



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

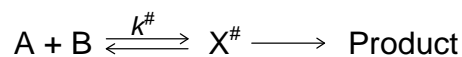
DEPARTMENT OF CHEMISTRY

UNIT – I – Advanced Chemical Kinetics – SCYA5202

1. ACTIVATED COMPLEX THEORY

Postulates of Activated Complex Theory

Activated complex is formed by the reactants A and B with an equilibrium constant k^\ddagger and such equilibrium reaction can be represented as:



The rate of the above reaction can be obtained by from the concentration of the two reactants and their equilibrium conditions as:

$$\text{Rate of formation of } X^\ddagger = k^\ddagger [A][B] \quad \dots (1)$$

The vibrational degrees of freedom of activated complex is highly unstable, which gives rise to the product and the frequency of such activated complex will be in the order of $k_b T$ and is given as:

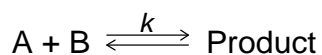
$$\gamma = \frac{k_b T}{h} \quad \dots (2)$$

The rate of reaction is therefore found to be:

The rate of formation of X^\ddagger = The frequency of vibration of X^\ddagger

$$\therefore \text{Rate of reaction} = k^\ddagger [A][B] \frac{k_b T}{h} \quad \dots (3)$$

The rate of reaction under an equilibrium condition may also be written as:



$$\text{Rate of reaction} = k[A][B] \quad \dots (4)$$

By comparing equation (3) and (4) to obtain rate equation under equilibrium condition as:

$$k[A][B] = k^\ddagger [A][B] \frac{k_b T}{h} \quad \dots (5)$$

$$(\text{or}) \quad k = k^\ddagger \frac{k_b T}{h} \quad \dots (6)$$

Where, k is the equilibrium constant; k_b is the Boltzmann constant; h is the Planck's constant and T is the absolute temperature.

Thermodynamic Formulation of Activated Complex Theory

The rate constant and the equilibrium constant for the activated complex is given by:

$$k = k^\ddagger \frac{k_b T}{h} \quad \dots (1)$$

The relationship between the free energy change and equilibrium constant for the formation of activated complex is given as:

$$-\Delta G^\ddagger = RT \ln k^\ddagger$$

$$\ln k^\ddagger = \frac{-\Delta G^\ddagger}{RT}$$

Taking exponentials on both the sides, we get:

$$e^{\ln k^\ddagger} = e^{\frac{-\Delta G^\ddagger}{RT}}$$

$$k^\ddagger = e^{\frac{-\Delta G^\ddagger}{RT}} \quad \dots (2)$$

We know that,

$$-\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Substituting ΔG^\ddagger in equation (2), we have:

$$k^\ddagger = e^{\left[\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT} \right]}$$

$$k^\ddagger = e^{\left[\frac{-\Delta H^\ddagger + T\Delta S^\ddagger}{RT} \right]}$$

$$k^\ddagger = e^{\left[\frac{-\Delta H^\ddagger}{RT} \right]} \cdot e^{\left[\frac{T\Delta S^\ddagger}{RT} \right]}$$

$$k^\ddagger = e^{\left[\frac{-\Delta H^\ddagger}{RT} \right]} \cdot e^{\left[\frac{\Delta S^\ddagger}{R} \right]} \quad \dots (3)$$

Substituting k^\ddagger in equation (1), we get:

$$k = \frac{k_b T}{h} \cdot e^{\frac{-\Delta H^\ddagger}{RT}} \cdot e^{\frac{\Delta S^\ddagger}{R}} \quad \dots (4)$$

The equation (4) is known as **Eyring equation**.

Taking logarithm on equation (1), we have:

$$\ln k = \ln \frac{k_b}{h} + \ln T + \ln k^\# \quad \dots (5)$$

Differentiating equation (5) with respect to T, we get:

$$\frac{d \ln k}{T} = \frac{d \left(\ln \frac{k_b}{h} \right)}{T} + \frac{d(\ln T)}{T} + \frac{d(\ln k^\#)}{T}$$

$$\frac{d \ln k}{T} = \frac{1}{T} + \frac{d(\ln k^\#)}{T} \quad \dots (6)$$

The Arrhenius equation for activated complex is given as:

$$k = A e^{-\frac{E_a}{RT}} \quad \dots (7)$$

Taking logarithm on both the sides, we have:

$$\ln k = \ln A + \ln e^{-\frac{E_a}{RT}} \quad \dots (8)$$

Differentiating equation (8) with respect to T, we get:

$$\frac{d \ln k}{T} = \frac{d \ln A}{T} - \frac{d \left[\frac{E_a}{RT} \right]}{T}$$

$$\frac{d \ln k}{T} = \frac{-E_a}{R} \left[-\frac{1}{T^2} \right]$$

$$\frac{d \ln k}{T} = \frac{E_a}{RT^2} \quad \dots (9)$$

Comparing (6) and (9), we have:

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{d \ln k^\#}{dT}$$

Multiplying the above equation with RT^2 on both the sides:

$$E_a = RT + \frac{d \ln k^\#}{dT} RT^2 \quad \dots (10)$$

According to Van't Hoff isochore

$$\frac{d \ln k^\#}{dT} = \frac{\Delta E^\#}{RT^2} \quad \dots (11)$$

Comparing equations (10) and (11), we have:

$$E_a = RT + \Delta E^\# \quad \dots (12)$$

We know that

$$\Delta H^\# = \Delta E^\# + P\Delta V$$

$$\Delta E^\# = \Delta H^\# - P\Delta V$$

$$\Delta E^\# = \Delta H^\# - \Delta nRT \quad \dots (13)$$

Substituting (13) in (12), we get:

$$E_a = RT + \Delta H^\# - \Delta nRT$$

Where Δn is the number of gaseous molecules going from reactants to products.

Limiting Cases

Case (1): For a bimolecular reaction, $\Delta n = -1$

$$\therefore E_a = RT + \Delta H^\# + RT$$

$$E_a = \Delta H^\# + 2RT$$

$$\Delta H^\# = E_a - 2RT$$

From Eyring equation, we have:

$$k = \frac{k_b T}{h} \cdot e^{\frac{-E_a + 2RT}{RT}} \cdot e^{\frac{\Delta S^\#}{R}}$$

$$k = \frac{k_b T}{h} \cdot e^{\frac{-E_a}{RT}} \cdot e^2 \cdot e^{\frac{\Delta S^\#}{R}}$$

$$k = \frac{k_b T}{h} \cdot e^{\frac{-E_a}{RT}} \cdot e^{2 + \frac{\Delta S^\#}{R}}$$

Case (2): For a unimolecular reaction, $\Delta n = 0$

$$\therefore E_a = RT + \Delta H^\#$$

$$\Delta H^\# = E_a - RT$$

From Eyring equation, we have:

$$k = \frac{k_b T}{h} \cdot e^{\frac{-E_a + RT}{RT}} \cdot e^{\frac{\Delta S^\#}{R}}$$

$$k = \frac{k_b T}{h} \cdot e^{\frac{-E_a}{RT}} \cdot e^1 \cdot e^{\frac{\Delta S^\ddagger}{R}}$$

$$k = \frac{k_b T}{h} \cdot e^{\frac{-E_a}{RT}} \cdot e^{1 + \frac{\Delta S^\ddagger}{R}}$$

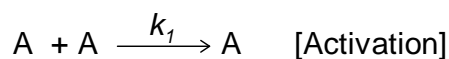
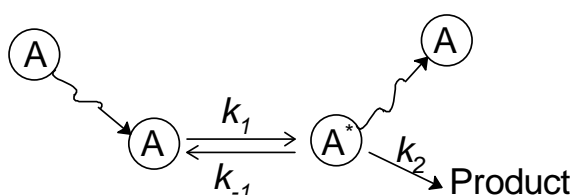
Exercise 1: The value of ΔS^\ddagger for a unimolecular reaction as obtained is $-80.5 \text{ JK}^{-1}\text{mol}^{-1}$. Find the exponential factor. [Ans: $17378 \text{ mol}^{-1} \text{ s}^{-1}$]

Exercise 2: The pre-exponential factor for bimolecular gaseous reaction occurring at 350°C is $8 \times 10^{10} \text{ mol}^{-1} \text{ s}^{-1}$. Calculate ΔS^\ddagger . [Ans: $-35 \text{ JK}^{-1}\text{mol}^{-1}$]

2. LINDEMAN'S MECHANISM OF UNIMOLECULAR REACTIONS

Postulates of Lindeman's Mechanism

- ❖ According to Lindemann's mechanism, at least two molecules must collide so that the kinetic energy of second molecule will get converted into the vibrational energy and to form an energised molecule.
- ❖ The energised molecule in turn gets deactivated with rate constant of k_{-1} or get decomposed with the rate constant of k_2 .



Derivation of Lindeman's Mechanism

$$k = \frac{-d[A^*]}{dt} = k_1[A][A] \quad \dots (1)$$

$$k = \frac{-d[A^*]}{dt} = k_{-1}[A^*][A] \quad \dots (2)$$

$$k = \frac{+d[P]}{dt} = \frac{-d[A^*]}{dt} = k_2[A^*] \quad \dots (3)$$

The concentration of any intermediate species can be determined by applying steady state approximation [SSA]. According to SSA,

Rate of formation of intermediate species = Rate of decomposition of intermediate species
 + Rate of deactivation of intermediate species

$$k_1[A][A] = k_{-1}[A^*][A] + k_2[A^*]$$

$$k_1[A][A] = k_{-1}[A^*]\{k_{-1}[A] + k_2\}$$

$$[A^*] = \frac{k_1[A]^2}{\{k_{-1}[A] + k_2\}} \quad \dots (4)$$

$$\therefore \text{The rate of reaction} = \frac{-d[A]}{dt} = k_2[A^*]$$

$$(\text{or}) \text{The rate of reaction} = \frac{-d[A]}{dt} = \frac{k_1 k_2 [A]^2}{\{k_{-1}[A] + k_2\}} \quad \dots (5)$$

Limiting cases

Case 1: At high pressures, the chances of collisions between A^* and A are greater, in turn deactivation is prominent than product formation. i.e., $k_{-1}[A] \gg k_2$. Hence, k_2 can be neglected.

$$\frac{-d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A]}$$

$$\frac{-d[A]}{dt} = \frac{k_1 k_2}{k_{-1}} [A]$$

$$\frac{-d[A]}{dt} = k_{\infty} [A] \quad \text{where } k_{\infty} = \frac{k_1 k_2}{k_{-1}}$$

$$\frac{-d[A]}{dt} \propto [A]$$

\therefore The rate is of first order at high pressures.

Case 2: At low pressures, the chances of collisions between A^* and A are lesser, in turn deactivation is less than product formation. i.e., $k_{-1}[A] \ll k_2$. Hence, $k_{-1}[A]$ can be neglected.

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

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

$$\frac{-d[A]}{dt} \propto [A]^2$$

\therefore The rate is of second order at low pressures.

Rearranging equation (5), we have:

$$-\frac{1}{[A]} \frac{d[A]}{dt} = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2} \quad \dots (6)$$

$$k' = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2}$$

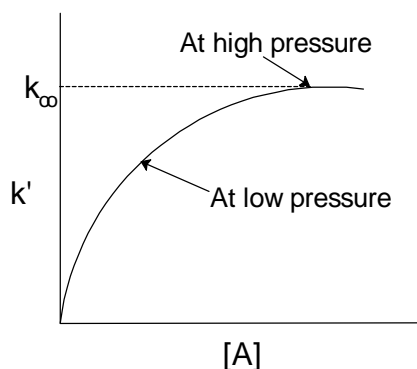
where $k' = -\frac{1}{[A]} \frac{d[A]}{dt}$, is known as first order rate coefficient

At high pressures, $k_{-1} [A] \gg k_2$, we have:

$$k' \propto [A]$$

At low pressures, $k_{-1} [A] \ll k_2$, we have:

$$k' \propto [A]^2$$



Limitations of Lindeman's Mechanism

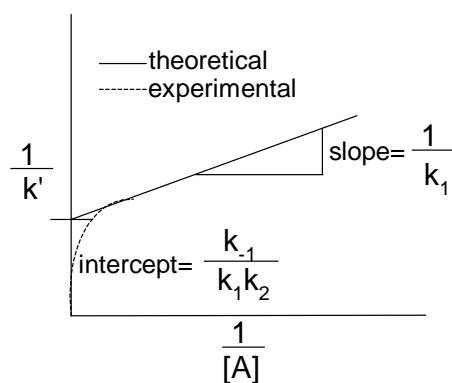
Taking reciprocals for the equation (6), we get:

$$\left[-\frac{1}{[A]} \frac{d[A]}{dt} \right]^{-1} = \frac{k_{-1} [A] + k_2}{k_1 k_2 [A]} \quad \dots (7)$$

$$\frac{1}{k'} = \frac{k_2}{k_1 k_2 [A]} + \frac{k_{-1} [A]}{k_1 k_2 [A]}$$

$$\frac{1}{k'} = \frac{1}{k_1 [A]} + \frac{k_{-1}}{k_1 k_2} \quad \dots (8)$$

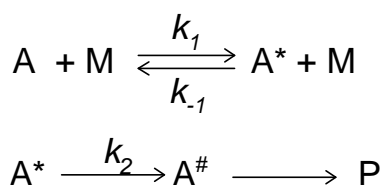
The equation (8) is a straight-line equation, and plotting $1/k'$ versus $1/[A]$ gives a straight line which yields a slope = $1/k_1$ and an intercept = $k_{-1}/k_1 + k_2$.



However, the experimental results prove that there is deviation from linearity.

3. HINSHELWOOD MECHANISM OF UNIMOLECULAR REACTIONS (LINDEMAN-HINSHELWOOD MECHANISM)

Hinshelwood modified Lindemann's mechanism as follows:



Where, M is the third molecule (can be another A or an inert molecule); A* is the energised molecule and A[#] is the activated molecule.

Those energised molecules which possess a very large internal degrees of vibrations (energy) will get converted into the product.

For a simple unimolecular reaction, the rate expression is given as:

$$k_1 = z_1 e^{\frac{-E_a^\#}{RT}}$$

Where, z_1 is the collision number for a bimolecular reaction.

And, for the complex molecule, Hinshelwood derived the rate expression as:

$$k_1 = \frac{z_1}{(S-1)!} \left[\frac{E_a^\#}{RT} \right]^{(S-1)} e^{\frac{-E_a^\#}{RT}}$$

Where S is the number of molecules which possess excess of vibrational energy and $\frac{z_1}{(S-1)!} \left[\frac{E_a^\#}{RT} \right]^{(S-1)}$ is the pre-exponential factor [f*].

$$\therefore k_1 = f * e^{\frac{-E_a^\#}{RT}}$$

$$\therefore \log k_1 = \log f^* - \frac{E_a^\#}{RT}$$

Exercise 1: Calculate the frequency factor for a reaction at 300K with an activation energy of 200kJ mol⁻¹ and S=6 assuming the collision number z₁=10¹² dm³ mole⁻¹s⁻¹.

[Ans: $f^*=2.6 \times 10^{19} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$].

Exercise 2: Calculate the value for k₁ assuming S=1, 3, and 6. Take z₁be =10¹² dm³ mole⁻¹s⁻¹, T=300K and E_a[#] = 60 kg/mol.

[Ans: When S=1, $f^* = 5 \times 10^{10}$ and $k_1 = 2$; When S=3, $f^* = 1446 \times 10^{10}$ and $k_1 = 578$; When S=6, $f^* = 5 \times 67119 \times 10^{10}$ and $k_1 = 134238$].

Limitations of Hinshelwood Mechanism

According to Hinshelwood theory, we have:

$$k_1 = \frac{z_1}{(S-1)!} \left[\frac{E_a^\#}{RT} \right]^{(S-1)} e^{-\frac{E_a^\#}{RT}}$$

$\frac{z_1}{(S-1)!} \left[\frac{E_a^\#}{RT} \right]^{(S-1)}$ which indicates the strong dependence of pre-exponential factor. But there is no experimental evidences for it.

The explanation of 1/k' versus 1/[A] (non-linearity) is not given in Hinshelwood mechanism.

In Hinshelwood theory, the S values are calculated by trial-and-error method. But the experimental results prove that S values are corresponding to half of the theoretical values.

4. TEMPERATURE DEPENDENCE OF PRE-EXPONENTIAL FACTOR FROM TRANSITION STATE THEORY (TST)

The transition state theory in terms of partition function is given as:

$$k = \left[\frac{k_b T}{h} \frac{Q_{AB}^\#}{Q_A^\# Q_B^\#} \right] e^{-\frac{E_a}{RT}}$$

Where, $Q_{AB}^\#$ is the total partition function of the activated complex AB[#]; Q_A and Q_B are total partition functions of the reactants A and b respectively.

Further, the term $\left[\frac{k_b}{h} T \frac{Q_{AB}^\#}{Q_A^\# Q_B^\#} \right]$ is known as temperature dependence of pre-exponential factor, which can be written as:

$$\left[A \propto T \frac{Q_{AB}^\#}{Q_A^\# Q_B^\#} \right]$$

It has been theoretically found that,

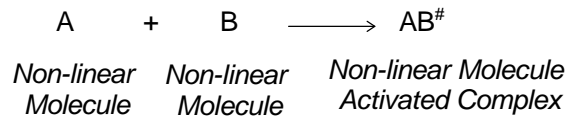
(i) q_T , the translational partition function, for each degree of freedom depends on $T^{\frac{1}{2}}$

- (ii) q_R , the rotational partition function, for each degree of freedom depends on $T^{\frac{1}{2}}$
- (iii) q_V , the vibrational partition function, for each degree of freedom depends on T^0 at low temperatures and T^1 at high temperatures.

These partition functions are used to calculate the temperature dependence of pre-exponential factor for various specific reactions.

Example:

Let us consider the following reaction:



The temperature dependence of pre-exponential factor from TST is given as:

$$A \propto T \frac{Q_{AB}^\#}{Q_A^\# Q_B^\#}$$

$$A \propto T^n$$

Where n is known as temperature exponent.

$$Q_A = q_T^3 q_R^3 q_V^{3(N_A)-6}$$

$$Q_A = q_T^3 q_R^3 q_V^{3(N_A)} q_V^{-6}$$

$$Q_B = q_T^3 q_R^3 q_V^{3(N_B)-6}$$

$$Q_B = q_T^3 q_R^3 q_V^{3(N_B)} q_V^{-6}$$

$$Q_{AB}^\# = q_T^3 q_R^3 q_V^{3(N_A+N_B)-7}$$

$$Q_{AB}^\# = q_T^3 q_R^3 q_V^{3(N_A)} q_V^{3(N_B)} q_V^{-7}$$

$$A \propto T \frac{q_T^3 q_R^3 q_V^{3(N_A)} q_V^{3(N_B)} q_V^{-7}}{q_T^3 q_R^3 q_V^{3(N_A)} q_V^{-6} q_T^3 q_R^3 q_V^{3(N_B)} q_V^{-6}}$$

$$A \propto T \frac{q_V^{-7}}{q_T^3 q_R^3 q_V^{-12}}$$

$$A \propto T \frac{q_V^5}{q_T^3 q_R^3}$$

$$A \propto T \frac{(T^1)^5}{\left(T^{\frac{1}{2}}\right)^3 \left(T^{\frac{1}{2}}\right)^3}$$

$$A \propto T^3$$

(or) $n = 3$.

Exercise 1: The absolute rate theory relates A on temperature T ($A \propto T^n$). Determine the value of exponent for the following reactions:

- (i) Atom + Linear Molecule \rightarrow Linear Activated Complex
- (ii) Linear Molecule + Linear Molecule \rightarrow Non-Linear Activated Complex

5. EFFECT OF SOLVENT ON REACTION RATES

The rates of reactions are affected by:

- (i) the nature of the solvent used and
- (ii) the nature and concentration of ionic species present in the reaction mixtures.

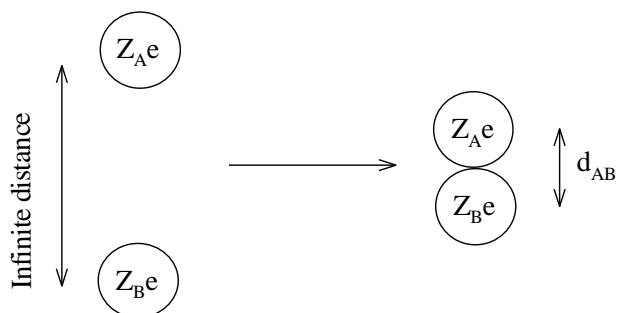
For the purpose of describing effect of solvent on reaction rates, the reactions can be generally grouped into three categories: Reaction between (i) two ions, (ii) an ion and a neutral molecule, and (iii) two neutral dipolar molecules.

Reaction Between Two Ions

Let us consider the reaction between two ions A and b with charges $Z_A e$ and $Z_B e$.

The interpretation of solvent effects on reaction rates based on electrostatic interactions.

Initially the ions are at infinite distance from one another, but they touch each other when form the activated complex.



Double sphere model for a simple ionic reaction

The work that must be done in bringing two ions together from infinity to a distance d_{AB} is given by:

$$w = \frac{Z_A Z_B e^2}{\epsilon d_{AB}} \quad \dots(1)$$

where ϵ is the dielectric constant of the solvent.

This work is equal to the electrostatic contribution to the Gibbs free energy increase where the ions are going from initial state to final state. If the signs of the on the ions are same, this work is positive, if they are different, it is negative.

According to thermodynamics, Gibb's free energy is the measure of useful work (activation work) and is given by:

$$\frac{\Delta G^\#}{N} = \frac{\Delta G_o^\#}{N} + \frac{Z_A Z_B e^2}{\epsilon d_{A-B}}$$

Where, $\Delta G_o^\#$ is the molar Gibbs free energy chnge of the solution.

Multiplying by N on both the sides, we have:

$$\Delta G^\# = \Delta G_o^\# + \frac{N Z_A Z_B e^2}{\epsilon d_{A-B}}$$

Multiplying by $\frac{-1}{RT}$ on both the sides, we get:

$$\frac{-\Delta G^\#}{RT} = \frac{-\Delta G_o^\#}{RT} - \frac{Z_A Z_B e^2}{RT \epsilon d_{A-B}} \quad \dots (2)$$

From TST, we have:

$$k = \frac{k_b T}{h} \cdot e^{\frac{-\Delta G^\#}{RT}}$$

$$k = \frac{k_b T}{h} \cdot e^{\frac{-\Delta G_o^\#}{RT} - \frac{Z_A Z_B e^2}{RT \epsilon d_{A-B}}}$$

$$k = \frac{k_b T}{h} \cdot e^{\frac{-\Delta G_o^\#}{RT}} \cdot e^{-\frac{Z_A Z_B e^2}{RT \epsilon d_{A-B}}}$$

Taking logarithm on both the sides, we have:

$$\log k = \log \frac{k_b T}{h} - \frac{\Delta G_o^\#}{RT} - \frac{Z_A Z_B e^2}{RT \epsilon d_{A-B}}$$

$$(or) \log k = \log k_o - \frac{Z_A Z_B e^2}{RT \epsilon d_{A-B}} \quad \dots (3)$$

$$\text{Where, } \log k_o = \log \frac{k_b T}{h} - \frac{\Delta G_o^\#}{RT}$$

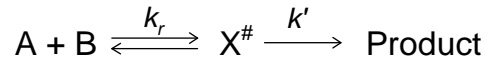
k_o is the rate constant of the solvent at zero concentration.

Equation (3) is the straight-line equation which explains the variation of rate constant with the effect of dielectric constant of the solvent. The measurement of this equation gives the slope in turn is used to calculate d_{A-B} .

