyst can be explained on the basis of Transition State Theory. "A catalyst provides an alternate path mechanism with a lower free energy of activation. The lowering of free energy may be due to the decrease in the energy of activation or high frequency factor or both. This causes a change in the rate of a catalysed reactions.

According to Transition state theory

$$k_f = \frac{RT}{c^0 N_a h} \exp\left(-\Delta G_f^{0\#} / RT\right) \qquad (2)$$

In the presence of a catalyst

$$k_f' = \frac{RT}{c^0 N_a h} \exp\left(-\Delta G^{0\#'} / RT\right) \qquad (3)$$

since $\Delta G^{\circ\#'}$ is less than $\Delta G^{0\#}$, $k_f^{'}$ becomes greater than k_f i.e. rate of the forward reaction is increased. (Fig. 15)

As can be seen in Fig. (15), the free energy of activation is lowered for both forward as well as backward reaction. **Hence a catalyst cannot alter the equilibrium constant of a reaction. But, the presence of homogeneous catalyst can change the equilibrium mole fractions of reactants and products.** Since a catalyst is present in small quantities, its effect on equilibrium composition is small.

The rate law for homogeneously calatysed reaction can be written as:-

$r = k_0 [A]^{\alpha} ... [D]^{\gamma} + k_{cat} [A]^{\alpha} ... [D]^{\gamma} [Catalyst]^{\delta}$

where k_0 is the rate constant in the absence of catalyst {[Cataylst] = 0} and k_{cat} is the rate constant for the catalysed reaction. **The order of reaction with respect to catalyst is one.**

If the lowering of E_a is significant, the first term in r is negligible compared with the second, unless concentration of the catalyst is extremely small. The activation energies for catalysed and uncatalysed reaction can be found from the temperature dependences of k_0 and k_{cat}.

Characteristics of Catalytic Reactions

1. In some cases, catalytic activity of a catalyst can be enhanced by adding a small quantity of another substance called **promotor.** The action of promoters can be explained on the basis that it increases the surface area. As a result the concentration of adsorbed reactant molecule increases and so is the rate of reaction.

Example :

In Haber process, Molybdenum (Mo) or Aluminum Oxide (Al_2O_3) act as promotor for Iron Catalyst.

$$N_2 + 3H_2 \xrightarrow[+Mo]{Fe} 2NH_3$$

2. Whereas, in some cases, presence of certain substances can decrease the catalystic activity of a catalyst. These are known as **Negative Catalyst or Inhibitor.** Their action can be explained on the basis that it either poisons the catalyst or breaks the chain reaction if occurring in the system.

Example :

Nitrogen trichloride (NCl_3) acts as a Inhibitor for chain reaction between Hydrogen and Chlorine to form Hydrogen Chloride.

$$Cl_2 \rightarrow Cl^{\bullet} + Cl^{\bullet}$$

$$H_2 + Cl^{\bullet} \rightarrow HCl + H^{\bullet}$$

$$H^{\bullet} + Cl_2 \rightarrow HCl + Cl^{\bullet}$$

NCl_3 breaks the chain of reactions by absorbing $Cl^{\bullet}$ species and the reaction stops.

$$NCl_3 + Cl^{\bullet} \rightarrow \frac{1}{2} N_2 + 2Cl_2.$$

3. The presence of certain substances can destroy the activity of a catalyst. These substances are known as **Poisons** and the phenomenon is called **Catalytic Poisoning.** It is explained on the basis that the poison is adsorbed on the surface of catalyst in preference to the reactant.

Example:- The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide(Fig. (16))

$$2H_2 + O_2 \xrightarrow[\text{Poisoned}]{Pt} 2H_2O$$

4. When one of the product formed during the reaction speeds up the rate of the reaction (Fig.17) This phenomenon is known as **auto catalysis.**

Example :- (i) An atomic bomb. The reaction sequence A + B → C + D followed by C + E → 2A + F is autocatalytic. where A is neutron.

(ii) During redox reaction between Oxalic acid and acidified permanganate, manganous sulphate formed, acts as the catalyst.

$$2KMnO_4 + 5H_2C_2O_4 + 3K_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Although there are different types of catalytic reaction but some **characteristics** are common.