6. EFFECT OF IONIC STRENGTH ON REACTION RATES

Primary Salt Effect: Bronsted-Bjerrum Equation

Let us consider the reaction:



Where A and B are the ionic species present in solution and $X^\#$ is the activated complex.

The equilibrium $[k]$ depends only on $[X^\#]$.

$$k = \frac{a_{X^\#}}{a_A \cdot a_B}$$

$$k = \frac{[X^\#]\gamma_{X^\#}}{[A]\gamma_A \cdot [B]\gamma_B}$$

$$k = \frac{[X^\#]}{[A] \cdot [B]} \cdot \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B}$$

$$[X^\#] = k[A][B] \cdot \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B} \quad \dots (1)$$

The rate of reaction for product formation is given by:

$$r = k'[X^\#]$$

$$r = k'k[A][B] \cdot \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B} \quad \dots (2)$$

The rate of reaction can be written as:

$$r = k_r[A][B] \quad \dots (3)$$

Comparing (2) and (3), we have:

$$k_r[A][B] = k'k[A][B] \cdot \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B}$$

$$k_r = k'k \cdot \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B}$$

Taking logarithm on both the sides, we have:

$$\log k_r = \log(k'k) \cdot \log \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B}$$

$$\log k_r = \log k_o + \log \frac{\gamma_{X^\#}}{\gamma_A \cdot \gamma_B} \quad \dots (4)$$

Where $k_o = k'k$, rate constant of reaction at infinite dilution.

The relationship between activity coefficient and ionic strength is given by Debye-Huckel Limiting Law as:

$$\log \gamma_i = -AZ_i^2 \sqrt{I}$$

Where, A is Debye-Huckel parameter and I is the ionic strength.

$$\log \gamma_A = -AZ_A^2 \sqrt{I}$$

$$\log \gamma_B = -AZ_B^2 \sqrt{I}$$

$$\log \gamma_{X^\#} = -AZ_{X^\#}^2 \sqrt{I}$$

$$\log \gamma_{X^\#} = -A(Z_A + Z_B)^2 \sqrt{I}$$

$$\log \frac{\gamma_A \gamma_B}{\gamma_{X^\#}} = 2AZ_A Z_B \sqrt{I} \quad (5)$$

Substituting equation (5) into equation (4) gives:

$$\log k_r = \log k_o + 2AZ_A Z_B \sqrt{I} \quad (6)$$

This is known as the *Bronsted-Bjerrum equation*. It explains the variation of specific rate with ionic strength, which in turn depends on the charges of reacting species.

Rearrangement of equation (6) gives:

$$\log \left(\frac{k_r}{k_o} \right) = 2AZ_A Z_B \sqrt{I} \quad (7)$$

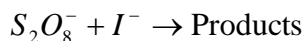
Case (1): When $Z_A Z_B = 0$, (i.e: one of the reactants is non-electrolyte), the rate constant would be independent of ionic strength.

Example: Reaction between iodoacetic acid and CNS^-

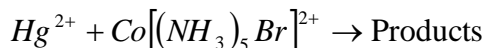


Case (2): When $Z_A Z_B = \text{Positive}$, (i.e: Z_A and Z_B are of opposite sign), the rate constant for such reaction would decrease with \sqrt{I} .

Example (1): Reaction between persulphate and iodide ion. The value of $Z_A Z_B = +1$.

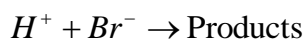


Example (2): Reaction between mercury ion and cobalto ammonium bromide ion. The value of $Z_A Z_B = +4$.

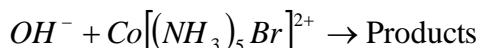


Case (3): When $Z_A Z_B = \text{Negative}$, (i.e: Z_A and Z_B are of same sign), the rate constant for such reaction would increase with \sqrt{I} .

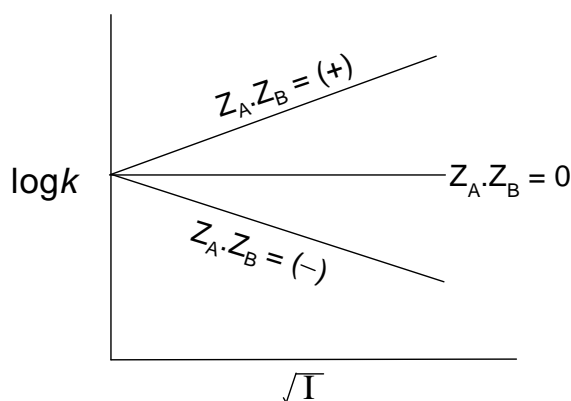
Example (1): Reaction between hydrogen and bromide ion. The value of $Z_A Z_B = -1$.



Example (2): Reaction between cobalto ammonium bromide ion and hydroxyl ion. The value of $Z_A Z_B = -2$.



Therefore, a plot of $\log\left(\frac{k_r}{k_o}\right)$ against \sqrt{I} is linear.



It is seen that for reactions between ions of like charge the slope is positive. Such reactions show a positive salt effect; that is, the reaction rate increases with increasing ionic strength.

For reactions between ions of opposite charge the slope is negative. This corresponds to a negative salt effect and the reaction rate decreases with increasing ionic strength.

A reaction between an ion and a neutral molecule such as the acid or alkaline hydrolysis of an ester does not exhibit a primary salt effect.

Secondary Salt Effect

In primary salt effect, addition of an electrolyte (salt) or variation of ionic strength affects the activity coefficients and hence the rate of reaction.

However, in a reaction where H^+ or OH^- ions produced from a weak acid or weak base act as catalysing agent, the addition of salt influences the concentration of H^+ or OH^- ions.

Since the rate of reaction depends upon the concentration of H^+ or OH^- , it will be affected by the salt concentration. This phenomenon is known as *secondary salt effect*.

Let us consider a reaction which is catalysed by H^+ produced by weak acid HA. The dissociation constant of acid is given as:



$$K = \frac{[H^+][A^-]}{[HA]} \times \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}}$$

(or)

$$[H^+] = K \frac{[HA]}{[A^-]} \times \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}}$$

(or)

$$[H^+] = K \times \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}}$$

where $K = \text{Constant} = K_a [HA]/[A^-]$; because $[HA]/[A^-]$ will remain constant for a given acid salt mixture.

Since the rate depends on $[H^+]$, the rate constant for a given acid salt ratio may be given as:

$$k = k_o \times \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}}$$

Where k_o is the rate constant in absence of secondary salt effect and includes the primary salt effect. The above equation at 25°C may be given as:

$$\log k = \log k_o + 1.018\sqrt{I}$$

When I is increased, the concentration of H^+ increases, and therefore, rate of acid catalysed reaction will also increase. Similar results are obtained for reactions catalysed by hydroxyl ions. The ionic strength must be kept constant when we examine a general acid/base catalysed reaction because, if ionic strength is not kept constant the rate constant will change in accordance with equation.

References

1. Keith J. Laidler, Chemical Kinetics, Pearson Education India, 3rd Edition, 2003.
2. John W. Moore and Ralph G. Pearson, Kinetics and Mechanism, Wiley, 3rd Edition, 1981.
3. F. Wilkinson, Chemical Kinetics and Reaction Mechanism, Van Nostrand Reinhold Co., 2000.

REVIEW QUESTIONS

1. Explain the postulated of activated complex theory.
2. Explain the postulated of Lindemann's mechanism of unimolecular reactions.
3. Explain the limitations of Lindemann's mechanism of unimolecular reactions.
4. Explain Lindemann-Hinshelwood mechanism of unimolecular reactions.
5. Determine the frequency factor for a reaction at 300K with an activation energy of 200kJmole^{-1} and $S=6$, assuming the collision number $Z_1 = 10^{12}\text{dm}^3\text{mole}^{-1}\text{s}^{-1}$.
6. Explain the limitations of Hinshelwood mechanism of unimolecular reaction.
7. Discuss the secondary salt effect.
8. The absolute rate theory relates the dependence A on temperature T ($A \propto T^n$). Determine the value of exponent for the following reaction:
Atom + Linear Molecule \rightarrow Activated Non-linear Molecule
9. Develop thermodynamic formulation of activated complex theory.
10. The value of ΔS^\ddagger for a reaction as obtained is $-80.5\text{JK}^{-1}\text{mole}^{-1}$. Determine the exponential factor for the temperature 400K for unimolecular reaction.
11. The pre-exponential factor for a bimolecular gaseous reaction occurring at 350°C is $8 \times 10^{10}\text{mole}^{-1}\text{s}^{-1}$. Determine ΔS^\ddagger .
12. Discuss Lindemann's mechanism of unimolecular reaction with limiting case.
13. Determine the value for k_1 assuming $S = 1, 3, 6$. Take Z_1 to be $5 \times 10^{12}\text{dm}^3\text{mole}^{-1}\text{s}^{-1}$; $T=300\text{K}$ and $E_a^\ddagger = 60\text{kJmole}^{-1}$.
14. Explain temperature dependence of pre-exponential factor from transition state theory.
15. Discuss the effect of solvent on reaction rates.
16. Explain the effect of ionic strength on reaction rate.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – II–Kinetics of Fast Reactions–SCYA5202

1. INTRODUCTION

When we carry out conventional studies of solution kinetics, we initiate reactions by mixing solutions. There are many reactions that are too fast to investigate by ordinary mixing techniques.

Some important examples are proton transfers, enzymatic reactions, and noncovalent complex formation. Prior to the second half of the 20th century, these reactions were referred to as instantaneous because their kinetics could not be studied.

It is now possible to measure the rates of such reactions. In this unit, we will find methods for measuring the fastest reactions that have half-lives of the order 10^{-12} s.

The techniques, which have been designed to monitor concentrations and to measure the rate coefficients, include flash photolysis, relaxation methods and flow techniques.

The other techniques including shock tubes and molecular beams have been used to explore the dependence of reaction rate on the state of rotational/ vibrational excitation of molecules or on the energy with which molecules collide and the rate at which the energy is changed from one form into another.

2. CLASSIFICATION OF CHEMICAL REACTIONS ON THE BASIS OF RATE OF THE REACTION

1. Fast/Instantaneous Reactions

The chemical reaction which completes in less than 1 ps (one pico second) (10^{-12} s) time, is known as the fast reactions. It is practically impossible to measure the speed of such reactions. The reason for a very fast rate of such reaction is that no chemical bonds are to be broken among the reactants.

Examples: ionic reactions, organic substitution reactions, neutralization reactions

2. Very Slow Reactions

Chemical reactions which complete in a long time from some minutes to some years are called slow reactions. The rates of such reactions are hardly of any physical importance.

Examples: rusting of iron, transformation of carbon into diamond etc.

3. Moderately Slow Reactions

Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions. These reactions proceed at a moderate speed which can be measured easily. Mostly these reactions are in molecular nature.

The values of rate constant give an idea about the speed of the reaction. Greater the value of the rate constant, faster is the reaction.

Table 2.1: Classification of Chemical Reactions

S. No.	Types of Reaction	Rate Constant ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Half Life (sec)
1.	Slow	10^{-7}	10^8
2.	Moderate	$10^{-4} - 10^{-1}$	$10^5 - 10^2$
3.	Fast	$10^1 - 10^5$	$10^{-1} - 10^{-4}$
4.	Ultrafast	$10^2 - 10^{11}$	$10^{-12} - 10^{-15}$

Characteristics of Fast Reactions

- ⇒ The chemical reactions in which the rate constant lies between $10^1 - 10^{11} \text{ s}^{-1}$ are called fast reactions. They have very short half-life of $10^{-1} - 10^{-15}$.
- ⇒ They are so fast that they occur as soon as the reactants are brought together.
- ⇒ The special experimental techniques used for measuring the rate constant of fast reactions include: Relaxation methods, Flow methods, Ultrasonic and Resonance techniques etc.

3. CHEMICAL RELAXATION METHODS

Types of Relaxation Techniques

Relaxation methods are classified into three groups based on the extent of perturbation to attain a new equilibrium. They include:

1. Small perturbation method

Examples: Temperature jump method and Pressure jump method

2. Large perturbation method

Examples: Shock tube method and Flash photolysis

3. Periodic perturbation method

Example: Ultrasonic method

- ⇒ In relaxation techniques, a chemical equilibrium is disturbed (perturbed) by a rapid change in one of the possible parameters like temperature or pressure or electric field intensity.
- ⇒ The relaxation is followed by using spectrometer or conductivity meter techniques.
- ⇒ The time during which the reaction gets relaxed from the equilibrium is called relaxation time.
- ⇒ The relaxation time can be determined by T-jump method or by P-jump method.

1. Chemical relaxation by Temperature Jump Method (T-Jump Method)

- ⇒ In T-jump method, a high voltage power supply charges the capacitor (C).
- ⇒ When a certain voltage is reached, the spark gap (G) breaks down and thereby discharging the capacitor and sending a strong current through the cell containing reactive system at equilibrium (Fig. 2.1).
- ⇒ As the current passes, the temperature of the reactive system rises by about 10°C in few microseconds. This temperature rise perturbs the system in such a way that the concentration of reactive species adjusts to a new equilibrium value.
- ⇒ The speed with which the system approaches new equilibrium is monitored through spectrometer in which the intensity of light leaving the cell is measured by using a suitable photodetector (Photo multiplier tube-PMT).
- ⇒ The output of PMT is displayed as the variation of concentration versus time on the oscilloscope screen.

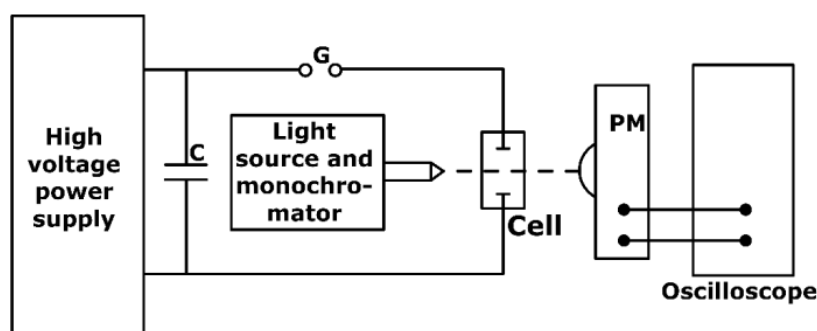
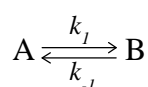


Fig. 2.1: Apparatus for the Temperature Jump Method

Kinetics of Small Perturbation Method (or) Rate Constant Expression for Fast Reactions by T-Jump Method

If the displacement from equilibrium is very small, the rate of relaxation (restoration of equilibrium) always follows the first order kinetics.

1. *Let us consider the reversible reaction is of first order:*



Let 'a' be the total concentration of A, and 'x' be the concentration of B at any interval of time 't'.

Therefore, the rate of reaction is given by:

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x \quad \dots (1)$$

At equilibrium $dx/dt = 0$ and $x = x_e$, and from the equation (1) we have:

$$0 = k_1(a - x_e) - k_{-1}x_e \quad \dots (2)$$

(or)

$$k_1(a - x_e) = k_{-1}x_e \quad \dots (3)$$

The deviation from equilibrium (Δx) may be defined as:

$$\Delta x = x - x_e$$

Where x_e is equilibrium concentration.

(or)

$$x = \Delta x + x_e \quad \dots (4)$$

The deviation of Δx with time is given by:

$$\frac{d(\Delta x)}{dt} = k_1(a - x) - k_{-1}x$$

But $x = \Delta x + x_e$ and hence, we have:

$$\frac{d(\Delta x)}{dt} = k_1[a - \Delta x - x_e] - k_{-1}[\Delta x + x_e] \quad \dots (5)$$

$$\frac{d(\Delta x)}{dt} = k_1a - k_1\Delta x - k_1x_e - k_{-1}\Delta x - k_{-1}x_e$$

$$\frac{d(\Delta x)}{dt} = k_1(a - x_e) - k_1\Delta x - k_{-1}\Delta x - k_{-1}x_e$$

$$\frac{d(\Delta x)}{dt} = k_1(a - x_e) - k_1\Delta x - k_{-1}\Delta x - k_{-1}x_e \quad \dots (6)$$

From equation (3), we have:

$$k_1(a - x_e) = k_{-1}x_e$$

Therefore, the equation (6) is written as:

$$\frac{d(\Delta x)}{dt} = k_{-1}x_e - k_1\Delta x - k_{-1}\Delta x - k_{-1}x_e$$

(or)

$$\frac{d(\Delta x)}{dt} = -\Delta x[k_1 + k_{-1}]$$

$$\frac{d(\Delta x)}{dt} = -\Delta x \cdot k_r \quad \dots (7)$$

Where $k_r = [k_1 + k_{-1}]$ is known as relaxation constant.

The reciprocal of relaxation constant is known as relaxation time (τ^*).

$$\tau^* = \frac{1}{k_r} = \frac{1}{[k_1 + k_{-1}]}$$

Rearranging equation (7), we have:

$$\frac{d(\Delta x)}{\Delta x} = -k_r dt \quad \dots (8)$$

Since the quantity Δx varies with time, integrating the equation (8) subjected to the boundary conditions $\Delta x = \Delta x_o \rightarrow \Delta x$ when $t = 0 \rightarrow t$, we have:

$$\int_{\Delta x = \Delta x_o}^{\Delta x = \Delta x} \frac{d(\Delta x)}{\Delta x} = -k_r \int_{t=0}^{t=t} dt$$

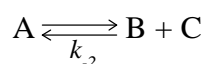
$$\ln \frac{\Delta x}{\Delta x_o} = -k_r t$$

$$\frac{\Delta x}{\Delta x_o} = e^{-k_r t}$$

$$\Delta x = \Delta x_o e^{-k_r t}$$

Where $k_r = k_1 + k_{-1}$.

2. *Let us consider a reaction involving first order forward reaction with second order reverse reaction:*



Let 'a' be total concentration of A, and 'x' be the concentration of B and C at any interval of time 't'. Therefore, the rate equation is given by:

$$\frac{dx}{dt} = k_1(a - x) - k_{-2}x^2 \quad \dots (1)$$

At equilibrium $dx/dt = 0$ and $x = x_e$, and from the equation (1) we have:

$$0 = k_1(a - x_e) - k_{-2}x_e^2 \quad \dots (2)$$

(or)

$$k_1(a - x_e) = k_{-2}x_e^2 \quad \dots (3)$$

The deviation from equilibrium (Δx) may be defined as:

$$\Delta x = x - x_e$$

Where x_e is equilibrium concentration.

(or)

$$x = \Delta x + x_e \dots (4)$$

The deviation of Δx with time is given by:

$$\frac{d(\Delta x)}{dt} = k_1(a - x) - k_{-2}x^2$$

But $x = \Delta x + x_e$ and hence, we have:

$$\frac{d(\Delta x)}{dt} = k_1[a - \Delta x - x_e] - k_{-2}[\Delta x + x_e]^2 \dots (5)$$

$$\frac{d(\Delta x)}{dt} = k_1a - k_1\Delta x - k_1x_e - k_{-2}\Delta x^2 - k_{-2}x_e^2 - 2k_{-2}\Delta xx_e$$

Since Δx^2 is very small, its value can be neglected and hence, we have:

$$\frac{d(\Delta x)}{dt} = k_1(a - x_e) - k_1\Delta x - k_{-2}x_e^2 - 2k_{-2}\Delta xx_e \dots (6)$$

From equation (3), we have:

$$k_1(a - x_e) = k_{-2}x_e^2$$

Therefore, the equation (6) is written as:

$$\frac{d(\Delta x)}{dt} = k_{-2}x_e^2 - k_1\Delta x - k_{-2}x_e^2 - 2k_{-2}\Delta xx_e$$

$$\frac{d(\Delta x)}{dt} = -k_1\Delta x - 2k_{-2}\Delta xx_e$$

(or)

$$\frac{d(\Delta x)}{dt} = -\Delta x[k_1 + 2k_{-2}x_e]$$

$$\frac{d(\Delta x)}{dt} = -\Delta x \cdot k_r \dots (7)$$

Where $k_r = [k_1 + 2k_{-2}x_e]$ is known as relaxation constant.

The reciprocal of relaxation constant is known as relaxation time (τ^*).

$$\tau^* = \frac{1}{k_r} = \frac{1}{[k_1 + 2k_{-2}x_e]}$$

Rearranging equation (7), we have:

$$\frac{d(\Delta x)}{\Delta x} = -k_r dt \dots (8)$$

Since the quantity Δx varies with time, integrating the equation (8) subjected to the boundary conditions $\Delta x = \Delta x_o \rightarrow \Delta x$ when $t = 0 \rightarrow t$, we have:

$$\int_{\Delta x = \Delta x_o}^{\Delta x = \Delta x} \frac{d(\Delta x)}{\Delta x} = -k_r \int_{t=0}^{t=t} dt$$

$$\ln \frac{\Delta x}{\Delta x_o} = -k_r t$$

$$\frac{\Delta x}{\Delta x_o} = e^{-k_r t}$$

$$\Delta x = \Delta x_o e^{-k_r t}$$

Where $k_r = k_1 + 2k_{-2}$.

Exercise: 1

The relaxation time for fast reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$ is $10 \mu s$ and the equilibrium constant is 1×10^{-3} . Calculate the rate constant for forward and reversible reaction.

The relaxation time for the given fast reaction is given as:

$$\tau^* = \frac{1}{[k_1 + k_{-1}]} = 10 \mu s = 10 \times 10^{-6} s = 10^{-5} s$$

Since the k_1 is far greater than k_{-1} ($k_1 \ll k_{-1}$),

$$\tau^* = \frac{1}{k_1}$$

(or)

$$10^{-5} s = \frac{1}{k_1}$$

$$k_1 = 10^5 s^{-1}$$

We know that the equilibrium constant (K) for the given reversible reaction is:

$$K = \frac{k_1}{k_{-1}}$$

Given that the equilibrium constant for the given fast reaction is 1×10^{-3} . Therefore, the rate constant for reversible reaction is:

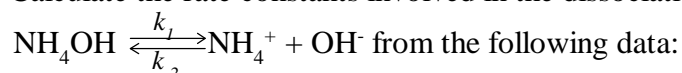
$$k_{-1} = \frac{k_1}{K}$$

$$k_{-1} = \frac{10^5}{1 \times 10^{-3}} s^{-1}$$

$$k_{-1} = 10^8 s^{-1}$$

Exercise: 2

Calculate the rate constants involved in the dissociation of:



A 0.1 M solution of NH_4OH is subjected to a sudden T-jump terminating at 25°C at which the equilibrium constant is $1.8 \times 10^{-5} \text{ mol dm}^{-3}$. The observed relaxation time is $0.109 \mu\text{s}$ and x_e is $4.1 \times 10^{-4} \text{ mol dm}^{-3}$.