(i) There in no change in the mass and composition of the catalyst after the completion of the reaction. However, it may undergo a physical change. **Example:-**The granular form of catalyst manganese dioxide (MnO_2) for thermal decomposition of potassium chlorate gets converted into powder form at the end of the reaction.

(ii) A small quantity of catalyst is required to produce almost unlimited reaction.

(iii) In heterogeneous catalysis, the solid catalyst is more effective when finely divided. Finely divided nickel is a better catalyst than lumps of solid nickel.

(iv) Different catalysts bring about completely different reactions for the same substance i.e. **Each catalyst is specific in its action.**

For example,

$$C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O$$

$$C_2H_5OH \xrightarrow{Cu} CH_2CHO + H_2$$

(v) The presence of a catalyst doesn't alter the equilibrium constant value. It helps in attaining the state of equilibrium in much lesser time by enhancing the rate of reaction.

(vi) The rate of a catalytic reaction increases with rise in temperature. But in some case, increase in temperature alter the physical state of a catalyst and hence its catalytic activity gets disturbed.

For example, colloidal solution of platinum coagulates at high temperatures. The rate of reaction increases up to a certain point and then gradually decreases The temperature at which rate of catalysed reaction is maximum is known as **optimum temperature.**

Examples of Homogeneous Catalysis

The important examples of homogeneous catalysis include:-

(i) Acid – Base Catalysis

(ii) Enzyme Catalysis

Acid - Base Catalysis:-

Acid catalysis involves an equilibrium reaction in which there occurs a transfer of proton from an acid to a substrate 'S'. The protonated substrate then reacts to give product and proton.

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^- \qquad (4)$$

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+ \qquad (5)$$

The rate of appearance of product is given by

$$\frac{d[P]}{dt} = k_2 [SH^+] [H_2O].$$

since water is present in excess.

$$\therefore \frac{d[P]}{dt} = k_2 [SH^+] \qquad (6)$$

The concentration of SH^+ can be determined by applying Steady Sate approximation.

Base Catalysis involves transfer of a proton from the substrate molecule to the base.

$$SH + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S^- + H_2O \qquad (7)$$

$$S^- \xrightarrow{k_2} P + OH^- \qquad (8)$$

It has been found that not only H^+ ions but **all Bronsted acid (proton donors) cause acid catalysis.** The general acid catalysts are:-

H^+, undissociated acid (CH_3 COOH), cations of weak bases $\left(NH_4^+\right)$ and water (H_3O^+) **Also, not only OH^- ions but all Bronsted bases (proton acceptors) cause base catalysis.**

Examples:-

(i) Inversion of cane sugar is an acid catalysed reaction

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

Cane sugar Glucose fructose

(ii) Decomposition of nitramide is a base catalysed reaction

$$NH_2NO_2 + OH^- \rightarrow H_2O + NHNO_2^-$$

$$NHNO_2^- \rightarrow N_2O + O\bar{H}$$

Enzyme Catalysis: This is the most important example of homogeneous catalysis. Enzymes are complex protein molecules which catalyse reactions occurring in the biological systems.

Example:- Conversion of glucose into ethanol by Zymase present in yeast

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Characteristics of enzyme catalyst reactions :-

(i) Enzymes catalysed reactions proceed at high rates and one molecule of an enzyme may transform one million molecules of the substrate per minute.

(ii) An enzyme is specific in action. If a compound exists in optically active isomeric forms, an enzyme which acts on one of the isomer is unable to act on the other.

(iii) The rate of enzyme catalysed reaction is maximum at the optimum temperature. In human body, the optimum temperature for enzyme reaction is 37°C (98.6F). At high temperatures all physiological reaction will cease due to the loss of enzymatic activity. **Therefore, high body temperature (Fever) is dangerous.**

(iii) **Rate of enzyme catalysed reaction is maximum at the optimum pH.** Many enzymes of the body function best at pH of about 7.4, the pH of blood and body fluids.

(iv) Enzyme activity is greatly influenced by the presence of other substances acting as inhibitors or poisons. The physiological activity of many drugs is related to their action as enzyme inhibitors in body. Example : sulpha drugs inhibit the action of several bacteria and prove effective in curing many diseases. Cyanide acts by blocking the enzyme cytochrome oxidase.

(v) The presence of activators or co-enzymes can enhance the enzyme activity as well.