Given:

$$K = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

$$x_e = 4.1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\tau^* = 0.109 \mu\text{s} = 0.109 \times 10^{-6} \text{ s}$$

The relaxation constant for the given reaction which is first order forward and second order reverse is given as:

$$k_r = k_1 + 2k_{-2}x_e \quad \dots (1)$$

Further, we know that the equilibrium constant (K) for the given reversible reaction is:

$$K = \frac{k_1}{k_{-2}} \quad \dots (2)$$

(or)

$$k_{-2} = \frac{k_1}{K} \quad \dots (3)$$

Substituting the equation (3) in equation (1), we get:

$$k_r = k_1 + 2 \frac{k_1}{K} x_e$$

(or)

$$k_r = k_1 \left[1 + \frac{2x_e}{K} \right]$$

(or)

$$k_1 = \frac{k_r}{\left[1 + \frac{2x_e}{K} \right]}$$

But,

$$k_r = \frac{1}{\tau^*}$$

(or)

$$k_r = \frac{1}{0.109 \times 10^{-6} \text{ s}} = 9.2 \times 10^6 \text{ s}^{-1}$$

Therefore,

$$k_1 = \frac{9.2 \times 10^6 \text{ s}^{-1}}{\left[1 + \frac{2 \times 4.1 \times 10^{-4}}{1.8 \times 10^{-5}} \right]}$$

$$k_1 = \frac{9.2 \times 10^6 s^{-1}}{46.5}$$

$$k_1 = 1.9 \times 10^5 s^{-1}$$

From equation (2), we have:

$$K = \frac{k_1}{k_{-2}}$$

(or)

$$k_{-2} = \frac{k_1}{K}$$

$$k_{-2} = \frac{1.9 \times 10^5 s^{-1}}{1.8 \times 10^{-5}}$$

$$k_{-2} = 1.05 \times 10^{10} s^{-1}$$

2. Chemical relaxation by Pressure Jump Method (P-Jump Method)

- ⇒ In P-jump method, the perturbation of a chemical system is achieved by rising the pressure from ambient to some higher values and a subsequent sudden drop back to the ambient pressure.
- ⇒ The sudden change in pressure shifts the chemical equilibrium which is described by Van't Hoff equation as:

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = - \frac{\Delta V^o}{RT}$$

Where ΔV^o is the change in volume by the application of pressure.

- ⇒ In P-jump method, the experimental liquid is placed in a flexible cell. It is provided with two electrodes and connected with a Wheatstone bridge to follow the attainment of new equilibrium. When pressure is dropped to the atmospheric pressure (Fig. 2.2).
- ⇒ The experimental cell is placed in a pressure vessel filled with an inert liquid such as xylene and by using a pressure gauge, a pressure of about 65 atmospheres is set up in the pressure vessel.
- ⇒ Now the pressure is reduced to one atmosphere in about 10^{-4} seconds by puncturing a thin metal disc set into the wall of the pressure vessel.
- ⇒ The sudden drop of pressure causes the sample to attain a new equilibrium, which is followed by measuring the electrical conductance of the liquid using the Wheatstone bridge.

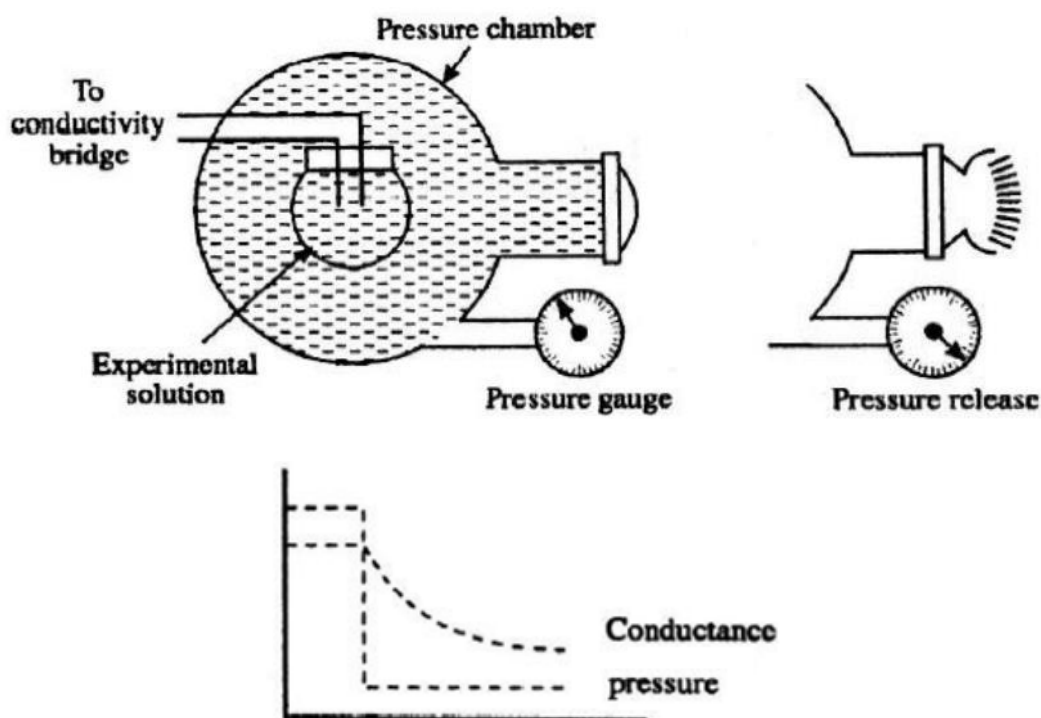


Fig. 2.2: Apparatus for Pressure-Jump Method: The Reaction is Followed by Measuring the Electrical Conductance

4. FLOW METHODS

In flow studies of fast reactions, streams of two reactant solutions are forced under pressure to meet in a mixing chamber, from which the mixed solution passes to an observation chamber. These methods have been reviewed by Caldin and Chance.

Flow methods function in the time range of (approximately) 1 millisecond to 10 second, so they very usefully extend the range of conventional batch mixing. Unlike relaxation kinetics, flow methods are applicable to irreversible reactions.

1. Continuous Flow Method

- ⇒ The continuous flow method was developed in 1923 by Hartridge and Roughton in aid of their study of the kinetics of the reaction between hemoglobin and oxygen.
- ⇒ The principle is shown schematically in Fig. 2.3.
- ⇒ In this method, the solutions of reactants A and B are forced by pistons into the mixing chamber, whose design contributes to rapid mixing.
- ⇒ The mixed solution flows into an observation tube, where detection by spectroscopy takes place a distance d downstream from the mixer.
- ⇒ With continuing injection of reactant solutions, a steady state is set up in the observation tube, the concentrations at any point being independent of time.

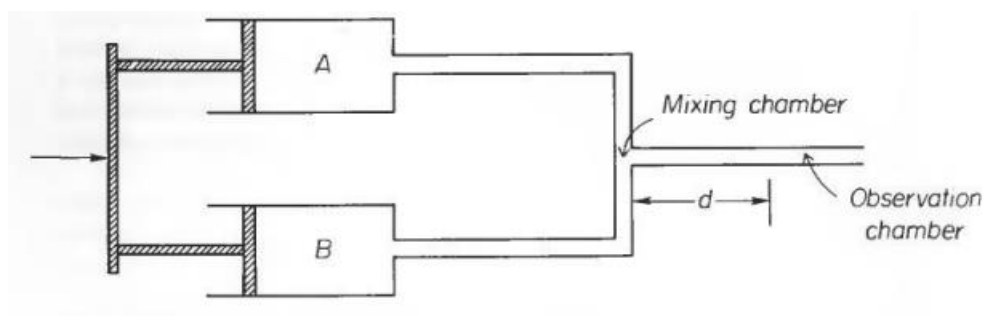


Fig. 2.3: Schematic diagram of continuous flow kinetic system. The quantity d is the distance from the mixer to the point of observation

⇒ If v is the flow velocity, the distance d is related to reaction time given by:

$$t = \frac{d}{v}$$

⇒ Thus, with a flow velocity of 10 m s^{-1} , a distance of 1 cm corresponds to 1 millisecond. The time course of the reaction is determined by varying d or v .

⇒ Continuous flow devices have undergone careful development, and mixing chambers are very efficient. Mixing is essentially complete in about 1 ms, and half-lives as short as 1 ms may be measured.

⇒ An interesting advantage of the continuous flow method is that the analytical method need not have a fast response, since the concentrations are at steady state. Of course, the slower the detection method, the greater the volumes of reactant solutions that will be consumed.

⇒ In 1923 several liters of solution were required, but now reactions can be studied with 10-100 ml.

⇒ Two techniques conceptually related to classical continuous flow make use of different injection methods.

⇒ In one of these, a reactant solution formed into a highspeed jet is injected through a sheet or film of the second solution. The jet speed is 40 ms^{-1} , and the mixing time is $1 \mu\text{s}$.

⇒ In the second technique, two streams of microdroplets (about $100 \mu\text{m}$ diameter, 40 kHz generation frequency, 15 ms^{-1} velocity) collide to form a single droplet stream, which is observed by Raman spectroscopy. The mixing time is $200 \mu\text{s}$.

Exercise:

Calculate the reaction time when the flow is made at 1, 5, and 10 cm distance along a tube with the flow rate of 20 ms^{-1} .

Given:

$$d = 1, 5, 10 \text{ cm}$$

$$v = 20 \text{ ms}^{-1} = 20 \times 100 \text{ cms}^{-1}$$

$$t = ?$$

We know from the continuous flow techniques, the flow velocity (v) and the distance d is related to reaction time given by:

$$t = \frac{d}{v}$$

When $d = 1$

$$t = \frac{1}{2000} = 5 \times 10^{-4} \text{ s}$$

When $d = 5$

$$t = \frac{5}{2000} = 2.5 \times 10^{-3} \text{ s}$$

When $d = 10$

$$t = \frac{10}{2000} = 5 \times 10^{-3} \text{ s}$$

2. Stopped Flow Method

- ⇒ Stopped flow is probably the most widely used of methods for the study of fast reactions, because stopped-flow apparatus is commercially available at modest cost.
- ⇒ As with continuous flow, the reactant solutions are forced from cylinders or syringes, they meet in a mixing chamber, and the mixture flows into an observation tube. However, in stopped flow method, after a few milliseconds the flow is abruptly stopped by forcing of a stopping piston against an arrest.

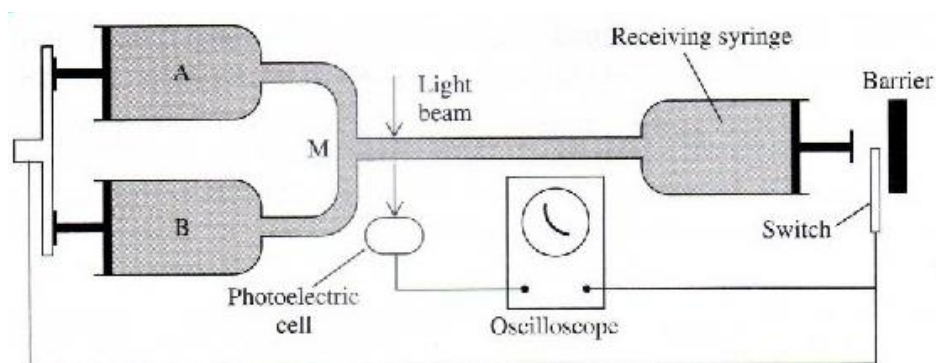


Fig. 2.4: Schematic diagram of stopped flow kinetic system

- ⇒ Progress of reaction is observed by a fast response analytical method (usually spectrophotometry or fluorimetry) is then made as a function of time by using an oscilloscope.
- ⇒ The stopped-flow method is, therefore, exactly analogous to conventional batch mixing kinetic studies.
- ⇒ The dead time is typically 3-5 milliseconds, so stopped flow is not quite as fast as continuous flow, but it requires less than a millilitre of each solution per run.

- ⇒ Stopped flow is sometimes described as concentration jump kinetics. Variations on the technique include the injection of solvent, the combination of stopped flow with T-jump, and the use of NMR as the analytical method so as to detect short lived intermediates.

5. KINETICS OF LARGE PERTURBATION METHODS

Flash photolysis and shock tube methods apply a large perturbation to a reactive system and thereby generating one or more reactive species as free radicals and intermediates. The reactions are followed by spectroscopic methods.

1. Shock Tube Method

- ⇒ A number of fast gaseous reactions have been investigated using shock tubes.
- ⇒ The reaction system is taken in a long metal tube, through which a shock wave is passed.
- ⇒ As the shock wave traverses an element of gas, the temperature of gas rises sharply and reaction occurs in and behind the shock front.
- ⇒ The course of reaction and temperature may be determined by various methods. Various designs of shock tubes have been employed and one such is shown schematically in Fig. 2.5.
- ⇒ The tube is divided into two parts, viz. a high pressure and low-pressure end, separated by a thin diaphragm made of a metal foil or other material.

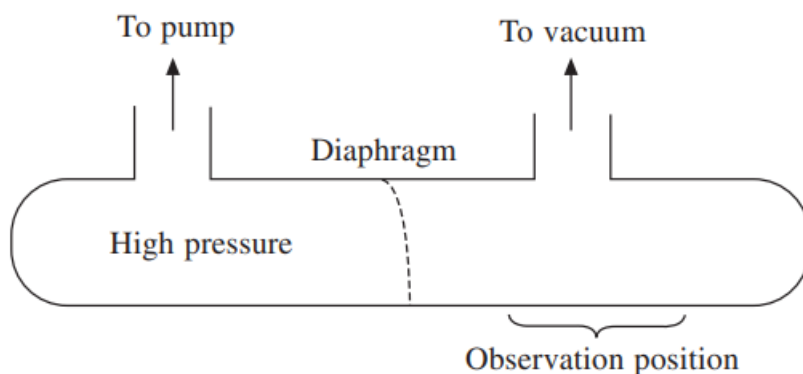


Fig. 2.5: Shock Tube

- ⇒ The appropriate reactants and precursors are kept in the low-pressure compartment while an inert gas is kept in a high-pressure compartment.
- ⇒ The diaphragm is burst either by mechanical means or by increasing the pressure.
- ⇒ To initiate the reaction, the diaphragm is punctured and a plane shock wave moves along the tube.
- ⇒ At start, wave is not sharp because of initial turbulence. After traveling a short distance, the wave becomes a true shock wave in which there is a very sharp boundary between high and low-pressure region.

- ⇒ As the wave travels, the gas is rapidly raised to a very high temperature and the reaction of the species produces excited states of atoms and free radicals. The reaction of these species is followed by observation of their absorption spectra using the mobile detector.
- ⇒ The sharp change in temperature, pressure, density or electrical conductivity etc. can also be used as tool for the detection of the arrival of the shock front.
- ⇒ The shock wave technique has successfully been applied to study the vibrational and rotational energy transfers between gaseous molecules.

2. Flash Photolysis

- ⇒ The reaction is initiated by an intense flash of visible or ultraviolet light generated by a photoflash lamp.
- ⇒ The duration of the flash, about 5 to 15 microseconds is shorter than the reaction time scale.
- ⇒ The intermediates generated can be probed in real time using spectroscopic methods. The absorption spectrum of the intermediate has to be determined at fixed intervals after the initial flash
- ⇒ The reaction cell (RC) is a quartz cylinder of length up to 1 m. Both the ends of the cylinder are plane windows (Fig. 2.6).

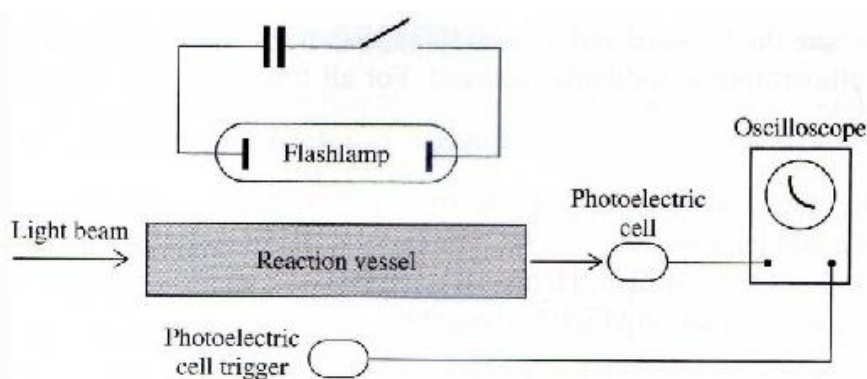


Fig. 2.6: Apparatus for Flash Photolysis

- ⇒ The photoflash lamp tube is parallel to the reaction cell. Suitably placed reflectors increase the intensity of light falling on the sample.
- ⇒ The photoflash lamp has a capacitor connected to the two electrodes of the lamp. For short flashes (ns) the energy dissipated from the lamp is small (microjoules) for millisecond flashes, the energy dissipated is several hundred joules.
- ⇒ The absorption spectrum of intermediates/products is obtained using a second lamp (the spectroflash) at one end of the reaction cell.
- ⇒ The spectroflash energy and duration have to be adjusted so that it does not interfere with the ongoing photochemistry in the reaction cell, but has sufficient intensity to be detected in the detector, kept at the other end.

6. KINETICS OF PERIODIC PERTURBATION METHODS

Ultrasonic Absorption Technique

- ⇒ In this technique, the sound waves are passed through the reaction mixture and the velocity (or) absorption of sound is measured for a series of frequency of the sound waves.
- ⇒ The periodic relaxation diagram can be drawn by plotting the absorption of ultrasonic wave through a mixture on its frequency (Fig. 2.7).

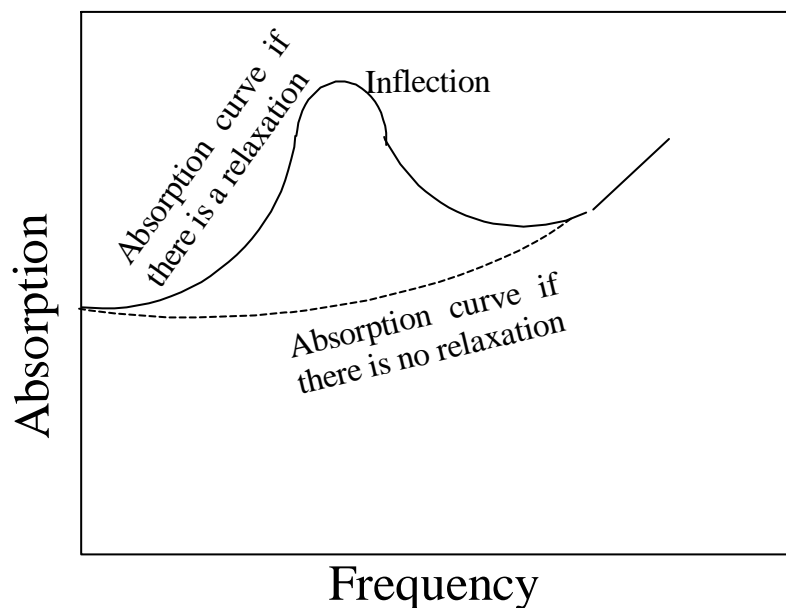


Fig. 2.7: Periodic Relaxation Diagram (Absorption versus Frequency)

- ⇒ From each point of inflection, the maximum relaxation time can be found directly and the rate constant can be calculated by using the expression, $\tau = 1/k$.

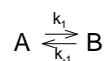
References

1. Keith J. Laidler, Chemical Kinetics, Pearson Education India, 3rd Edition, 2003.
2. John W. Moore and Ralph G. Pearson, Kinetics and Mechanism, Wiley, 3rd Edition, 1981.
3. C. Kalidas C, Chemical Kinetic Methods, New Age International, 1996.
4. F. Wilkinson, Chemical Kinetics and Reaction Mechanism, Van Nostrand Reinhold Co., 2000.

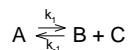
REVIEW QUESTIONS

1. Explain stopped flow method for studying kinetics of fast reactions.
2. Explain the fast reactions with their characteristics.
3. Discuss pressure jump method for studying fast reactions.
4. Discuss how a fast reaction can be initiated and studied by flash photolysis.
5. Discuss how a fast reaction can be initiated and studied by shock tube method.
6. Discuss ultrasonic absorption technique for studying fast reactions.
7. Explain with a neat diagram, how a fast reaction kinetics studied by temperature jump method.

8. Compare stopped flow and continuous flow methods for studying fast reactions.
9. Illustrate the technique used in studying kinetics of fast reactions. What is meant by the term relaxation time?
10. Explain flow methods for studying fast reactions.
11. Develop the relationship between relaxation time and rate constant for the following reaction?
What is relaxation time?



12. Develop the relationship between relaxation time and rate constant for the following reaction?
What is relaxation time?



13. Discuss chemical relaxation technique with reference to jump methods.
14. Explain large perturbation methods for studying the kinetics of fast reactions.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – III –Kinetics of Polymerisation–SCYA5202

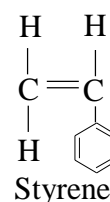
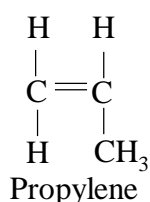
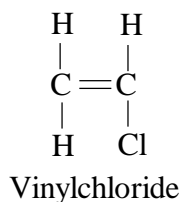
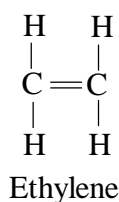
1. INTRODUCTION TO POLYMER SCIENCE

1. Monomer

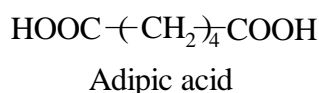
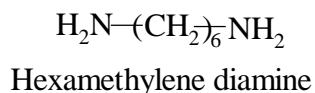
Definition: Monomer is a simple molecule consisting of two or more bonding sites through which it interacts with other simple molecules to form a polymer. All simple molecules do not qualify as monomers. The essential requirements of a simple molecule to qualify as a monomer are:

- ❖ It must possess at least two active centres (bonding sites) in the form of double bonds. (or)
- ❖ It must have at least two reactive, same or different functional groups.

Examples of Type-I Monomers



Examples of Type-II Monomers



2. Polymer

Definition: Polymer is a macromolecule formed by the combination of large number of one or more types of small molecules of low molecular weight called monomer.

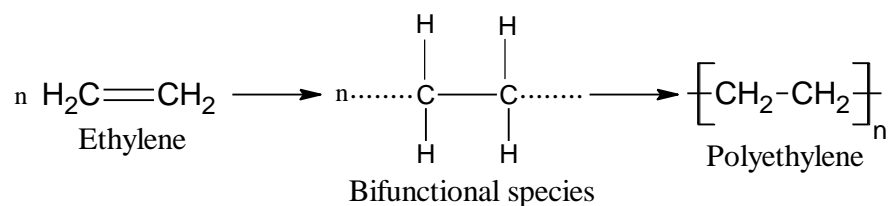
3. Addition (or) Chain Growth Polymerisation

Monomers having multiple bonds (double or triple bond) undergo addition polymerisation. Monomers combine to give addition polymer through addition reaction and no other by-products. Therefore, molecular weight of the resulting polymer will be an integral multiple of the molecular weight of monomers.

❖ Examples of Condensation Polymerisation

Polymerisation of Ethylene

Polyethylene is obtained by polymerisation of ethylene monomers. The ethylene monomer can be obtained by dehydrogenation of ethane and by dehydration of ethyl alcohol. The first step in the polymerisation is molecular rearrangement to produce a bi-functional molecule. In presence of suitable catalysts, these activated molecules join together to form a long chain polyethylene.



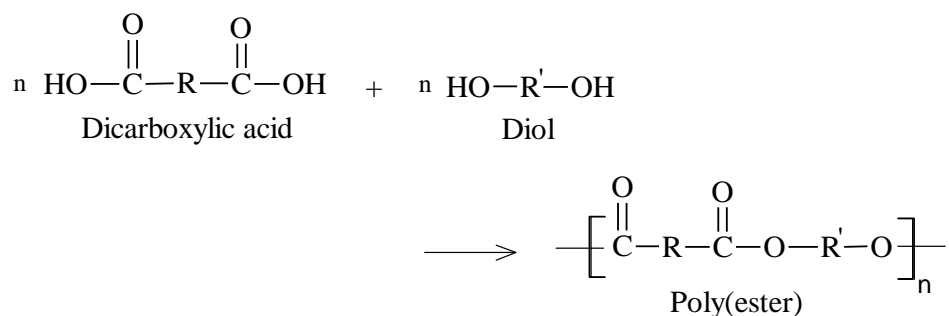
4. Condensation (or) Step Polymerisation

- Monomers having same type or different type of functional groups undergo condensation polymerisation.
- The polymerisation proceeds by step wise reaction between reactive functional groups and small molecules are eliminated.
- Therefore, molecular weight of polymer will not be an integral multiple of the molecular weight of monomers.
- Condensation polymers are hard, strong and more brittle. They are insoluble in almost all organic solvents because of strong bonds and cross linking.

❖ Examples of Condensation Polymerisation

Polyesters

Polyester is obtained by the reaction of a dicarboxylic acid with a diol.



2. MECHANISM OF ADDITION POLYMERISATION

1. Free Radical Mechanism

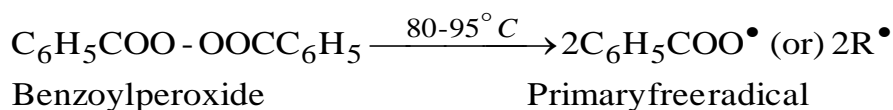
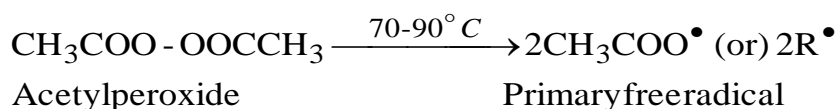
Free radical mechanism follows three main steps:

- (i) Chain initiation
- (ii) Chain propagation and
- (iii) Chain termination.

1. Chain Initiation

Chain initiation involves two reactions:

Production of primary free radical by homolytic dissociation of thermal initiator.



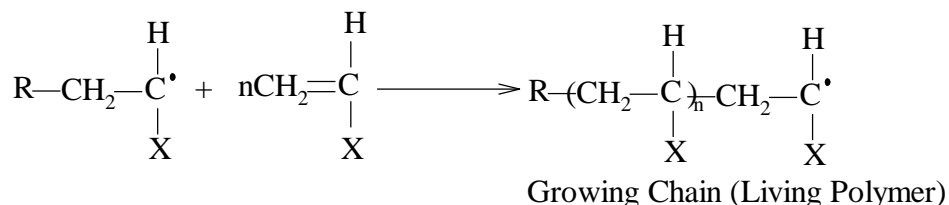
- represents free radical.

(i) Addition of this free radical to the first monomer to produce chain initiating species.



2. Chain Propagation

Propagation consists of the growth of chain initiating species by successive addition of large number of monomer molecules one by one.

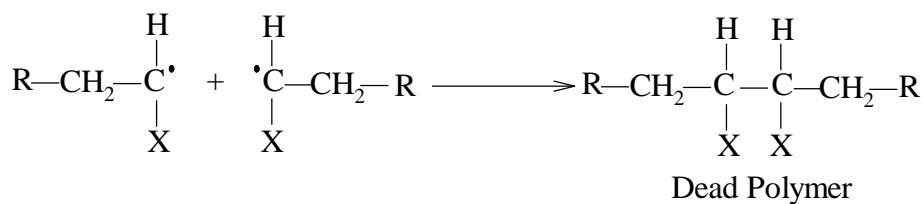


The growing chain of the polymer is known as **living polymer**.

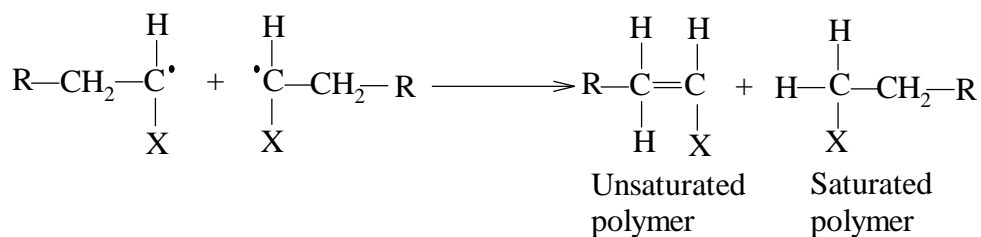
3. Chain Termination

Termination of living polymer may occur due to:

Combination or Coupling of free radical of one chain end to another free radical forming a macromolecule.



Disproportionation involves transfer of a hydrogen atom of one chain end to another to form two macromolecules (one saturated and another unsaturated).



The product of addition polymerisation is called as **dead polymer**.

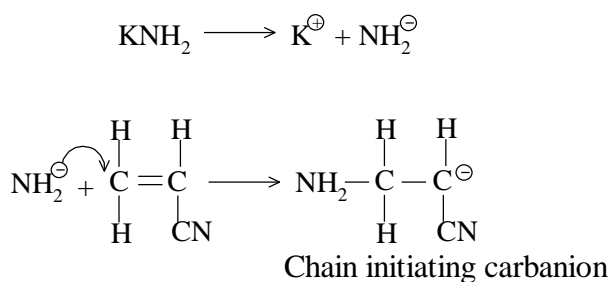
2. Anionic Mechanism

Monomers containing electronegative groups like Cl^- , CN^- at one of the carbon atoms connected by the double bond follow this mechanism. The catalysts used to initiate the reaction are KNH_2 , NaNH_2 (Lewis bases).

❖ **Examples:** Vinyl chloride, Acrylonitrile.

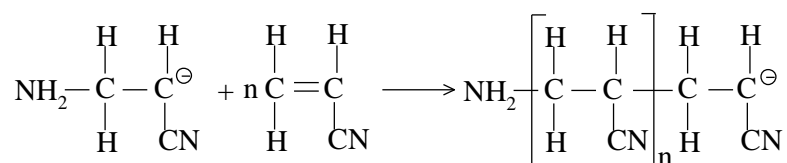
1. Chain Initiation

It involves the formation of chain initiating **carbanion**.



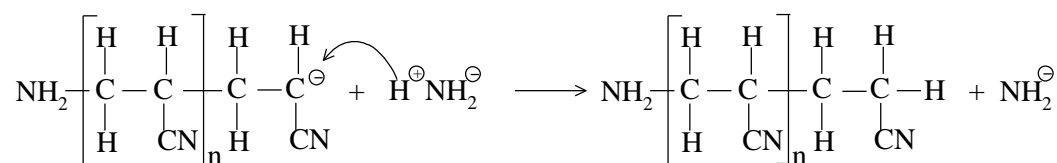
2. Chain Propagation

It involves the growth of chain initiating **carbanion** by successive addition of large number of monomers one by one. The growth involves the transfer of negative charge along the chain.



3. Chain Termination

Termination of growing chain occurs by the reaction of growing **carbanion** chain with the medium of the polymerisation like ammonia.



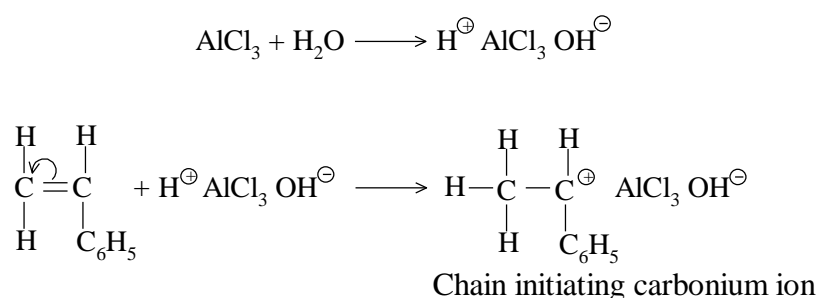
3. Cationic Mechanism

Monomers containing electropositive groups like CH_3 , C_6H_5 at one of the carbon atoms connected by the double bond follow this mechanism. The catalysts used to initiate the reaction are AlCl_3 , BF_3 (Lewis acids).

❖ **Examples:** Isoprene, Styrene.

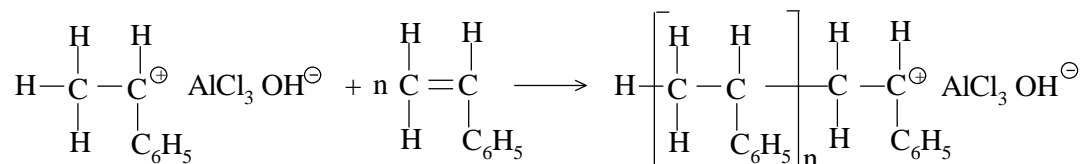
1. Chain Initiation

It involves the formation of chain initiating **carbonium ion**.



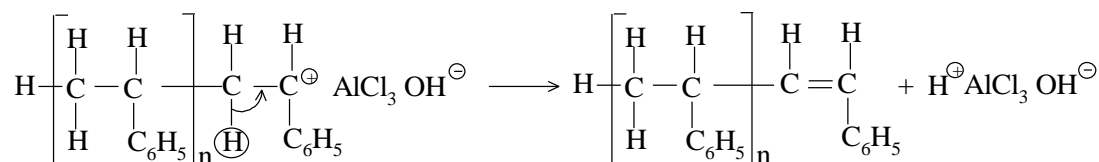
2. Chain Propagation

It involves the growth of chain initiating **carbonium** ion by successive addition of large number of monomers one by one. The growth involves the transfer of positive charge along the chain.



3. Chain Termination

It involves the splitting of the catalyst from the growing chain of polymer.



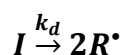
3. KINETICS OF FREE RADICAL POLYMERISATION

Kinetics of free radical polymerization involves three steps:

Step 1: Chain Initiation

It consists of two steps: In the first step, the initiator I dissociates into two molecules of primary free radicals (R^{\bullet}).

$$I = I_0 - e^{-kt} \quad \dots \dots (1)$$



The rate of dissociation of the initiator, I is given by:

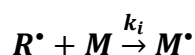
$$\frac{-d[I]}{dt} = k_d[I] \quad \dots (1)$$

Or) the rate of formation of free radical is given as:

$$\frac{+d[R^\bullet]}{dt} = 2k_d[I] \quad \dots (2)$$

Since the reaction takes place by two events.

In the second step, the primary free radical combines with the first monomer M to give chain initiating carrier.



Further, the rate of formation of chain carrier is given by:

$$\frac{d[M^\bullet]}{dt} = k_i[R^\bullet][M] \quad \dots (3)$$

Applying steady state approximation with respect to R^\bullet , we have:

The rate of formation of R^\bullet = The rate of conversion of R^\bullet into M^\bullet

$$2k_d[I] = k_i[R^\bullet][M]$$

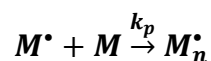
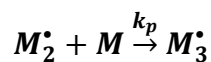
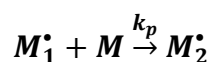
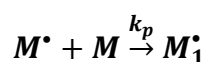
$$\frac{d[M^\bullet]}{dt} = 2k_d[I]$$

Therefore, the rate of chain initiation is given as:

$$R_i = 2k_d[I] \quad \dots (4)$$

Step 2: Chain Propagation

It involves the growth of chain initiating carrier by successive addition of large number monomers one by one.



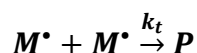
Since the chain growth is independent of chain length, all these steps take place with a rate constant of k_p .

Therefore, the rate of propagation is given as:

$$R_p = k_p [M^\bullet] [M] \quad \dots (5)$$

Step 3: Chain Termination

It takes place by mutual combination of chain carriers, and it proceeds with the rate constant, k_t .



Therefore, the rate of chain termination is given as:

$$R_t = 2k_t [M^\bullet]^2 \quad \dots (6)$$

In any number of terminations, two number of chain carriers are involved.

Applying SSA to M^\bullet in order to evaluate in terms of measurable quantities, we have:

Rate of formation of M^\bullet = Rate of termination of M^\bullet

$$R_i = R_t$$

$$2k_d[I] = 2k_t [M^\bullet]^2$$

$$[M^\bullet]^2 = \frac{k_d[I]}{k_t}$$

$$[M^\bullet] = \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} \quad \dots (7)$$

But, the rate of polymerisation depends upon the rate of propagation, and hence:

The rate of polymerisation = $k_p [M^\bullet] [M]$

$$R_p = k_p \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M]$$

(or)

$$R_p = k_p \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} f^* [I]^{\frac{1}{2}} [M] \quad \dots (8)$$

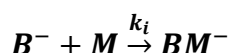
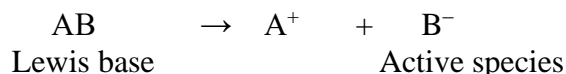
Where f^* the fraction of R^\bullet which is efficient for the production of chain carrier $[M^\bullet]$.

4. KINETICS OF ANIONIC POLYMERISATION

The monomers like vinyl chloride, acrylonitrile follow anionic polymerisation. The Lewis base like NaNH_2 or KNH_2 acts as the catalyst. The kinetics of anionic polymerisation also involves three steps.

Step 1: Chain Initiation

In the first step Lewis base dissociates to give the active species. The active species in turn attacks the the first monomer to give a carbanion chain carrier.



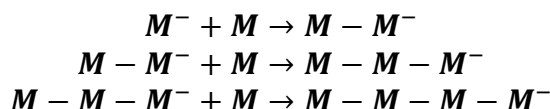
Where, BM^- is a carbanion chain carrier.

Therefore, the rate of initiation is given by:

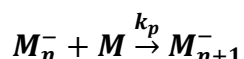
$$R_i = k_i[\text{B}^-][\text{M}] \quad \dots (1)$$

Step 2: Chain Propagation

It consists of the growth of anionic chain carrier by successive addition of large number of monomers one by one.



(or)

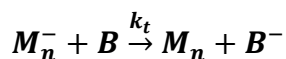


Therefore, the rate of propagation is given by:

$$R_p = k_p[\text{M}_n^-][\text{M}] \quad \dots (2)$$

Step 3: Chain Termination

The growing chain can be terminated by using excess of suitable solvent.



Therefore, the rate of termination is given by:

$$R_t = k_t[\text{M}_n^-][\text{B}] \quad \dots (3)$$

Applying SSA to the intermediate species M_n^- , we have:

The rate of formation of M_n^- = The rate of termination of M_n^-

$$k_i[B^-][M] = k_t[M_n^-][B]$$

$$[M_n^-] = \frac{k_i[B^-]}{k_t[B]}[M] \quad \dots (4)$$

We know that,

The rate of polymerisation = The rate of propagation

$$R_p = k_p[M_n^-][M] \quad \dots (5)$$

Substituting $[M_n^-]$ in equation (5), we get:

$$R_p = k_p \frac{k_i[B^-]}{k_t[B]} [M]^2 \quad \dots (6)$$

The kinetic chain length of polymers is defined as the average number of monomers reacting with active species to form a polymer from initiation to termination.

(or)

$$\text{The kinetic chain length} = \frac{\text{Rate of polymerisation}}{\text{Rate of initiation}}$$

$$KCL = \frac{k_p \frac{k_i[B^-]}{k_t[B]} [M]^2}{k_i[B^-][M]}$$

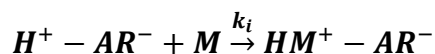
$$KCL = \frac{k_i[M]}{k_t[B]}$$

5. KINETICS OF CATIONIC POLYMERISATION

The monomers like propylene, styrene follow anionic polymerisation. The Lewis acid like $AlCl_3$ or BF_3 acts as catalyst and water is used as co-catalyst. The kinetics of cationic polymerisation involves three steps.

Step 1: Chain Initiation

In the first step Lewis acid reacts with the cocatalyst to give the active species. The active species in turn attacks the first monomer to give a carbonium ion chain carrier.



Where, $HM^+ - AR^-$ is a carbonium ion chain carrier.

Therefore, the rate of initiation is given by:

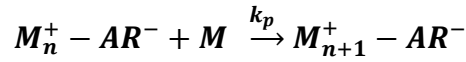
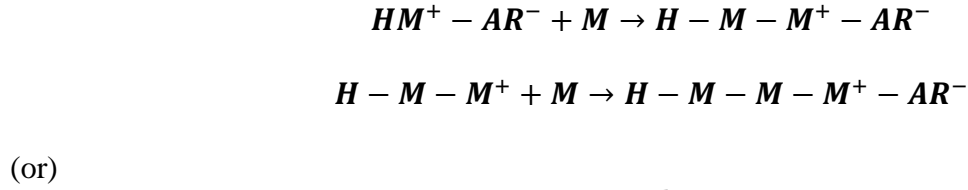
$$R_i = k_i[H^+ - AR^-] [M]$$

(or)

$$R_i = k_i k[A] [RH][M] \quad \dots (1)$$

Step 2: Chain Propagation

It consists of the growth of cationic chain carrier by successive addition of large number of monomers one by one.

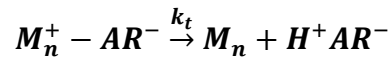


Therefore, the rate of propagation is given by:

$$R_p = k_p[M_n^+ - AR^-] [M] \quad \dots (2)$$

Step 3: Chain Termination

It involves the transfer of H⁺ ion from the end of growing chain to AR⁻.



Therefore, the rate of termination is given by:

$$R_t = k_t[M_n^+ - AR^-] \quad \dots (3)$$

Applying SSA to the intermediate species $M_n^+ - AR^-$, we have:

The rate of formation of $M_n^+ - AR^-$ = The rate of termination of $M_n^+ - AR^-$

$$k_i k[A] [RH][M] = k_t[M_n^+ - AR^-]$$

$$[M_n^+ - AR^-] = \frac{k k_i}{k_t} [A] [RH][M] \quad \dots (4)$$

We know that,

The rate of polymerisation = The rate of propagation

$$R_p = k_p[M_n^+ - AR^-] [M] \quad \dots (5)$$

Substituting $M_n^+ - AR^-$ in equation (5), we get:

$$R_p = k_p \frac{k k_i}{k_t} [A] [RH] [M]^2 \quad \dots (6)$$

The kinetic chain length of polymers is defined as the average number of monomers reacting with active species to form a polymer from initiation to termination.

(or)

The kinetic chain length = $\frac{\text{Rate of polymerisation}}{\text{Rate of initiation}}$

$$KCL = \frac{k_p \frac{k k_i}{k_t} [A] [RH] [M]^2}{k_i k [A] [RH] [M]}$$

$$KCL = \frac{k_p}{k_t} [M]$$

6. MOLECULAR WEIGHT OF POLYMERS

Polymers are normally a mixture consisting of different chain lengths. Hence it is not possible to assign a definite molecular weight to a polymer. In practice, statistical methods are adopted for assigning average molecular weight of polymers.

1. Number Average Molecular Weight (\overline{M}_n)

It is defined as the ratio of sum of molecular weights of individual molecules to the total number of molecules in the mixture.

If a polymer mixture contains n_1 molecules with molecular weight M_1 , n_2 molecules with molecular weight M_2 till n_i molecules with molecular weight M_i then,

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + \dots + n_i M_i}{n_1 + n_2 + \dots + n_i}$$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

2. Weight Average Molecular Weight (\overline{M}_w)

It is defined as the ratio of sum of weights of individual polymer molecules to the total weight of polymer molecules in the mixture.

In a polymer mixture, if w_1 is the weight of polymer with molecular weight M_1 , w_2 is the weight of polymer with molecular weight M_2 till w_i is the weight of polymer with molecular weight M_i then,

$$\overline{M}_w = \frac{w_1 M_1 + w_2 M_2 + \cdots + w_i M_i}{w_1 + w_2 + \cdots + w_i}$$

$$\overline{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

But, number of moles $n = \frac{w}{M}$ and $w = nM$.

Therefore, replacing w_1 by $n_1 M_1$, w_2 by $n_2 M_2$, and w_i by $n_i M_i$, then we have:

$$\overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + \cdots + n_i M_i^2}{n_1 M_1 + n_2 M_2 + \cdots + n_i M_i}$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum n_i M_i}{\sum n_i}$$

3. Viscosity Average Molecular Weight

From the measurements of viscosity of solutions of polymers, it is possible to determine the average molecular weight of the polymer.

The molecular weight of a polymer is proportional to the intrinsic viscosity of its solution (η_i) when the polymer molecular chain is extended to its full contour length.

The relationship between intrinsic viscosity and molecular weight is given by Mark-Hownik's equation.

$$\eta_i = K M^\alpha$$

Where,

- ✓ K and α are constants that depend on the polymer, solvent and temperature.
- ✓ M is the average molecular weight of the polymer.

(or)
$$\log M = \frac{\log \eta_i - \log K}{\alpha}$$

➤ The intrinsic viscosity of the polymer can be determined by U-tube viscometer.

$$\eta_i = \frac{1}{C} \times \left[\frac{\eta}{\eta_o} - 1 \right]$$

Where,

- ✓ η_o and η are the viscosity of the solvent and the solution respectively.
- ✓ C is the concentration of the polymer, usually in wt. %.

7. DETERMINATION OF MOLECULAR WEIGHT OF POLYMERS BY LIGHT SCATTERING METHOD

1. Determination of Molecular Weight of Polymers by Light Scattering Method

⇒ Light scattering method is useful in case of polymers of very high molecular weights, particularly above 10,000 – 1,00,000.

⇒ This method is based on the scattering of light by a colloidal solution, i.e., Tyndal effect.

⇒ The fraction of incident light scattered in all direction increases with the increase in the number and size of particles in the solution and this causes the turbid appearance of the most of the polymer or colloidal solution.

⇒ The intensity of transmitted light (I) can be obtained from well-known Beer-Lambert's and is given by:

$$I = I_o - e^{-Tl} \quad \dots\dots(1)$$

- ✓ Where I_o is the intensity of incident light falling on solution column;
- ✓ I is the intensity of transmitted light after travelling length l in solution column
- ✓ and T is solution turbidity.

⇒ Polymer solution turbidity is defined as the fraction of incident light scattered per centimeter length of solution through which it passes.

⇒ The polymer solution turbidity can be determined by measuring the decrease in intensity of transmitted light from the intensity of incident light after scattering.

⇒ Turbidity of polymer solution is related to molecular weight of the macromolecule by the equation:

$$T = HCM \quad \dots\dots(2)$$

$$(or) \quad \frac{1}{M} = \frac{HC}{T} \quad \dots\dots(3)$$

⇒ Where T is solution turbidity and is inversely is inversely proportional to the fourth power of the wave length of light used (λ); M is the molecular weight of macromolecule; C is the concentration of sol (gm/cc) and H is constant.

⇒ The constant H is defined as:

$$H = \frac{32\pi^3 n_o^2 \left(\frac{n - n_o}{C} \right)}{3N\lambda^4} \quad \dots\dots(4)$$

where n_o is the refractive index of the pure solvent, n is the refractive index of the polymer solution, dn/C is the refractive index increment of the solute/solvent system, λ is the wavelength of the light used and N is the Avogadro's number.

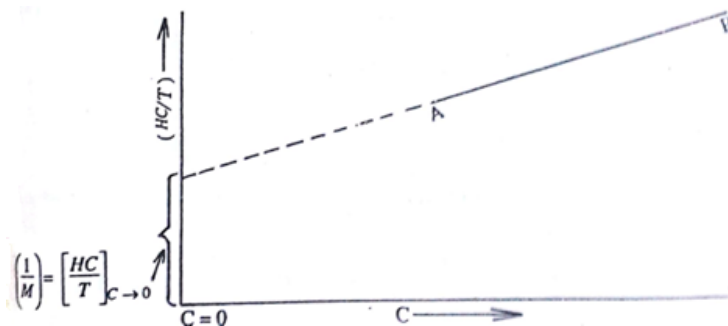
⇒ The refractive index increment is a measure of the optical contrast between the solute molecules and the solvent. The value of refractive index increment dn/C can be determined by measuring the refractive index of solutions of different concentrations of the solute molecules.

⇒ Equation (3) is strictly valid when $C \rightarrow 0$, so we get:

$$(or) \quad \frac{1}{M} = \left(\frac{HC}{T} \right)_{C \rightarrow 0} \dots\dots(5)$$

⇒ In order to determine M of the polymer, we must find out T values at different dilutions of the polymer solution so that the quantity HC/T can be calculated for different concentrations.