Mechanism :

The mechanism of enzyme catalysed reactions was initially proposed by Michaelis and Menten. The long chains of the enzyme molecules are coiled to make a rigid colloidal particle with cavities on the surface. The cavities containing active groups like $-NH_2$, –COOH, –SH or – OH are termed as **active sites.** It then acts on a substrate**.** The substrate binds to the active site to form an **enzyme substrate complex**. While bound to the enzyme, the substrate is converted to a product which is then released from the enzyme.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \qquad (9)$$

where E is the free enzyme, S is the substrate, ES is the enzyme substrate complex and P is the product.

The enzyme concentration is much less than the substrate concentration i.e. [E] << [S]. Hence, the concentration of ES is much less than that of S and the steady state approximation can be applied for evaluating the value of rate constant.

$$r_0 = \frac{k_2 [E]_0 [S]_0}{k_M + [S]_0} \qquad (10)$$

where k_M = Michaelis constant

$= (k_{-1} + k_2) / k_1$

Equation (10) is known as Michaelis – Menten equation.

Many experimental studies on enzyme kinetics give a rate law in agreement with this equation. But this mechanism is over simplified. As such another model has been proposed.

$$E + S \rightleftharpoons ES \rightleftharpoons EP \rightleftharpoons E + P \qquad (11)$$

While substrate is bound to the enzyme, it undergoes chemical change before being released as product.

The limitations of these models are it takes the catalytic reactions as $S \rightleftharpoons P$ whereas most enzyme catalysed reactions involve two substrates and two products.

$$A + B \rightleftharpoons P + Q \qquad (12)$$

The enzyme then has two active sites, one on each substrate. With two substrates, there are many possible mechanisms.

Enzyme catalysed reactions are fast but these can be studied using "classical methods" by keeping [E] and [S] very low such that [S] / [E] is large to ensure steady state approximation. Detailed information (rate constants for individual steps) can be obtained by employing fast methods like rapid flow or relaxation.

Heterogeneous Catalysis

Most heterogeneous catalysts are metals, metal oxides or acids. Many metallic catalyst are transition metals with partly vacant 'd' orbitals. e.g. Fe, Co, Ni, Cr, Mn, Cu. Common metal oxide catalyst are Al_2O_3, Cr_2O_3, V_2O_5, ZnO, Fe_2O_3 and NiO. Common acid catalysts are H_3PO_4 and H_2SO_4.

A **good catalyst** should have **moderate values for the enthalpies** of adsorption of the reactants. The **adsorption** is **chemisorption** in nature where the adsorbed molecules are held to the surface by valence forces. These forces make the bonds within the molecule weak and hence its reactivity is increased. In general, the catalytic effect depends upon the surface area available for adsorption and so a **powder form of catalyst is more effective.**

The **mechanism** of only a few heterogeneously catalysed reactions are known. In case of reaction in the liquid phase catalysed by solid catalyst, the various steps involved are :

(i) Diffusion of reactant molecules to the solid's surface.

(ii) chemisorption of at least one reactant species on the surface.

(iii) Chemical reaction between molecules adsorbed on the adjacent sites or between an adsorbed molecule and liquid phase molecules colliding with the surface.

(iv) Desorption of products from the surface.

(v) Diffusion of products into the bulk fluid.

When step (iii) is between species chemisorbed on the surface, the reaction is said to occur by **Langmuir – Hinshelwood mechanism.** If step (iii) involves a chemisorbed species reacting with liquid phase, the mechanism is called **Rideal – Eley Hinshelwood mechanism.**

Suggested Reading:-

(i) Physical Chemistry :- I.N. Levine

(ii) Physical Chemistry :- G.W. Castellan

(iii) Physical Chemistry :- P.W. Atkins

(iv) Physical Chemistry :- Marron and Pruton

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Keywords:- Chemical Kinetics; Kinetics and Thermodynamics; Classification of reactions on reaction time; Rate of reaction; Factors affecting rate of reaction; Measurement of reaction rate, Rate law and order of reaction; Molecularity; Integrated rate equation for zero, first and second order reactions; Methods for the determination of order of reaction; Complicating factors in reaction kinetics; Stationary State; Steady state approximation; Simple reaction mechanism, Effect of temperature on reaction rate; Theories of reaction rates: Collision Theory and Transition State Theory; Catalysis, Homogeneous catalysis, Acid Base catalysis, Enzyme catalysis, Heterogeneous Catalysis.