⇒ If a graph is plotted between HC/T against C , a straight line is obtained. When this line is extrapolated to zero concentration, we get the intercept on HC/T -axis which gives value of $1/M$, and thus the molecular weight is calculated.



2. Determination of Molecular Weight of Polymers by Ultracentrifuge Method (Sedimentation Velocity Method)

Principle

⇒ When a colloidal solution is left in vessel, the solution particles tend to settle to bottom under the influence of gravity. This phenomenon is called sedimentation.

⇒ Unless the solution particles are large, the sedimentation under gravity occurs at very slow rate.

⇒ However, the rate of sedimentation can be highly increased if the solution is put under very large gravitational force, which can be artificially created by means of ultracentrifuge. This technique was introduced by Svederg.

⇒ Ultracentrifuge is a very high-speed centrifuge in which the sedimentation occurs under very high centrifugal force of rotation.

⇒ The speed of rotation is so high that an acceleration as high as million times that of gravity is attained.

⇒ The polymer solution is kept in ultracentrifuge and the rate of sedimentation is noted.

⇒ Knowing rate of sedimentation (velocity of sedimentation), it is possible to calculate the molecular weight of polymer.

⇒ The determination of molecular weight of polymers by ultracentrifuge can be done by two methods: Sedimentation velocity method and Sedimentation equilibrium method.

Sedimentation Velocity Method

⇒ The acceleration in a centrifugal field is given by:

$$\text{Acceleration in a centrifugal field} = \omega^2 x \quad \dots\dots(1)$$

Where,

ω is the angular velocity (radian/sec) = $2\pi \times$ revolutions per second (speed of rotation of centrifuge);

x is the distance of setting particles from the axis of rotation.

⇒ The velocity of sedimentation under centrifugal field is given by:

$$\frac{dx}{dt} = \frac{2r^2(d_p - d_m)\omega^2 x}{9\eta} \quad \dots\dots(2)$$

Where,

dx/dt is velocity of sedimentation;

r is the radius of the particle (cm);

d_p is the density of particle (gm/cc);

d_m is the density of medium (solvent) and

η is the viscosity of medium (poise).

⇒ Rewriting equation (2)

$$\frac{dx}{x} = \frac{2r^2(d_p - d_m)\omega^2 dt}{9\eta} \quad \dots\dots(2)$$

⇒ On integration

$$\int_{x_1}^{x_2} \frac{dx}{x} = \frac{2r^2(d_p - d_m)\omega^2}{9\eta} \int_{t_1}^{t_2} dt \quad \dots\dots(3)$$

$$\ln x_2 - \ln x_1 = \frac{2r^2(d_p - d_m)\omega^2(t_2 - t_1)}{9\eta} \quad \dots\dots(4)$$

$$\frac{\ln\left(\frac{x_2}{x_1}\right)}{\omega^2(t_2 - t_1)} = \frac{2r^2(d_p - d_m)}{9\eta} \quad \dots\dots(5)$$

$$(or) S = \frac{2r^2(d_p - d_m)}{9\eta} \quad \dots\dots(6)$$

$$where S = \frac{\ln\left(\frac{x_2}{x_1}\right)}{\omega^2(t_2 - t_1)} \quad \dots\dots(7)$$

⇒ **S is called sedimentation constant of coefficient.**

⇒ The sedimentation constant S can be calculated by equation (7) knowing x and t at two stages of sedimentation and speed of rotation of centrifuge (ω).

⇒ Knowing S , the radius of particle (r) can be calculated by using the equation (6).

⇒ Assuming the polymer particle to be spherical, its volume can be taken as the mass of the particle and is given by:

$$M = \frac{4}{3} \pi r^3 \quad \dots\dots(8)$$

⇒ Molecular Weight = Mass of Particle (mass = volume \times density) $\times N$ (where N is Avogadro's number)

$$M = \frac{4}{3} \pi r^3 d_p N \quad \dots\dots(9)$$

⇒ This method gives weight average molecular weight of polymer. It is important to note that the equation (6) applies to uniform spherical particles of polymer.

References

1. Keith J. Laidler, Chemical Kinetics, Pearson Education India, 3rd Edition, 2003.
2. John W. Moore and Ralph G. Pearson, Kinetics and Mechanism, Wiley, 3rd Edition, 1981.
3. F. Wilkinson, Chemical Kinetics and Reaction Mechanism, Van Nostrand Reinhold Co., 2000.
4. V.R. Gowarikar, N.V. Vishwanathan and Jayadev Sreedhar, Polymer Science, 2nd Edition, New Age International Publishers, 2006.
5. F.W. Billmeyer, Textbook of Polymer Science, John Wiley & Sons, 3rd Edition, 1990.

REVIEW QUESTIONS

1. Distinguish chain growth and step growth polymerization.
2. Explain the mechanism of cationic polymerization.
3. Explain carbanion mechanism of addition polymerization.
4. Illustrate number average molecular weight.
5. Explain weight average molecular weight of polymers.
6. Explain the kinetic chain length of polymers.
7. Discuss free radical mechanism of addition polymerization.
8. Discuss the kinetics of free radical polymerization.
9. Discuss the kinetics of anionic polymerization. What is kinetic chain length?
10. Discuss the kinetics of cationic polymerization. What is kinetic chain length?
11. Explain different ways for expressing molar masses of polymers.
12. Discuss light scattering method for determining the molar mass of polymers.
13. Explain an ultracentrifuge method for the determination of molecular weight of polymers.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – IV – Adsorption – SCYA5202

1. ADSORPTION ISOTHERMS

⇒ The amount of gas adsorbed on the surface of adsorbent depends on pressure and temperature, i.e., the amount of gas adsorbed is a function of temperature and pressure only. If 'x' is the amount gas adsorbed on mass 'm' of adsorbent at pressure (P) and temperature (T), it may be mathematically expressed as:

$$\frac{x}{m} = f(P, T) \quad \dots(1)$$

⇒ This mathematical equation is called adsorption curve. The equation (1) gives three types adsorption curves under different conditions of P, T and x/m.

1. Adsorption Isotherm: If T is kept constant, then the equation (1) becomes:

$$\frac{x}{m} = f(P) \quad \dots(2)$$

Equation (2) explains the variation of x/m with pressure at constant temperature. Adsorption isotherm is defined as the variation of amount of substance adsorbed per unit mass of adsorbent with pressure at constant temperature.

2. Adsorption Isobar: If P is kept constant, then the equation (1) becomes:

$$\frac{x}{m} = f(T) \quad \dots(3)$$

Equation (3) explains the variation of x/m with temperature at constant pressure. Adsorption isobar is defined as the variation of amount of substance adsorbed per unit mass of adsorbent with temperature at constant pressure. Equation (3) is called adsorption isobar. It explains the variation of adsorption with temperature at constant pressure.

3. Adsorption Isostere: If the amount of adsorbed gas x/m is kept constant, then the equation (1) becomes:

$$P = f(T) \quad \dots(4)$$

The equation (4) is called adsorption isostere. It explains the variation of pressure with temperature when the amount of gas adsorbed is kept constant.

Types of Adsorption Isotherms

⇒ A plot obtained between the amounts of substance adsorbed per unit mass of the adsorbent and the equilibrium pressure (in the case of a gas) or concentration (in the case of solution) at constant temperature is known as adsorption isotherm.

⇒ Five different types of adsorption isotherms have been observed in the adsorption of gases on solids. In the case of chemisorption, only Type I is observed while in the case of physical adsorption all the five isotherms are observed.

1. Type I Adsorption Isotherm

⇒ Type 1 adsorption isotherm is a typical Langmuir isotherm because the adsorption leads to monolayer formation. The curve represents that after certain value of P , there is no change in x/m with the increase of pressure. i.e., it shows limiting or saturation state after certain value of P (Fig. 4.1).

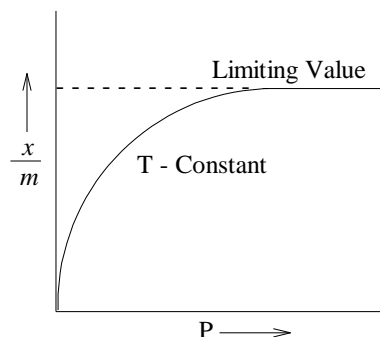


Fig. 4.1: Type I Adsorption Isotherm: Adsorption of N_2 on charcoal at $-183^\circ C$

2. Type II Adsorption Isotherm

⇒ It represents a multi-molecular layer physical adsorption on non-porous materials. The curve shows that there is a transition point, B that represents the pressure at which the formation of monolayer is complete and that of multilayer is being started (Fig. 4.2).

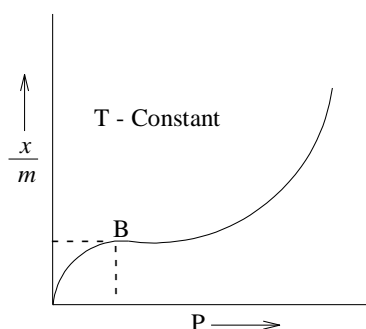


Fig. 4.2: Type II Adsorption Isotherm: Adsorption of N_2 on silica gel at $-195^\circ C$

3. Type III Adsorption Isotherm

⇒ It represents a case of physical adsorption on porous materials. The curve represents that multi molecular layer formation starts even before the completion of monomolecular layer formation (Fig. 4.3).

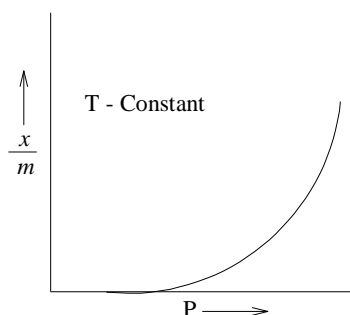


Fig. 4.3: Type III Adsorption Isotherm: Adsorption of I_2 vapours on silica gel at $83^\circ C$

4. Type IV Adsorption Isotherm

⇒ It also represents a case of physical adsorption on porous materials accompanied by capillary condensation. This isotherm indicates that there is a tendency for saturation state to be reached in the multi molecular region (Fig. 4.4).

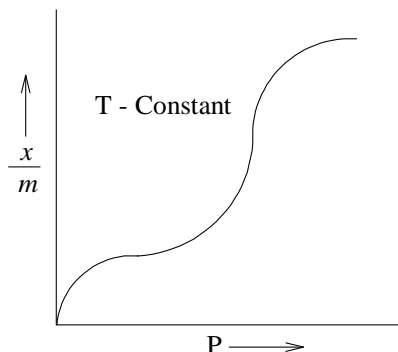


Fig. 4.4: Type IV Adsorption Isotherm: Adsorption of benzene vapours on ferric oxide gel at 50°C

5. Type V Adsorption Isotherm

⇒ It also represents a case of physical adsorption on porous material. It indicates that the formation of multi molecular layer starts in the beginning (Fig. 4.5).

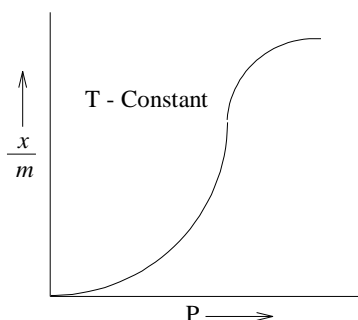


Fig. 4.5: Type V Adsorption isotherm: Adsorption of water vapour on charcoal at 100 °C

2. THE LANGMUIR ADSORPTION ISOTHERM

Postulates Assumptions of Langmuir Adsorption Isotherm

- ⇒ The adsorbed gas forms only a unimolecular layer on the solid adsorbent (i.e.: adsorbed gas is unimolecular in thickness).
- ⇒ The adsorbed molecules on the surface do not interact with each other.
- ⇒ The molecules of a gas are adsorbed only on vacant sites of the adsorbent surface. Each site can hold only one molecular species of the adsorbate.
- ⇒ The process of adsorption is a dynamic process, which consists of two opposite processes.

- Condensation (Adsorption) Process: It involves the condensation (adsorption) of molecules of the gas on the surface of the solid.
- Evaporation (Desorption) Process: It involves evaporation (desorption) of molecules of the adsorbate from the surface of the adsorbent.

Derivation of Langmuir Adsorption Isotherm

⇒ Consider an adsorbing surface of area 1 square centimeter is exposed to a gas (Fig. 4.6). Molecules of the gas will strike the surface and stick for an appreciable time due to condensation while other gas molecules will evaporate from the surface due to thermal agitation.

⇒ If θ is the fraction of surface area covered by gas molecules at any instant, then the fraction of the remaining surface available for adsorption is $(1-\theta)$.

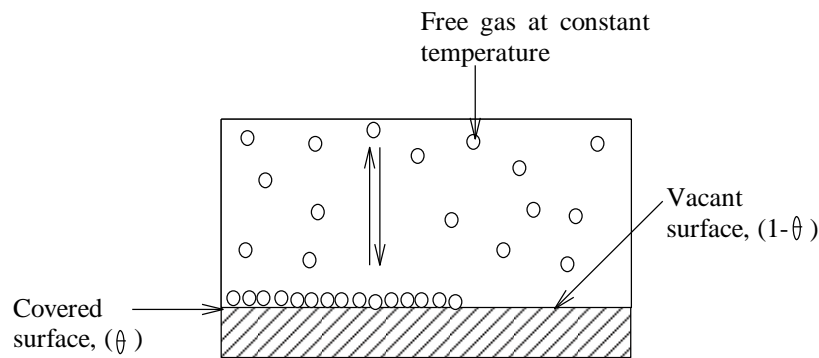


Fig. 4.6: Equilibrium between free molecules and adsorbed molecules

⇒ If P is the pressure of the gas, then the rate of condensation (adsorption) molecules is expected to be proportional to the pressure, P and fraction of uncovered surface, $(1-\theta)$. Hence,

$$\text{The rate of adsorption} = k_1(1-\theta)P \quad \dots(1)$$

⇒ The rate at which gas molecules evaporates from the surface (desorption) will depend on the fraction of the surface covered by the gas molecules, (θ) . Hence,

$$\begin{aligned} \text{The rate of evaporation of gas} &= k_2\theta \\ \text{molecules} & \end{aligned} \quad \dots(2)$$

where k_1 and k_2 are proportionality constants for a given system.

⇒ At equilibrium, the rate of adsorption and the rate of evaporation are equal, then,

$$k_1(1-\theta)P = k_2\theta$$

$$k_1P - k_1P\theta = k_2\theta$$

$$k_1P = k_2\theta + k_1P\theta$$

$$k_1P = \theta(k_2 + k_1P)$$

$$\theta = \frac{k_1 P}{k_2 + k_1 P} \quad \dots(3)$$

⇒ Dividing the numerator and denominator of the right-hand side of equation (3) by k_2 , we get:

$$\theta = \frac{\left(\frac{k_1}{k_2}\right)P}{1 + \left(\frac{k_1}{k_2}\right)P}$$

$$\theta = \frac{bP}{1 + bP} \quad \dots(4)$$

where $b = k_1/k_2$ and is called adsorption coefficient.

⇒ If x is the amount of gas adsorbed on the mass m of the adsorbent, then x/m is the amount of gas adsorbed per unit mass of the adsorbent.

⇒ Since the amount of gas adsorbed per unit mass of adsorbent (x/m) is proportional to the fraction (θ) of the surface covered, then

$$\frac{x}{m} \propto \theta$$

$$\frac{x}{m} = k \theta$$

$$\theta = \frac{x}{km} \quad \dots(5)$$

where k is proportionality constant.

⇒ Substituting the value of θ in equation (4), we have

$$\frac{x}{km} = \frac{bP}{1 + bP}$$

$$\frac{x}{m} = \frac{kbP}{1 + bP}$$

$$\frac{x}{m} = \frac{aP}{1 + bP} \quad \dots(6)$$

where the constant $a = kb$.

⇒ Equation (6) relates the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as the Langmuir adsorption isotherm.

⇒ The constant a and b depend on the nature of the system and on the temperature. In order to test this isotherm, the *equation (6)* is divided by P on both sides, we get:

$$\frac{\left(\frac{x}{m}\right)}{P} = \frac{1}{P} \left[\frac{aP}{1 + bP} \right] \quad \dots(7)$$

⇒ Further taking reciprocals, we get:

$$\frac{P}{\left(\frac{x}{m}\right)} = \frac{P(1 + bP)}{aP}$$

$$\frac{P}{\left(\frac{x}{m}\right)} = \frac{(1 + bP)}{a}$$

$$\frac{P}{\left(\frac{x}{m}\right)} = \frac{1}{a} + \left(\frac{b}{a}\right) P \quad \dots(8)$$

⇒ This equation is similar to an equation for a straight line ($y = mx + c$). Hence if $P/(x/m)$ is plotted against P , a straight line should be obtained with a slope equal to (b/a) and intercept equal to $(1/a)$.

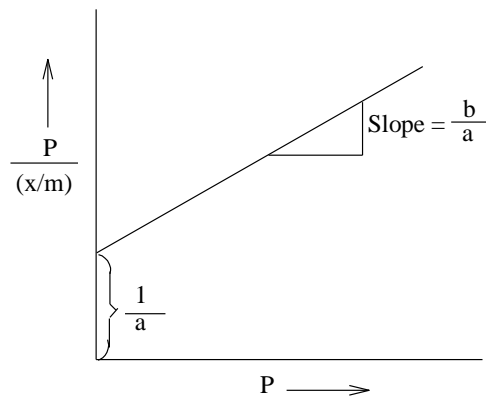


Fig. 4.7: Langmuir Adsorption Isotherm

❖ Testing of Langmuir Adsorption Isotherm

⇒ We shall now consider three special cases of Langmuir isotherm.

$$\frac{P}{\left(\frac{x}{m}\right)} = \frac{1 + bP}{a} \quad \dots(9)$$

Case 1: At very low pressures, bP can be neglected in comparison with unity (i.e: $bP \ll 1$) and hence,

$$\frac{P}{\left(\frac{x}{m}\right)} = \frac{1}{a}$$

$$\frac{x}{m} = a P$$

At very low pressures, the amount of gas adsorbed is directly proportional to the pressure.

Case 2: At high pressures $bP \gg 1$, and hence 1 can be neglected in comparison with bP .

$$\frac{P}{\left(\frac{x}{m}\right)} = \left(\frac{b}{a}\right) P$$

$$\frac{x}{m} = \frac{a}{b} \quad \dots(10)$$

At very high pressures, the extent of adsorption at a given temperature is independent of pressure of the gas. This condition arises when the surface of the adsorbent is completely covered by the unimolecular layer of gas molecules.

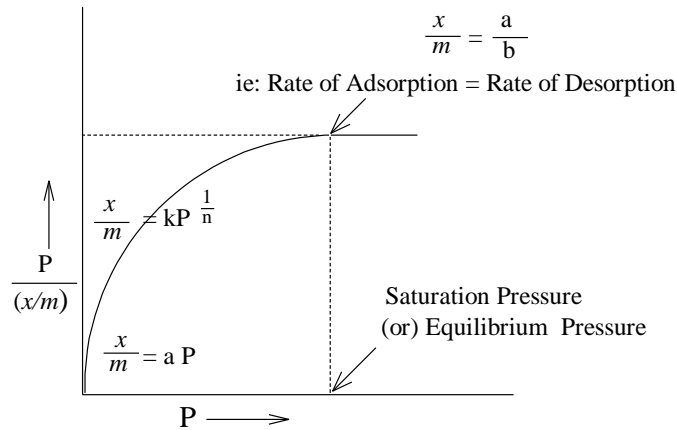


Fig. 4.8: Testing of Langmuir Adsorption Isotherm

Case 3: At intermediate pressure, Langmuir equation becomes Freundlich equation.

At very low pressure,

$$\frac{x}{m} \propto P$$

$$\frac{x}{m} = k P$$

At very high pressure,

$$\frac{x}{m} = k$$

At intermediate pressure, the equation becomes:

$$\frac{x}{m} = k P^{\frac{1}{n}}$$

where the value n lies between 0 and 1. This equation is known as *Freundlich equation*.

3. THE BET THEORY OF MULTIMOLECULAR LAYER ISOTHERM AND DETERMINATION OF SURFACE AREA OF ADSORBENTS

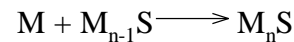
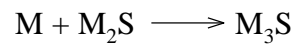
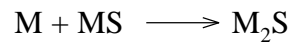
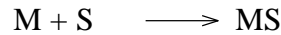
Postulates of Brunauer-Emmett-Teller (BET) adsorption isotherm

- ⇒ The adsorption involves the formation of multimolecular layer of adsorbate molecules on the surface of solid adsorbent.
- ⇒ The multilayer adsorption takes place the following manner:

Vapour + Free surface of adsorbent	————>	Monolayer
Vapour + Monolayer	————>	Bimolecular layer
Vapour + Bimolecular layer	————>	Trimolecular layer
Vapour + Trimolecular layer	————>	Multimolecular layer
- ⇒ Langmuir assumption applies to each layer and there is a dynamic equilibrium exists between the successive layer. Further, the rate of from the first layer is equal to the rate of condensation of preceding layer.
- ⇒ The heat of adsorption in each layer (except the first layer) is involved in each of the evaporation process. After the formation of first layer, the heat of adsorption is equal to the latent heat of condensation of vapours.

Derivation BET adsorption isotherm

- ⇒ We can represent the formation of multilayer of gas molecules on the surface of adsorbent can be explained with following equilibrium equations:



- ⇒ Where M is the unadsorbed gas molecules and S is the active sites on the adsorbent surface; MS is the single layer formed; M₂S is the second layer formed and so on. There is always an equilibrium exists between the adsorbate and adsorbent.

- ⇒ The equilibrium constant can be written as:

$$k_1 = \frac{[MS]}{[M][S]}; \quad k_2 = \frac{[M_2S]}{[M][MS]}; \quad k_3 = \frac{[M_3S]}{[M][M_2S]} \quad \text{and so on} \quad (1)$$

- ⇒ We know that P is the pressure of gas molecules and M is the un-adsorbed molecules. Further, let θ_0 be free surface area available for adsorption; θ_1 is fraction of free surface area available after formation of monolayer; θ_2 is fraction of free surface area available after formation of second layer; θ_3 is fraction of free surface area available after formation of third layer and so on.

⇒ Therefore, the adsorption of unadsorbed molecule on the surface of adsorbent, $[S] \propto P$ and $[M] = \theta_o$; $[MS] = \theta_1$; $[M_2S] = \theta_2$; $[M_3S] = \theta_3$ and so on.

⇒ Substituting the above θ values in equation (1), we have:

$$k_1 = \frac{\theta_1}{P\theta_o}; \quad k_2 = \frac{\theta_2}{P\theta_1}; \quad k_3 = \frac{\theta_3}{P\theta_2} \quad (2)$$

⇒ The value of k_1 is usually very large as compared to the other equilibrium constant. This is due to the increase in distance from the adsorbent surface and the interaction gas molecules and solid adsorbent.

⇒ Therefore, k_2, k_3, k_4 etc. much smaller than k_1 .

⇒ So, $k_2 \approx k_3 \approx k_L$ (3)

⇒ where k_L is the equilibrium constant corresponding to saturated vapour liquid equilibrium system and it may be represented mathematically as:

$$k_L = \frac{1}{P_o} \quad (4)$$

⇒ Where P_o is the total vapour pressure using approximation of (3), and the various equilibria of (2) can be written as:

$$k_1 = \frac{\theta_1}{P\theta_o}; \quad k_2 = \frac{\theta_2}{P\theta_1} = k_L; \quad k_3 = \frac{\theta_3}{P\theta_2} = k_L \quad \text{and so on} \quad (5)$$

⇒ Rearranging the above equation by making use of (4), we have:

$$\theta_1 = k_1 P \theta_o; \quad \theta_2 = k_L P \theta_1; \quad \theta_3 = k_L P \theta_2 \quad \text{and so on} \quad (6)$$

⇒ If we assume that the entire adsorbent surface is covered, then the total coverage of the first layer is given by:

$$\theta_{tot} = \theta_o + \theta_1 + \theta_2 + \theta_3 + \dots = 1 \quad (7)$$

⇒ Substituting (6) in (7), we get:

$$\theta_{tot} = \theta_o + k_1 P \theta_o + k_1 P \left(\frac{P}{P_o} \right) \theta_o + k_1 P \left(\frac{P}{P_o} \right)^2 \theta_o + \dots$$

$$\theta_{tot} = \theta_o \left[k_1 P + k_1 P \left(\frac{P}{P_o} \right) + k_1 P \left(\frac{P}{P_o} \right)^2 + \dots \right]$$

$$\theta_{tot} = \theta_o \left[1 + k_1 P \left\{ 1 + \left(\frac{P}{P_o} \right) + \left(\frac{P}{P_o} \right)^2 + \dots \right\} \right] \quad (8)$$

$$1 = \theta_o \left[1 + \frac{k_1 P}{1 - \left(\frac{P}{P_o} \right)} \right] \quad \because 1 + x + x^2 + \dots = \frac{1}{1 - x}$$

$$\theta_o = \frac{1}{1 + \frac{k_1 P}{1 - \left(\frac{P}{P_o} \right)}}$$

$$\theta_o = \frac{1 - \left(\frac{P}{P_o} \right)}{1 - \left(\frac{P}{P_o} \right) + k_1 P} \quad (9)$$

\Rightarrow Let V_{tot} be the total number of molecules adsorbed by unit mass of adsorbent and V_m be the total number of surface sites occupied by the adsorbed molecules per unit mass of the adsorbent. Further $V_m \theta_1$ is the number of sites carrying one molecule thick, $V_m \theta_2$ is the number of sites carrying two molecules thick and so on and hence,

$$\therefore V_{tot} = V_m (\theta_1 + 2\theta_2 + 3\theta_3 + \dots) \quad (10)$$

\Rightarrow Substituting $\theta_1, \theta_2, \theta_3$ values in equation (10), we have

$$\therefore V_{tot} = V_m \left[k_1 P \theta_o \left\{ 1 + 2 \left(\frac{P}{P_o} \right) + 3 \left(\frac{P}{P_o} \right)^2 + \dots \right\} \right] \dots \dots \dots (11)$$

$$V_{tot} = V_m \left[k_1 P \theta_o \frac{1}{\left(1 - \frac{P}{P_o} \right)^2} \right] \quad \because 1 + 2x + 3x^2 + \dots = \frac{1}{(1 - x)^2} \quad \dots \dots \dots (12)$$

\Rightarrow Substituting θ_o in (12), we get

$$V_{tot} = V_m \left[\frac{k_1 P}{\left(1 - \frac{P}{P_o} \right)^2} \times \frac{\left(1 - \frac{P}{P_o} \right)}{\left(1 - \frac{P}{P_o} \right) + k_1 P} \right] \quad \dots \dots \dots (13)$$

$$V_{tot} = V_m \left[\frac{k_1 P}{\left(1 - \frac{P}{P_o} \right) \left(1 - \frac{P}{P_o} \right) + k_1 P} \right] \quad \dots \dots \dots (14)$$

⇒ Expansion of P in terms of partial pressure can be written as:

$$P = P_o \times \frac{P_o}{P_o} = P_o \left(\frac{P}{P_o} \right) = \frac{1}{k_L} \left(\frac{P}{P_o} \right) \quad \because k_L = \frac{1}{P_o}$$

⇒ Replacing P by $1/k_L (P/P_o)$ in equation (14), we get

$$V_{tot} = V_m \left[\frac{\left(\frac{k_1}{k_L} \right) \left(\frac{P}{P_o} \right)}{\left(1 - \frac{P}{P_o} \right) \left(1 - \frac{P}{P_o} \right) + \left(\frac{k_1}{k_L} \right) \left(\frac{P}{P_o} \right)} \right] \quad \dots\dots\dots(15)$$

$$V_{tot} = \left[\frac{V_m c \left(\frac{P}{P_o} \right)}{\left(1 - \frac{P}{P_o} \right) \left[1 - \left(\frac{P}{P_o} \right) + c \left(\frac{P}{P_o} \right) \right]} \right] \quad \text{where } c = \left(\frac{k_1}{k_L} \right) \quad \dots\dots\dots(16)$$

⇒ Equation (16) is the required equation for adsorption of gaseous molecules on adsorbent surface and it is known as BET adsorption equation for multi-molecular layer formation.

Determination of surface area covered using BET adsorption equation (Testing of BET adsorption equation)

⇒ Let P/P_o as x and hence BET equation may be represented as:

$$V_{tot} = \left[\frac{V_m c x}{(1-x)[1-x+cx]} \right] \quad \dots\dots\dots(1)$$

$$\frac{V_{tot}(1-x)}{x} = \left[\frac{V_m c}{1-x+cx} \right] \quad \dots\dots\dots(2)$$

$$\frac{x}{V_{tot}(1-x)} = \frac{1-x+cx}{V_m c}$$

$$\frac{x}{V_{tot}(1-x)} = \frac{1+x[-1+c]}{V_m c}$$

$$\frac{x}{V_{tot}(1-x)} = \frac{1}{V_m c} + \frac{x[c-1]}{V_m c}$$

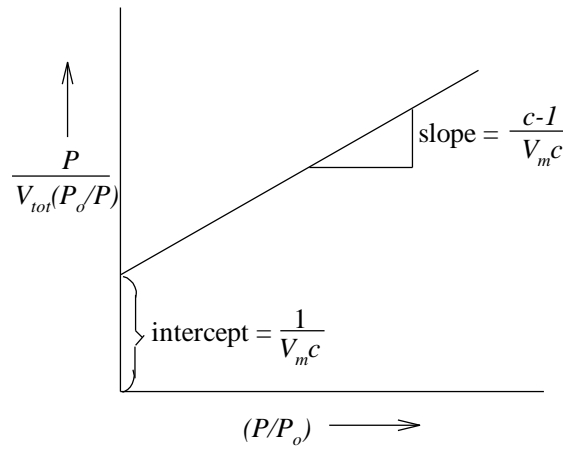
$$\frac{x}{V_{tot}(1-x)} = \frac{1}{V_m c} + \frac{x[c-1]}{V_m c}$$

$$\left(\frac{P}{P_o}\right) \frac{1}{V_{tot} \frac{(P_o - P)}{P}} = \frac{1}{V_m c} + \frac{[c-1]}{V_m c} \left(\frac{P}{P_o}\right)$$

$$\frac{P}{V_{tot}(P_o - P)} = \frac{1}{V_m c} + \frac{[c-1]}{V_m c} \left(\frac{P}{P_o}\right) \quad \dots(3)$$

⇒ Where P/P_o is the relative pressure of the adsorbate; V_{tot} is the total number of gas molecules adsorbed; V_m is the total number of sites occupied by adsorbed molecules per unit mass of the adsorbent; and c is the characteristic constant which depends on nature of adsorbent and adsorbate.

⇒ If we plot $\frac{P}{V_{tot}(P_o - P)}$ versus $\left(\frac{P}{P_o}\right)$, we get slope = $\frac{[c-1]}{V_m c}$ and intercept = $\frac{1}{V_m c}$.



⇒ Adding slope and intercept, we get:

$$\text{slope} + \text{intercept} = \frac{[c-1]}{V_m c} + \frac{1}{V_m c}$$

$$\text{slope} + \text{intercept} = \frac{c-1+1}{V_m c}$$

$$V_m = \frac{1}{\text{slope} + \text{intercept}} \quad \dots(4)$$

⇒ At standard temperature and pressure,

22.4 L will have = N_A molecules

$$V_m \text{ L will have} = \frac{V_m N_A}{22.4} \quad \dots(5)$$

⇒ Let one molecule of an adsorbate occupies an surface area = σ

⇒ Total number of molecules present in one volume will occupy surface area, $S = \frac{\sigma V_m N_A}{22.4}$

4. THE GIBBS ADSORPTION ISOTHERM

❖ Relationship between surface tension of the solution and the concentration of the solute

- ⇒ Excess concentration of solute present at the surface of liquid is called Gibb's surface excess, τ .
- ⇒ Surface tension is due to the presence of unbalanced forces in the surface of liquid; the liquid contracts the area and attain minimum value of surface energy (forces of surface tension).
- ⇒ For a system consisting of a solvent (n_1 – number of moles) and a solute (n_2 – number of moles) [two component system], the Gibb's free energy is given by:

$$G = n_1\mu_1 + n_2\mu_2 + \gamma S \quad \dots(1)$$

- ⇒ Where μ_1 and μ_2 are the chemical potentials of the two components respectively and S is the surface area and γ is the surface energy per unit area.
- ⇒ The complete differential of equation (1) gives the variation of the total Gibb's free energy and is given by:

$$dG = n_1d\mu_1 + \mu_1dn_1 + n_2d\mu_2 + \mu_2dn_2 + \gamma dS + Sd\gamma \quad \dots(2)$$

- ⇒ Therefore the free energy G depends upon five independent variables: $G = f(T, P, n_1, n_2, S)$. Taking partial differentials of (2), we get:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, S} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, S} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, S} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, S} dn_2 + \left(\frac{\partial S}{\partial T}\right)_{T, P, n_1, n_2} dS \quad \dots(3)$$

- ⇒ According to thermodynamics, the partial derives are represented as:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S; \quad \left(\frac{\partial G}{\partial P}\right)_T = V; \quad \left(\frac{\partial G}{\partial n_1}\right) = \mu_1; \text{ and } \left(\frac{\partial G}{\partial n_2}\right) = \mu_2 \quad \dots(4)$$

- ⇒ Substituting (4) in (3), we have:

$$dG = -SdT + VdP + \mu_1dn_1 + \mu_2dn_2 + \gamma dS \quad \dots(5)$$

- ⇒ At constant T and constant P, the equation (5) reduces to:

$$(dG)_{T, P} = \mu_1dn_1 + \mu_2dn_2 + \gamma dS \quad \dots(6)$$

- ⇒ Comparing (2) and (6),

$$n_1d\mu_1 + \mu_1dn_1 + n_2d\mu_2 + \mu_2dn_2 + \gamma dS + Sd\gamma = \mu_1dn_1 + \mu_2dn_2 + \gamma dS \quad \dots(7)$$

$$\therefore n_1d\mu_1 + n_2d\mu_2 + Sd\gamma = 0 \quad \dots(8)$$

⇒ The expression for the free energy change in the bulk phase (devoid of surface energy) is given by:

$$n_1^o d\mu_1 + n_2^o d\mu_2 = 0 \quad \dots(9)$$

$$d\mu_1 = -\frac{n_2^o}{n_1^o} d\mu_2 \quad \dots(10)$$

⇒ Substituting (10) in equation (8), we get,

$$n_1 \left[\frac{-n_2^o}{n_1^o} d\mu_2 \right] d\mu_1 + n_2 d\mu_2 + S d\gamma = 0 \quad \dots(11)$$

$$d\mu_2 \left[n_2 - \frac{n_2^o}{n_1^o} \right] + S d\gamma = 0 \quad \dots(12)$$

$$S d\gamma = -d\mu_2 \left[n_2 - \frac{n_2^o}{n_1^o} \right] \quad \dots(13)$$

$$-\frac{d\gamma}{d\mu_2} = \frac{\left(n_2 - \frac{n_2^o}{n_1^o} \right)}{S} \quad \dots(14)$$

⇒ The above equation involves the difference of two terms: i.e., the amount of solute associated with liquid at the surface and in the bulk phase. The numerator term gives the excessive concentration of solute present at the surface and when it is divided by S gives the excessive concentration of solute per unit surface area, τ_2 .

$$-\frac{d\gamma}{d\mu_2} = \tau_2 \quad \dots(15)$$

⇒ Further the chemical potential of the solute is given by Van't Hoff equation as:

$$\mu_2 = \mu^* + RT \ln a_2 \quad \dots(16)$$

⇒ The equation (16) upon differentiation,

$$d\mu_2 = RT d \ln a_2 \quad \dots(17)$$

⇒ Substituting $d\mu_2$ in (15), we have

$$-\frac{d\gamma}{RT d \ln a_2} = \tau_2$$

$$\frac{-d\gamma}{RT} \times \frac{a_2}{da_2} = \tau_2$$

$$\therefore d(\ln a_2) = \frac{da_2}{a_2} \quad (or) \quad \frac{1}{d(\ln a_2)} = \frac{a_2}{da_2}$$

⇒ For very dilute solution, the term activity is replaced by concentration, c. So, the above equation may be written as:

$$\tau_2 = \frac{-c_2}{RT} \times \frac{d\gamma}{dc_2} \quad \dots(18)$$

⇒ The equation (18) is the require Gibb's adsorption isotherm.

5. SURFACTANTS

Surface-active materials (or surfactants) consist of molecules containing both polar and non-polar parts (amphiphilic).

Classification of Surfactants

1. **Anionic surfactants:** The head-group of an anionic surfactant is negatively charged, which is electrically neutralized by an alkali metal cation. The soaps ($\text{RCOO}^- \text{Na}^+$), alkyl sulfates ($\text{RSO}_4^- \text{Na}^+$) and alkyl benzene sulfonates ($\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$) are the well known examples of the anionic surfactants. These surfactants readily adsorb on the positively charged surfaces.
2. **Cationic surfactants:** The head-group of a cationic surfactant has a positive charge. The cationic surfactants are useful for adsorption on negatively charged surfaces.

Some well known cationic surfactants are, long chain amines ($\text{RNH}_3^+ \text{X}^-$), quaternary ammonium salts [$\text{RN}(\text{CH}_3)_3^+ \text{X}^-$] and quaternary salts of polyethylene oxide-amine derivatives [$\text{RN}(\text{CH}_3)\{(\text{C}_2\text{H}_4\text{O})_x\text{H}\}_2^+ \text{Cl}^-$].

3. **Zwitterionic surfactants:** These surfactants have both positive and negative charges on the surface-active part of the molecule. The long chain amino acids ($\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$), sulfobetaine, [$\text{RN}^+(\text{CH}_3)_2(\text{CH}_2)_x\text{SO}_3^-$] are the well known examples of the zwitterionic surfactants.

The main advantage of these surfactants is that they are compatible with both anionic and cationic surfactants due to the presence of both positive and negative charges.

4. **Non-ionic surfactants:** The nonionic surfactants are second most widely used surfactants in the industry. They do not have any significant electric charge on their surface-active part. Therefore, there is very little or no electrical interaction between the head-groups. These surfactants are stable in presence of electrolytes

The alkyl phenol ethoxylate [$\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$], alcohol ethoxylates [$\text{R}(\text{OC}_2\text{H}_4)_x\text{OH}$], polyoxyethylene mercaptants [$\text{RS}(\text{C}_2\text{H}_4\text{O})_x\text{H}$] are the well known examples of the Non-ionic surfactants.

Formation of Micelles

- ⇒ One fundamental property of the surfactants is to adsorb at the interfaces. Surfactants have another very important property-the property of **self-assembly**.
- ⇒ When sufficient amount of a surfactant is dissolved in water, the surfactant molecules form colloidal clusters. For many ionic surfactants, typically 40–100 surfactant molecules assemble to form such clusters. These are called **micelles**, and the process of formation of micelles is known as **micellization** (Fig.4.9).
- ⇒ The number of surfactant molecules in a micelle is known as **aggregation number**. These clusters can have a wide variety of shape such as spherical, cylindrical and lamellar.

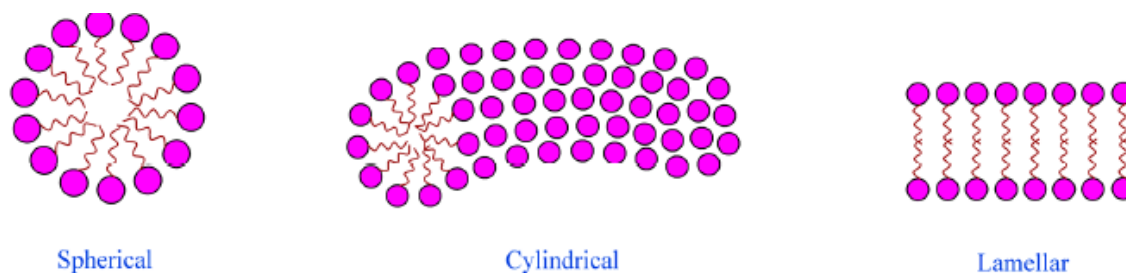


Fig. 4.9: Micelles of various Types

Critical Micelle Concentration (CMC)

- ⇒ The threshold concentration at which the formation of micelle begins is known as **critical micelle concentration (CMC)**.

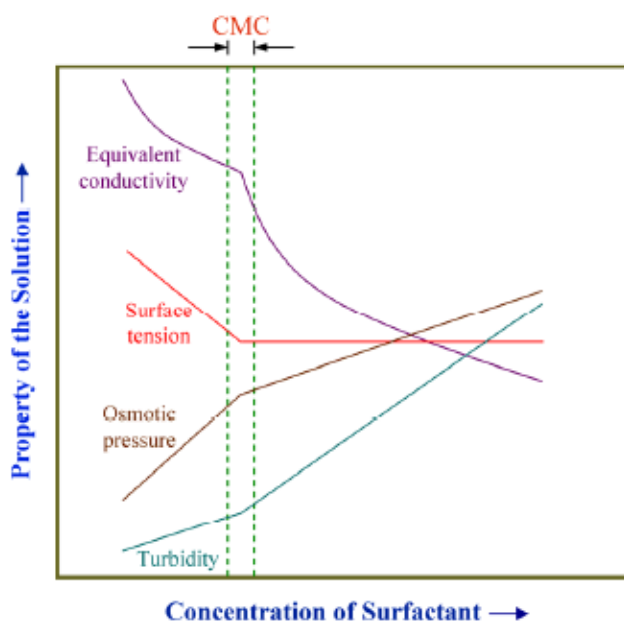


Fig. 4.10: Variation of properties of surfactant solution near the CMC

- ⇒ Several properties of surfactant solution show sharp change in the vicinity of CMC, such as surface tension, equivalent conductivity, osmotic pressure and Turbidity (Fig. 4.10).

- ⇒ These variations can be explained as follows. Near the CMC, the surface is almost saturated by the adsorption of the surfactant molecules. Therefore, the surface tension ceases to decrease when the surfactant concentration is increased beyond the CMC.
- ⇒ The equivalent conductivity of the solution decreases at the CMC owing to the lower mobility of the micelles as compared to the surfactant molecules.
- ⇒ When the critical micelle concentration is approached, the slope of the osmotic pressure curve decreases and the slope of the turbidity curve increases due to the increase in the average molecular weight of the solute.

Thermodynamics of Micellization

- ⇒ Let us consider a surfactant which is represented as S . If the surfactant is ionic, it represents the surface-active part. The effects associated with counterions (e.g., their binding effects) are not considered in the following derivation for simplicity.
- ⇒ When the micelle (S_N) forms, the clustering can be represented by the following reaction.



Where, N is the aggregation number. The aggregation number actually has a statistical distribution rather than a single value as used here.

- ⇒ The reaction represented by Eq. (1) is reversible. The equilibrium constant for this reaction is given by,

$$K = \frac{a_{micelle}}{a_S^N} \quad \dots\dots(2)$$

Where, a represents activity in Eq. (2), expressed in terms of mole fraction. The standard Gibbs free energy change for micelle formation per mole of surfactant is given by,

$$\Delta G^\circ = -\frac{RT \ln K}{N} = -\frac{RT}{N} \ln a_{micelle} + RT \ln a_S \quad \dots\dots(3)$$

- ⇒ At the critical micelle concentration, $a_S = a_{CMC}$. Since N is large, Eq. (3) becomes,

$$\Delta G^\circ \approx RT \ln a_{CMC} \quad \dots\dots(4)$$

- ⇒ The standard Gibbs free energy change due to micellization can be calculated from Eq. (4). The activity is expressed as the product of mole fraction and activity coefficient. For most surfactants, the critical micelle concentration is small ($< 1 \text{ mol/m}^3$). Setting the activity coefficient to unity under the assumption of ideal behavior of the surfactant solution at CMC, Eq. (4) becomes,

$$\Delta G^\circ \approx RT \ln x_{CMC} \quad \dots\dots(5)$$

where x_{CMC} is the mole fraction of surfactant in the solution at CMC. The experimentally determined value of CMC (expressed as mole fraction) can be put in Eq. (5) to calculate ΔG° .

- ⇒ The optimum HLB number for forming an emulsion depends to some extent on the nature of the particular system. Suppose that 20 percent sorbitan tristearate (HLB 2.1) plus 80 per cent polyoxyethylene sorbitan monostearate (HLB 14.9) is the optimum composition of a mixture of these emulsifiers for preparing a particular O/W emulsion. The HLB of the mixture is, therefore, $(0.2 \times 2.1) + (0.8 \times 14.9) = 12.3$. The theory is that an HLB of 12.3 should be optimum for the formation of this particular O/W emulsion by use of other emulsifier systems; for example, the optimum proportions in a mixture of sorbitan mono-oleate (HLB 4.3) and polyoxyethylene sorbitan monopalmitate (HLB 15.6) should be approximately 30 per cent and 70 percent, respectively.

6. EMULSIONS

- ⇒ An emulsion is a dispersed system in which the phases are immiscible or partially miscible liquids.
- ⇒ If the oil is the dispersed phase, the emulsion is termed an oil-in-water (O/W) emulsion; if the aqueous medium is the dispersed phase, the emulsion is termed a water-in-oil (W/O) emulsion.
- ⇒ The emulsions are generally prepared by shaking strongly the mixture of two colloids and these emulsions are generally unstable. The substances added to stabilize the emulsions are called emulsifiers or emulsifying agent.
- ⇒ Emulsions are also classified according to the size of the dispersed droplets.
- ⇒ **Macroemulsions:** At least one immiscible liquid dispersed in another as drops whose diameters generally exceed 100 nm. The stability is improved by the addition of surfactants and/or finely divided solids. Considered only kinetically stable.
- ⇒ **Miniemulsions:** An emulsion with droplets between 100 and 1000 nm, reportedly thermodynamically stable.
- ⇒ **Microemulsions:** A thermodynamically stable, transparent solution of micelles swollen with solubilizate. Microemulsions usually require the presence of both a surfactant and a co-surfactant (e.g. short chain alcohol).
- ⇒ Typical O/W macroemulsions are milk, water-soluble paint, body lotion and mayonnaise, whereas butter and certain skin creams are W/O macroemulsions.
- ⇒ Emulsion is the dispersion of one liquid into another liquid in the form of droplets in presence of one or more surfactants, which act as stabilizer.
- ⇒ Depending on the liquid that forms the dispersed phase, emulsions are classified as oil-in-water (O/W) and water-in-oil (W/O) emulsions. These emulsions have relationship with the HLB values of the surfactants which stabilize them

Hydrophilic–Lipophilic Balance (HLB)

- ⇒ A major commercial use of the surfactants is to formulate emulsion-stabilizing agents, or *emulsifiers*.

- ⇒ Emulsions can be divided into two types: oil-in-water (O/W) emulsions, and water-in-oil (W/O) emulsions. In the oil-in-water type of emulsions, oil droplets are dispersed in the continuous aqueous phase whereas, in water-in-oil type of emulsions, the aqueous phase is dispersed in the continuous oil phase.
- ⇒ Some surfactants stabilize the O/W emulsions whereas the other surfactants are more efficient in stabilizing the W/O emulsions. A rule of thumb is that the most stable emulsion is formed when the surfactant has higher solubility in the continuous phase.
- ⇒ Therefore, according to this rule, a water-soluble surfactant should stabilize oil-in-water emulsions more than water-in-oil emulsions, and the reverse is expected for a surfactant that is soluble in oil. This rule is known as **Bancroft's rule**.
- ⇒ **Griffin** (1949) developed a method to correlate the structural properties of the surfactants with their ability to act as emulsifiers. This method is known as *hydrophilic-lipophilic balance (HLB) method*.
- ⇒ The solubility of surfactants in water varies depending on their HLB value,

Table 4.2: HLB Values and Types of Emulsion Formed

Range of HLB value	Solubility in water	Emulsion type
1–4	Insoluble	Water-in-oil
4–7	Poor unstable dispersion	Water-in-oil
7–9	Stable opaque dispersion	-
10–13	Hazy solution	Oil-in-water
13 and higher	Clear solution	Oil-in-water

- ⇒ As the name suggests, the balance between the hydrophilic and lipophilic parts of the surfactant molecule is important in this method. Values have been assigned to these parts for various surfactants. A group-number method is used for calculating the HLB value of a surfactant from its chemical formula.

$$HLB = \sum \text{Hydrophilic group numbers} - \sum \text{Group number per } CH_2 \text{ group} + 7$$

Stability of Emulsions

- ⇒ Emulsions are thermodynamically unstable systems and their free energy of formation (ΔG_f) is greater than zero. Therefore, they show a tendency to destabilize.
- ⇒ This instability is a result of the energy associated with the large interfacial area of the droplets and γ the interfacial tension between the aqueous and nonaqueous area of the droplets and phases. This energy term outweighs the entropy of formation, ΔS_f associated with the formation of the droplets from the bulk constituents
- ⇒ The free energy of formation of the emulsion is given by,

$$\Delta G_f = \gamma A - T \Delta S_f$$

- ⇒ The interfacial tension in emulsions is generally in the range of 1–10 mN/m. The product of interfacial tension and the large interfacial area produces a large positive interfacial energy term.

- ⇒ The entropy of formation of emulsions is not very large because the number of droplets formed is rather small in entropic terms. These two factors result in $\Delta G_f > 0$, which leads to the thermodynamic instability of the emulsions.
- ⇒ Emulsions are, however, kinetically stable due to the presence of an adsorbed layer of surfactant molecules at the oil–water interface. This layer may provide electrostatic (in the case of an ionic surfactant) or steric (for a nonionic surfactant) repulsion when the droplets approach each other. These monolayers therefore act as barriers and prevent the emulsion droplets from coming into direct contact. They serve to stabilize the thin film of liquid between two adjacent droplets. Coalescence occurs when this thin film becomes unstable and then ruptures. Therefore, the presence of adsorbed surfactants can reduce the likelihood of rupture.
- ⇒ As a result of their thermodynamic instability, emulsions tend to reduce their total free energy through an increase in droplet diameter, and hence reduce their total interfacial area. This leads to the degradation of the emulsion.

References

1. Julian R.H. Ross, Heterogeneous Catalysis: Fundamentals and Applications, Elsevier, 1st Edition, 2011.
2. G.C. Bond, Heterogeneous Catalysis: Principles and Application. Oxford University Press, USA, 1987.
3. B. Vishwanathan, S. Sivasankar and A.V. Ramaswamy, Catalysis: Principles and Applications, Narosa Publishing House, New Delhi, 2004.
4. R. Aveyard and D.A Haydon, An Introduction to the Principles of Surface Chemistry, Cambridge University Press, 1973.

REVIEW QUESTIONS

1. Explain different types of adsorption isotherms.
2. Develop an expression for the determination of surface area of an adsorbent by BET method?
3. Predict and explain the condition under which Langmuir isotherm becomes Freundlich adsorption isotherm.
4. Discuss the postulates of Langmuir adsorption isotherm.
5. Explain the classification of surfactants.
6. Discuss the concept of Hydrophilic-Lipophilic Balance.
7. Discuss critical micelle concentration.
8. Explain the formation of micelles.
9. Discuss in detail emulsions.
10. Discuss Langmuir adsorption isotherm with the limiting cases.
11. Develop BET adsorption isotherm.
12. Develop Gibb's adsorption isotherm.
13. Discuss thermodynamics of micellization.
14. Discuss in detail surfactants.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – V – Catalysis – SCYA5202

1. CATALYSTS / CATALYSIS

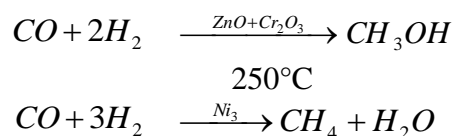
⇒ A catalyst is a substance which alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction. This phenomenon is called catalysis. Those catalysts which increase the reaction rate are called positive catalysts while those which slow down the reaction rate are called negative catalysts or inhibitors.

Criteria of Catalytic Reactions

The following are the general characteristics of most catalysts and catalytic reactions.

1. A catalyst remains unaltered in amount and in chemical composition at the end of the reaction; however it may undergo physical changes.
For example, granular MnO_2 used as the catalyst in the thermal decomposition of potassium chlorate and it recovered back as a fine powder at the end of the reaction.
2. A small amount of catalyst is generally sufficient to change the rate of reaction.
For example, 10^{-3} gm. ions/litre of Cu^{2+} is sufficient to change the rate of oxidation of sodium sulphate by oxygen in an aqueous solution.
3. A catalyst cannot initiate a reaction. It can only accelerate or retard the speed of a chemical reaction by decreasing or increasing the energy of activation.
4. A catalyst does not alter the equilibrium state of a reversible reaction: It simply alters the rate of both the forward and backward reactions so that the equilibrium condition is reached more quickly.
5. Every catalyst has a specific action. For a particular reaction, there is a particular catalyst. Even the same reactants in presence of different catalysts give different products.

For example, hydrogen and carbon monoxide combine in presence of different catalysts to produce different products.



6. A catalyst can be poisoned by the presence of small amount of certain substances called catalytic poison.
Examples of catalytic poisons are carbon monoxide, arseneous oxide, hydrogen cyanide, hydrogen sulphide etc.
7. The activity of a catalyst is enhanced by the presence of substances called promoters.
Examples of catalytic promoters are molybdenum, bismuth, zinc oxide, chromium oxide etc.

2. CLASSIFICATION OF CATALYSIS

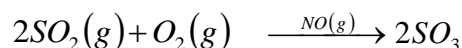
Catalyzed reactions are divided into two classes namely homogeneous and heterogeneous depending on the physical state of reactants, products and catalysts.

1. Homogeneous Catalysis

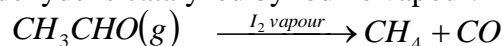
⇒ In homogeneous catalysis, the catalyst is present in the same phase as the reactants. It can occur in gas or liquid phase.

- **Homogeneous catalysis in gas phase**

(a) Oxidation of sulphur dioxide in lead chamber for the manufacture of sulphuric acid is catalyzed by gaseous nitric oxide.



(b) Decomposition of acetaldehyde is catalyzed by iodine vapour.



- **Homogeneous catalysis in liquid phase: Acid-base catalysis**

⇒ Homogeneous catalyzed reactions in a solution are mostly catalyzed by acids or bases. These are often referred to as acid-base catalysis. The most common acid catalyst in water solution is the hydronium ion; the most common base is hydroxyl ion.

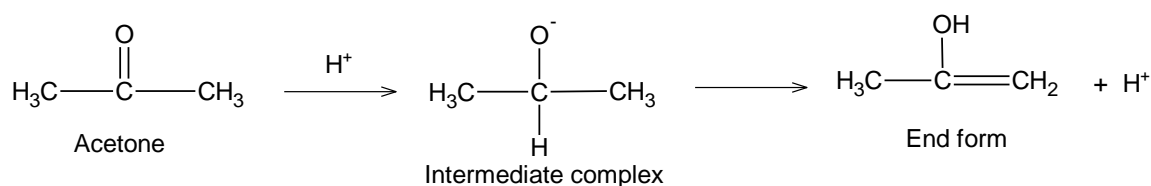
⇒ If any acid catalyses the reaction, it is referred to as general acid catalysis. Similarly if any base catalyses the reaction, it is referred to as general base catalysis. If only certain acids or hydroxyl ions are effective, the phenomenon is called specific acid or specific base catalysis.

- **General acid catalysis**

⇒ Under general acid catalysis, not only H^+ ions catalyses the reactions but also all Bronsted acids (proton donors) can catalyze the reaction. *Examples:* H^+ ions; undissociated acid (CH_3COOH); cations of weak base (NH_4^+) etc.

⇒ In general acid catalysis, the H^+ ion or a Bronsted acid transfers a proton to the reactant to form an intermediate complex which then decomposes and gives back the proton.

⇒ **Examples:** The mechanism of keto-enol tautomerism of acetone.

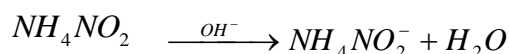


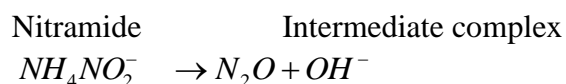
- **General base catalysis**

⇒ Under general base catalysts, not only OH^- ions catalyses the reactions but also all Bronsted bases (proton acceptors) can catalyse the reaction. *Examples:* OH^- ions; anions of weak acid (CH_3COO^-); undissociated base.

⇒ In general base catalysis, the OH^- ion or a Bronsted base accepts a proton to form an intermediate complex which then decomposes to regenerate OH^- or Bronsted base.

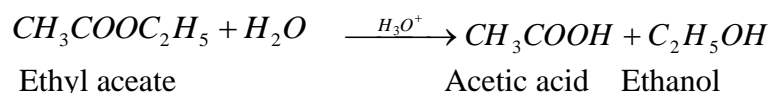
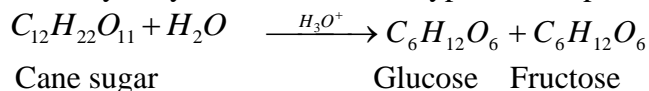
⇒ **Examples:** Decomposition of nitramide by OH^- ions.





- **Specific acid catalysis**

⇒ Inversion of cane-sugar and hydrolysis of ester are the typical examples of specific acid catalysis.

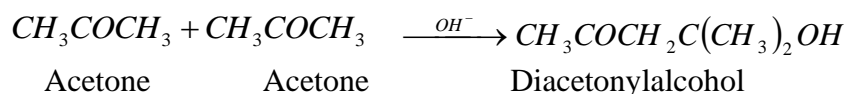


⇒ The reactions are catalysed by certain acids or H_3O^+ ions only. However, different acids have different activities.

⇒ For example, HCl has a greater activity than CH_3COOH . It is evident that the actual catalysts are H^+ or H_3O^+ ions. The rate of reaction is found to be proportional to the concentrations of H_3O^+ ions and the concentration of the reacting molecules or ions.

- **Specific base catalysis**

⇒ Conversion of acetone to diacetonyl alcohol is an example of specific base catalysis. This reaction is catalysed by OH^- ions only.

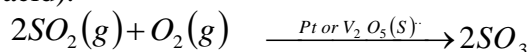


2. Heterogeneous Catalysis

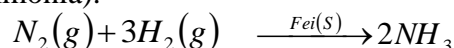
⇒ In heterogeneous catalyzed reactions, the catalyst is present in a different phase from that of the reactants. In most of the cases, gaseous reactants are catalyzed by solid catalysts and the reactions proceed at the surface of the solid catalysts. This type of process is referred to as *contact catalysis*.

Some important examples of heterogeneous catalysis are given below.

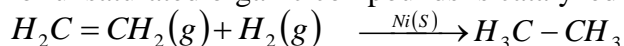
(i) Combination of SO_2 and oxygen in the presence of finely divided platinum or V_2O_5 (Contact process for sulphuric acid).



(ii) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for ammonia).



(iii) Hydrogenation of unsaturated organic compounds is catalyzed by finely divided nickel.



3. CONCEPT OF LANGMUIR-HINSHELWOOD MECHANISM

Surface reactions: Involve the reactions between gaseous reactants catalysed by solid state catalysts.

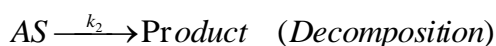
⇒ According to Langmuir-Hinshelwood mechanism (LHM), a gaseous reaction takes place on the surface of a solid catalyst. That is, the surface reaction involves the following elementary steps and these steps are consecutive (taking place one after another):

1. Diffusion of reactants to the surface (very fast)
2. Adsorption of reactants at the surface
3. Chemical reaction at the surface (decomposition) (slowest and rate determining step-RDS)
4. Desorption of products from the surface
5. Diffusion of products from the surface (very fast)

Assumptions of LHM

1. RDS is the chemical reactions at the surface i.e., decomposition
2. Chemisorption plays an important role in heterogeneous catalysis. Chemical bonds are formed between the adsorbate and the surface, which results into the formation of a monolayer (Langmuir adsorption)
3. The reaction rate per unit surface area is proportional to the fraction of the surface covered, θ which is calculated by the Langmuir adsorption isotherm.

Kinetics of Surface Reaction (Unimolecular Surface Reaction)



⇒ According to Langmuir-Hinshelwood hypothesis:

$$\Rightarrow \text{Rate of the reaction, } r = k_2 \theta \quad (1)$$

Where θ is the fraction of surface covered.

⇒ Assuming steady state approximation for the intermediate $[AS]$, we have:

$$\Rightarrow k_1[A][S] - k_{-1}[AS] - k_2[AS] = 0$$

$$\Rightarrow k_1[A][S] = [k_{-1} + k_2][AS]$$

$$\Rightarrow [AS] = \frac{k_1[A][S]}{[k_{-1} + k_2]} \quad (2)$$

Let, θ is the fraction of sites occupied; $1-\theta$ is the fraction of sites which are unoccupied and C_s is the total concentration of active sites on the surface

$$\Rightarrow \therefore \text{Concentration of reactant sites, } [S] = (1 - \theta)C_s \quad (3)$$

\Rightarrow and the concentration of sites occupied by A is given as :

$$\Rightarrow [AS] = \theta C_s \quad (4)$$

\Rightarrow From equations (2), (3) and (4), we have,

$$\Rightarrow \theta C_s = \frac{k_1[A][S]}{[k_{-1} + k_2]}$$

$$\Rightarrow (or) \quad \theta = \frac{1}{C_s} \times \frac{k_1[A][S]}{[k_{-1} + k_2]} \quad (5)$$

\Rightarrow Putting the equation (3) in (5), we get

$$\Rightarrow \theta = \frac{1}{C_s} \times \frac{k_1[A](1 - \theta)C_s}{[k_{-1} + k_2]}$$

$$\Rightarrow \theta = \frac{k_1[A](1 - \theta)}{[k_{-1} + k_2]}$$

$$\Rightarrow \frac{(1 - \theta)}{\theta} = \frac{[k_{-1} + k_2]}{k_1[A]}$$

$$\Rightarrow \frac{1}{\theta} - 1 = \frac{[k_{-1} + k_2]}{k_1[A]} \quad (or) \quad \frac{1}{\theta} = 1 + \frac{[k_{-1} + k_2]}{k_1[A]}$$

$$\Rightarrow \frac{1}{\theta} = \frac{k_1[A] + k_{-1} + k_2}{k_1[A]}$$

$$\Rightarrow \theta = \frac{k_1[A]}{k_1[A] + k_{-1} + k_2} \quad (6)$$

\Rightarrow Substituting the value of θ in rate of reaction equation (1), we get

$$\Rightarrow r = \frac{k_2 k_1 [A]}{k_1 [A] + k_{-1} + k_2} \quad (7)$$

\Rightarrow For gaseous adsorbates, concentration is expressed in terms of partial pressures.

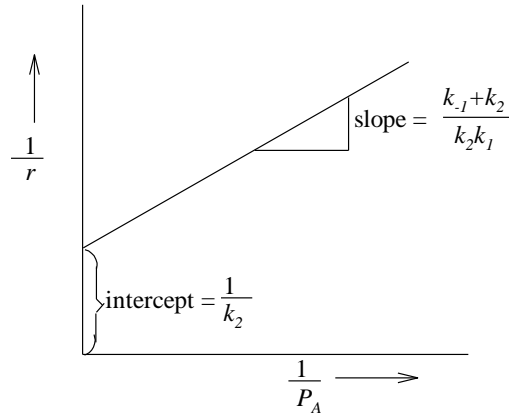
$$\Rightarrow \therefore r = \frac{k_2 k_1 P_A}{k_1 P_A + k_{-1} + k_2} \quad (8)$$

⇒ The equation (8) can be rearranged and written as:

$$\Rightarrow \frac{1}{r} = \frac{k_1 P_A}{k_2 k_1 P_A} + \frac{k_{-1} + k_2}{k_2 k_1 P_A}$$

$$\Rightarrow \text{(or)} \quad \frac{1}{r} = \frac{1}{k_2} + \frac{k_{-1} + k_2}{k_2 k_1} \frac{1}{P_A} \quad (9)$$

⇒ The equation (9) is corresponding to $y = mx + c$



❖ Limiting cases

⇒ **Case 1:** When $k_2 \gg (k_{-1} + k_1 P_A)$

$$\Rightarrow r = \frac{k_2 k_1 P_A}{k_2}$$

⇒ $r = k_1 P_A$ The reaction is of first order.

⇒ **Case 2:** When $k_2 \ll (k_{-1} + k_1 P_A)$

$$\Rightarrow r = \frac{k_2 k_1 P_A}{k_{-1} + k_1 P_A}$$

⇒ Dividing both the numerator and denominator of RHS by k_{-1} , we get,

$$r = \frac{k_2 k_1 P_A / k_{-1}}{k_{-1} + k_1 P_A / k_{-1}}$$

$$\Rightarrow r = \frac{\frac{k_2 k_1}{k_{-1}} P_A}{\frac{k_{-1}}{k_{-1}} + \frac{k_1 P_A}{k_{-1}}}$$

$$\Rightarrow r = \frac{K k_2 P_A}{1 + K P_A} \quad (10)$$

Where, $K = \frac{k_1}{k_{-1}}$ and is known as adsorption equilibrium constant.

1. *At low pressures, the reactants are slightly adsorbed, i.e., $\theta \rightarrow 0$ and $K P_A \ll 1$.*

$\Rightarrow \therefore$ The equation (10) reduces to :

$$\Rightarrow r = K k_2 P_A$$

$\Rightarrow r = k P_A$ i.e : The reaction is of first order
where $k = K k_2$

$$\Rightarrow \therefore r = \frac{-dP_A}{dt} = k P_A$$

$$\Rightarrow (or) P_A = P_A^o \exp(-kt)$$

\Rightarrow That is the partial pressure of gas decreases exponentially with time.

2. *At high pressures, the reactants are strongly adsorbed, i.e., $\theta \rightarrow 1$ and $K P_A \gg 1$.*

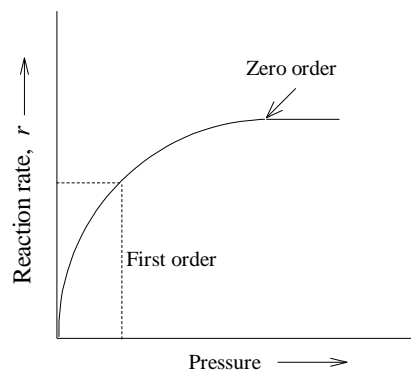
$$\Rightarrow r = \frac{K k_2 P_A}{K P_A}$$

$\Rightarrow r = k_2$ i.e : The reaction is of zero order

$$\Rightarrow \therefore r = \frac{-dP_A}{dt} = k_2$$

$$\Rightarrow (or) P_A = P_A^o - k_2 t$$

\Rightarrow That is the partial pressure of gas decreases linearly with time.



4. PHOTOCATALYSIS USING SEMICONDUCTING OXIDES

Photocatalysis

\Rightarrow **Photocatalyst:** A photocatalyst is a semiconducting substance that mediates a chemical reaction on its surface when activated by *uv* or visible light.

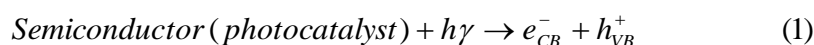
- ⇒ **Photocatalysis**: Photocatalysis is a catalytic reaction which occurs in the presence of light and a photocatalyst, semiconductor.
- ⇒ **Photocatalytic reactions** are initiated by the absorption of a photon with appropriate energy that is equal to or higher than the band gap energy of the photocatalyst.
- ⇒ There are two types of photocatalysis: homogeneous and heterogeneous.
- ⇒ **Homogeneous photocatalysis**: When the reactant and photocatalyst exist in the same phase, the reaction is called homogeneous photocatalysis. Coordination compounds, dyes, natural pigments are the most common examples of homogenous photocatalysts.
- ⇒ **Heterogeneous photocatalysis**: In this type, the reactant and photocatalyst exist in different phases. Transition metal chalcogenides are the most common examples of heterogeneous photocatalysts.

Semiconducting Materials for Photocatalysis

- ⇒ **Binary semiconductors** such as TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS can be used as photocatalysts because of a favorable combination of their electronic structure, light absorption properties, charge transport characteristics, and excited-state lifetime.
- ⇒ Apart from the binary chalcogenides, some **ternary chalcogenides** such as SrZrO_3 , PbCrO_4 , CuInS_2 , Cu_2SnS_3 can also be used as photocatalysts.
- ⇒ Examples of **quaternary oxides and sulfides** as photocatalysts are Bi_2AlVO_7 , $\text{Cu}_2\text{ZnSnS}_4$, $\text{FeZn}_2\text{Cu}_3\text{O}_{6.5}$

Basic Principle and Mechanism of Photocatalysis

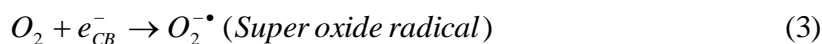
- ⇒ Photocatalysis involves the absorption of photons energy ($h\nu$) equal to or greater than the band gap energy (E_g) of a semiconductor material, and generate electron hole pairs.
- ⇒ The absorbed photon creates a charge separation as the electron (e^-) is elevated from the valence band (VB) of a semiconductor to the conduction band (CB), creating a hole (h^+) in the VB (Equation 1).



- ⇒ But in most of cases the holes and electrons can recombine and discharge the energy in the form of heat (Equation 2).



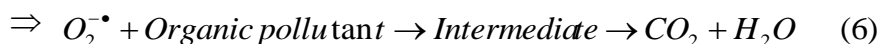
- ⇒ This excited electron can reduce any substrate or react with electron acceptors such as O_2 present on the semiconductor surface or dissolved in water, reducing it to an unstable superoxide radical anion $\text{O}_2^{\cdot-}$ (Equation 3)



- ⇒ On the other hand, the hole can oxidize the organic molecule to form R^+ , or react with H_2O , or OH^- , oxidizing them to an unstable $\cdot\text{OH}$ radicals (Equation 4).



⇒
 ⇒ These unstable radicals further react with the organic pollutant and subsequently mineralize it to carbon dioxide and water, forming a number of intermediate products (Equations 5 and 6).



⇒
 ⇒ The overall photocatalytic process involves three major steps:
 (i) Absorption of light by the semiconductor to generate of electron-hole pairs,
 (ii) Charge separation and migration to the surface of the semiconductor and
 (iii) Surface reaction for the water reduction or oxidation reactions.

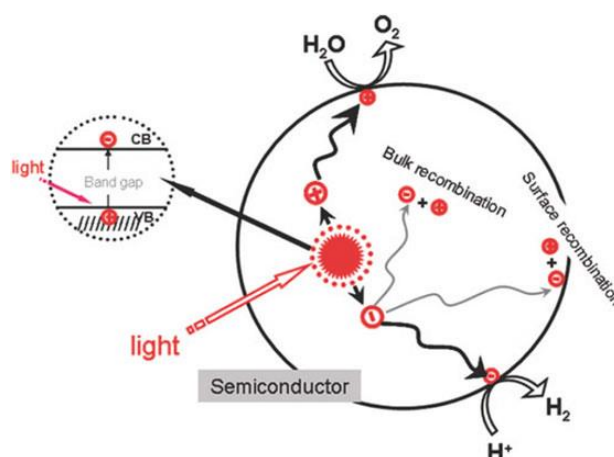


Fig. 5.1: Basic Principle and Mechanism of Photocatalysis

⇒ The main drawback of this process is low efficiency due to recombination of charge carriers.

Application of Photocatalysis in Water Remediation

⇒ Photocatalysis has been widely used for photocatalytic degradation of all kinds of organic pollutants in water such as dye and microbial pathogens.

⇒ In a photocatalysis procedure, electrons and holes are generated from semiconductors under light irradiation, organic molecules are oxidized by photo-generated holes, and reactive radical species such as $O_2^{\bullet -}$, $\bullet OH$ are formed from the reduction of O_2 . Because all these radical species are strong oxidizing agents, all organic molecules in water could be non-selectively destroyed.

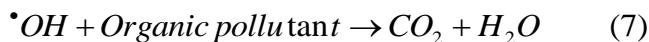
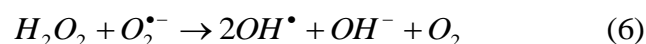
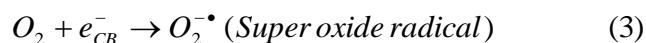
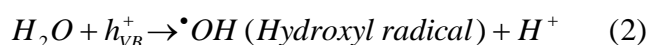
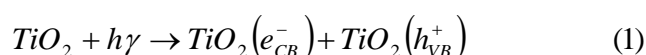
⇒ Under a certain pH condition, the photogenerated hole has a stronger oxidation capacity when the VB potential is more positive while photogenerated electron exhibits more powerful reduction capacity when the CB potential is more negative.

⇒ Therefore, a semiconductor photocatalyst should have a suitable energy band structure in order to remove organic pollutants effectively.

⇒ It is generally accepted that the VB should have a potential of +1.0 to +3.5 V versus the normal hydrogen electrode (NHE) and the CB should have a potential of +0.5 to -1.5 V versus the NHE.

Role of TiO₂ as photocatalyst in water remediation

- ⇒ TiO₂, a typical semiconductor photocatalyst is considered to be one of the best candidates for water purification, because of strong oxidising power at ambient temperature and pressure; high photocatalytic activity for degrading a wide range of environmental pollutants; chemical inertness; physical stability; non-toxicity; super hydrophilicity and cheapness and ready availability.
- ⇒ In case of heterogenic photocatalysis organic compounds present in aqueous phase are transformed into by-product and finally mineralized to carbon dioxide and water at proper radiation.
- ⇒ Photochemical degradation of various chemical compounds such as phenols, chlorophenols, dyes, pesticides, herbicides, humic and fulvic acids, pharmaceuticals, endocrine disruptors, heavy metals and other inorganic compounds on TiO₂ surface can be done.
- ⇒ The aromatic compounds are hydroxylated by reactive OH[•] radicals and undergo oxidation/addition which is finished with the ring opening. The byproducts obtained like aldehydes and carboxylic acids are next oxidized to carbon dioxide and water.
- ⇒ Some key steps during photocatalysis are given as follows.



- ⇒ It is also possible to use TiO₂ as photocatalyst for the destruction of microorganisms. All microorganisms such as bacteria cell consisting of water (70–90%) and major cell compounds like polysaccharides, lipids, lipopolysaccharides, proteins and nucleic acids can be attacked by oxygen containing radicals and completely destroyed.
- ⇒ The viruses like *Streptococcus natuss*, *Streptococcus cricetus*, *faecalis* and *aureus*, *Escherichia coli* and total *Coli*, *Scaccharomyces cerevisisas*, *Lactobacillus acidophilus*, *Enterobacter cloacae*, *Chlorella vulgaris*, *Candida albicans*, *Fusarium solami*, *Aspergillusniger*, *Polio 1 virus* have been successfully inactivated using heterogenic photocatalysis.

Application of Photocatalysis in Air Purification

- ⇒ Photocatalysis is a promising technique used for removing nitrogen oxides (NO_x), sulphur oxides (SO_x) and volatile organic compounds (VOCs) from polluted urban air and for reducing concentrations of toxic and irritating ozone.
- ⇒ The photocatalysis process has great potential applications to contaminant control in indoor environments such as residences, office buildings, factories, aircrafts, and spacecrafts. Disinfection is of importance in indoor air applications because of the risk of exposure to harmful airborne contaminants.
- ⇒ Bioaerosols are a major contributor to indoor air pollution, and more than sixty bacteria, viruses, and fungi are documented as infectious airborne pathogens. Diseases transmitted via bioaerosols include tuberculosis, Legionnaires, influenza, colds, mumps, measles, rubella, small pox, aspergillosis, pneumonia, meningitis, diphtheria, and scarlet fever. Photocatalytic oxidation can destroy these infectious airborne pathogens.
- ⇒ Titanium dioxide (TiO_2) nanoparticles can act as a photocatalyst to form reactive hydroxyl ($\bullet OH$) radicals in the presence of atmospheric moisture. These radicals can oxidize and destroy most pollutant molecules.
- ⇒ For example airborne pollutant molecules adsorb on the TiO_2 particle surface, where they react with adsorbed hydroxyl radicals until they are fully oxidized (benzene, C_6H_6 ultimately forms six CO_2 molecules and three H_2O molecules).
- ⇒ TiO_2 nanoparticles can also catalyze the breakdown of oxides of nitrogen (NO_x) and sulfur (SO_x).
- ⇒ Nanocrystalline materials like TiO_2 and ZnO show good photocatalytic activities to uv light and hence they are used to characterize the photocatalytic rates and reaction pathways for various polluting volatile organic compounds such as benzene, toluene, terpenes, etc. that act as smog precursors. To make them work at visible light (wavelength >420 nm), non-metals like C, S, N and B as well as Mn and other transition metals are used as dopants.

5. HETEROGENEOUS CATALYSIS BY INTERCALATION COMPOUNDS

Graphite Intercalation Compounds as Model Compounds in Catalysis Research

- ⇒ Graphite is able to react with both elements and compounds to form interstitial compounds, in which the reactant is found between the graphite layers and the layer structure of the graphite crystal is sealed.
- ⇒ These interstitial compounds will not have all the characteristic graphite properties such as bond distance, bond direction and stacking frequency, however, it retains the strong bond by which each carbon atom is coupled to its three nearest-neighbor atoms.
- ⇒ As the graphite layer structure is sealed, formation of most interstitial compounds is a reversible process.

- ⇒ The graphite can readily intercalate with alkali metals, transition metal chlorides or combinations of these materials. Alkali metal-graphite intercalation compounds can be considered as electron donor-acceptor (EDA) complexes, which have been shown to possess catalytic activity for a number of interesting reactions.
- ⇒ Graphite intercalation compounds have been used as model compounds in catalysis research for studying reaction mechanisms, graphitization reactions, structural aspects, and radiation damage.
- ⇒ The catalytic activity of the graphite intercalation compounds has also been used for dimerization, oligomerization, and polymerization reactions.
- ⇒ In addition, graphite intercalation compounds are used for chemical separations, oxidation inhibitors, electrode reactions, graphite synthesis, battery components, and semipermeable membranes.

The Interstitial Compounds of Graphite

- ⇒ In chemistry, intercalation describes the reversible insertion of guest species into a lamellar host structure with maintenance of the structural features of the host. The interstitial compounds of graphite can be divided into three main classes:
 1. The first class of interstitial compounds is known non-conducting compounds as they lack completely the metallic properties of graphite. These compounds contain graphite oxide and graphite monofluoride. In these compounds covalent bonding exists between the intercalated substance and the carbon layer planes. The possible use of these compounds as catalysts is poor because of their thermal instability.
 2. In the second class of interstitial compounds, the bonding is predominantly ionic in character. In these compounds, all the characteristic properties of graphite are retained. The group mainly comprises the alkali metal-graphite compounds and the molecular compounds of graphite with metal halides, metal oxides and sulfides.
 3. The third class of interstitial compounds is formed by the decomposition of a lamellar compound leaving behind a residue of the intercalated material in the graphite. These compounds cannot be considered as true compounds because their properties generally differ substantially from graphite itself.

Types of Ionic Compounds

- ⇒ Both elements and molecular compounds are capable of forming ionic lamellar compounds with graphite.
- ⇒ The ionic compounds can be subdivided into three groups: the alkali metal-graphite compounds, the halogen-graphite compounds and the molecular graphite compounds.

1. Alkali Metal-Graphite Intercalate Compounds

- ⇒ Graphite intercalation compounds of potassium, rubidium and cesium can be easily prepared by heating the metal with finely divided graphite in vacuum at 300-400°C or in an inert gas at 100-200°C.

⇒ These intercalation compounds can have stoichiometric compositions C_8Me , $C_{24}Me$, $Ca_{36}Me$, $C_{48}Me$, and $C_{60}Me$ ($Me = K, Rb, Cs$).

2. Halogen-Graphite Compounds

⇒ Although the halogens often behave similarly, their reactivities towards graphite differ.

⇒ Only fluorine and bromine react readily with graphite.

⇒ Fluorine yields only covalent compounds.

⇒ When bromine in either the liquid or vapor phase is brought into contact with graphite, the compound C_8Br is formed. In addition, the existence of C_9Br , $C_{10}Br$, and $C_{16}Br$ has been reported.

⇒ Reaction of graphite with chlorine takes place under favorable conditions (low temperature) leading to the formation of C_8Cl .

⇒ In compare, iodine does not intercalate at all.

3. Molecular Graphite Intercalation Compounds

⇒ Molecules that can be intercalated are metal halides, metal oxides, and sulfides.

⇒ Preparations of molecular graphite compounds are usually carried out by simply heating mixtures of the reactants at temperatures between 200 and 600°C.

⇒ The most extensively studied molecular compound is graphite-ferric chloride.

Structural Aspects of Graphite Intercalation Compounds

⇒ The layered structure of the graphite intercalation compounds offers unique properties of both activity and selectivity of a catalytic reaction through a geometric effect.

⇒ A necessary condition that has to be satisfied for these compounds to act as catalysts is the presence of sufficient and proper surface sites that can act as adsorption centers for the reactants participating in the reaction.

⇒ Moreover, these compounds must also possess a high thermal stability, since catalytic reactions often have to be carried out at elevated temperatures.

⇒ Therefore, only two groups of intercalation compounds are considered for application in catalysis, the alkali metal-graphite intercalates and the molecular graphite compounds.

⇒ In the former case, the alkali metal atoms themselves are considered to act as the catalytic sites whereas in the latter case, the metals are either present in the intercalated molecules (halides, oxides, sulfides) or generated by suitable reduction of the molecular compound.

- ⇒ *Stage 1 of lamellar structure of K-, Rb-, and Cs-graphite intercalation compounds:* X-ray studies carried out by Schleede and Wellmann (1932) on C_8K revealed that in the first stage compound, every interlayer space is filled with a layer of potassium atoms (Fig. 5.2).
- ⇒ As a result of this intercalation, the interplanar distance is increased from 3.34 in graphite to 5.40 Å.
- ⇒ The metal atoms are located above the centers of alternate carbon hexagons, forming a regular triangular net with an edge of 4.91 Å.
- ⇒ Four orientations are possible (α , β , γ , δ , refer Fig. 2a) for the location of the metal layers with respect to each other.
- ⇒ The period of the metal lattice in the c -axis direction therefore comprises four layers.

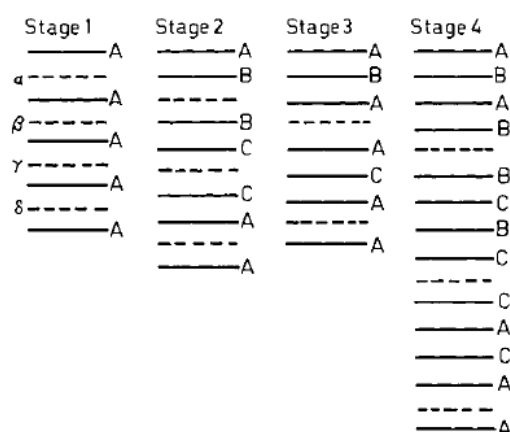


Fig. 5.2: Lamellar structure of K-, Rb-, and Cs-graphite intercalation compounds
 (—) carbon layer, (---) K, Rb, or Cs layer
 A, B, C denote graphite stacking sequence; and
 α , β , γ , δ denote alkali metal stacking sequence in C_8Me

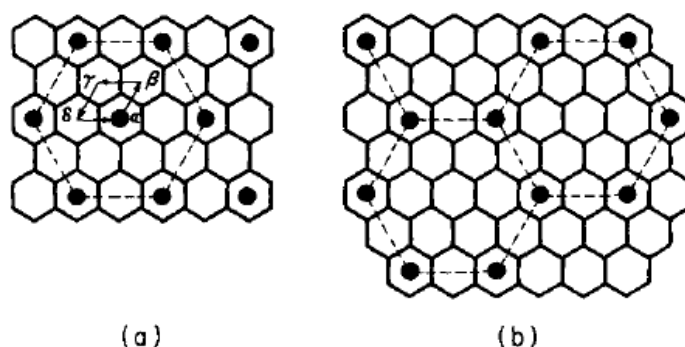


Fig. 5.2 (a) Arrangement of metal atoms (●) within each intercalate layer of Stage 1 K-, Rb-, Cs- graphite compounds

Fig. 5.2 (b) Arrangement of metal atoms in Stages 2–5 according to Rüdorff and Schulze (1954) and Herold (1955); the hexagons are carbon hexagon

- ⇒ **Staging sequence according to Rüdorff and Schulze & Daumas and Herold models:** In Stages 2–5, according to Rüdorff and Schulze (1954), intercalation of metal atoms is taking place in each 2nd, 3rd, 4th and 5th interlayer space, respectively as shown in Fig.5. 2a.
- ⇒ X-ray diffraction studies showed that the carbon layer planes are exactly superimposed when in contact with the intercalate layer in contrast to the stacking sequence of the carbon layers in graphite which is either *ABAB* . . . (hexagonal) or *ABC ABC* . . . (rhombohedral).
- ⇒ Since in the higher Stages, the metal content of each inserted layer has been reduced by one-third, the triangular arrangement of potassium atoms in C₈K does not apply to these compounds.
- ⇒ For these Stages Herold and Rüdorff and Schulze proposed a hexagonal pattern, which results from the triangular net with every third metal atom removed (Fig. 5.2b).
- ⇒ However, recent X-ray investigations reveal that the potassium atoms are distributed irregularly over the centers of the carbon hexagons. Lowering the temperature results in ordering of the intercalate structure in the Stage 2 compound; however the final structure was not the one proposed by Herold and Rüdorff.
- ⇒ Daumas and Herold proposed the structure depicted in Fig. 5.3. In this model the metal layers extend only themselves over certain short distances and the transition from one stage to another becomes a relatively easy process.

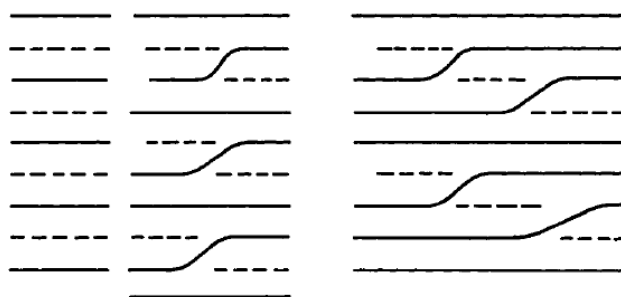


Fig.5.3: Interlamellar structure of alkali metal-graphite intercalation compounds according to Daumas and Herold; (—) carbon layer; (---) alkali metal layer.

2. Structural Aspects of Molecular-Graphite Intercalation

- ⇒ As most of the molecular compounds are formed with the metal halides, we discuss with the structural analysis of FeCl₃–graphite intercalation compounds. The other molecular compounds are analogous.
- ⇒ The FeCl₃ molecule, which crystallizes into a layer lattice, tends to preserve its layer structure when intercalated into graphite (Fig. 5.4a).
- ⇒ The Fe³⁺ ions, which are centered between the carbon layers, form a hexagonal net, as in crystalline FeCl₃. Even the distance between the Fe³⁺ is nearly the same as in FeCl₃.
- ⇒ A preferred orientation of the Fe³⁺ ions with respect to the carbon atoms does not exist, because the dimensions of the carbon and iron networks do not agree with each other.

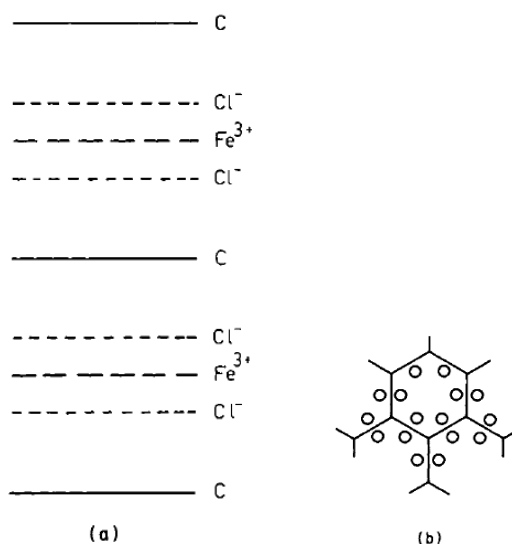


Fig. 5.4: (a) Lamellar structure of Stage 1 FeCl_3 -graphite
(b) Preferred positions of chlorine atoms (O) relative to carbon atoms in FeCl_3 -graphite

- ⇒ For the chlorine atoms of the first-stage FeCl_3 compound, the preferred positions have been observed (Fig. 5.4b). Due to excessive distortion, however, more than half of the atoms cannot occupy these preferred positions.
- ⇒ Consequently, they are distributed, more or less at random, among the chloride planes.

Catalytic Reactions

- ⇒ Two factors have to be considered when evaluating the change in catalytic activity of a compound upon intercalation into the graphite lattice.
- ⇒ First, it can be expected that the electronic properties will be altered by the exchange of electrons between the intercalated substance and graphite.
- ⇒ Hence, for the alkali metal-graphite compounds, the increase in conductivity in the a -axis direction is due to the electron transfer from the alkali metal to the upper π bond of graphite.
- ⇒ Since these levels possess an anti-bonding character, the transfer should result in an increase of the C-C bond distance of the graphite hexagons.
- ⇒ In the case of K-graphite, the effect of this change in electronic characteristics of the intercalated substance is an altered adsorption behavior with the pure substance.
- ⇒ Second, the geometrical arrangement of the catalytic sites may be altered by intercalation.
- ⇒ In pure compounds, the distance between the active centers as well as their chemical environment are determined mainly by the crystal lattice parameters.
- ⇒ Although both the geometry and electronic properties can be modified in introducing lattice imperfections, this is not a convenient method for affecting the activity pattern of a catalyst.
- ⇒ With the intercalation compounds, however, the distance between the catalytic sites in the c -axis direction can be altered by using different stages of the same intercalate.

- ⇒ Figure 5.5a corresponds to a first-stage compound, the distance between the catalytic sites in the *c*-axis has a fixed value.
- ⇒ This distance may influence the higher catalytic activity of intercalate; and it can be altered by forming the second- or higher-stage compounds (Figure 5.5 *b*).
- ⇒ Moreover, it is possible in some cases to intercalate two different molecules at the same time in the lattice, which means that the geometrical environment in the *a*-axis direction can also be changed (Fig. 5.5c). This geometric effect explains some remarkable catalytic features of alloy systems, may greatly enhance the selectivity of a catalytic reaction.

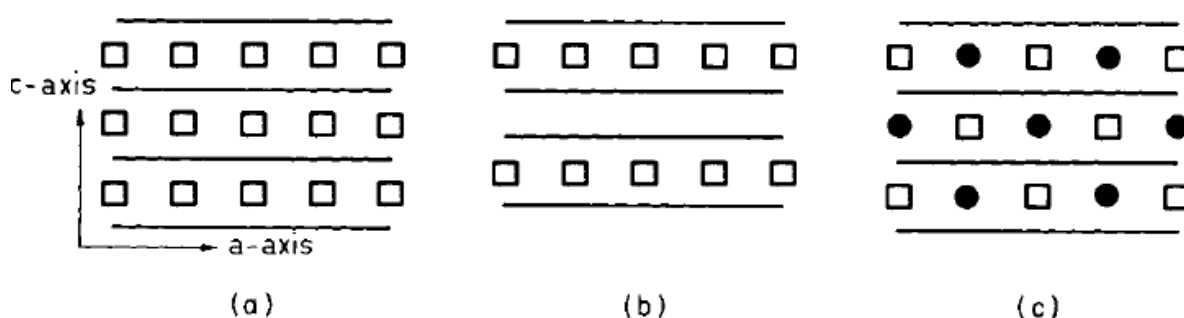


Fig. 5.5: Geometric effects in catalytic reactions with intercalation compounds,
(a) Stereochemical features of reactants play a role in determining the final structure of the product. Since large molecules sterically hinder each other, activity is lower compared with Part b.
(b) Since no steric hindrance of reactant molecules occurs, compound displays higher activity per gram of intercalated material compared with Part a.
(c) Simultaneous intercalation of two substances may increase selectivity of a reaction, which takes place on □. The atom (●) is assumed to be inactive.

Examples of Catalytic Reactions Catalyzed by Metal-Graphite Intercalation Compounds

1. Exchange Reactions

- ⇒ The exchange reaction of propylene with deuterium can be done using $C_{24}K$ catalyst.
- ⇒ From the product distribution in the initial stage of the reaction, it is concluded that from the four possible geometrical propylene- d_1 isomers, only the 3- d_1 species where exchange is taking place with hydrogen in the methyl group.
- ⇒ By simultaneously studying the formation of the propylene- d_2 species, in the initial stage of the reaction, which yielded a mixture of 50% $CHD_2-CH=CH_2$ and 50% $CH_2D-CH=CHD$ (25% *cis*-1, 3 and 25% *trans*-1,3) concluded that the reaction proceeds via an π -allyl intermediate.

2. Hydrogenation

- ⇒ The alkali metal intercalates possess high catalytic activity for the hydrogenation of aromatic compounds.
- ⇒ With C_8K and $C_{24}K$, high yields (80%) and selectivities (99.9%) are obtained for the hydrogenation of benzene at hydrogen pressures of 100-150 bars and temperatures of 250-300°C.

3. Alkylation of Alkylaromatics

⇒ When the alkylation alkyl aromatics are carried out in the presence of a potassium metal catalyst like C₈K and C₈Cs with propylene at 50-70 bars, an additional cyclization reaction occurs which lead to the formation of indanes.

4. Dimerization

⇒ The dimerization of propylene to methylpentenes and isobutylene to 2,4,4-trimethylpentenes reactions may be carried out continuously or in batches (reaction time 20 hr) at 120-160°C and 100-125 bars un presence of catalysts like C_nK (*n* = 8, 24, 36, 48, 60) and C₆₄Na.

5. Polymerization

⇒ Polymerization of butadiene with C₈K and C₂₄K mainly yields polymers with a 1,2- and *trans*-1,4- addition structure. The selectivity to *trans* 1,4 polybutadiene can be raised (up to 78%) by using ternary compounds consisting of potassium, an alkyl amine and graphite, while graphite compounds with lithium and THF give more 1,2- addition products.

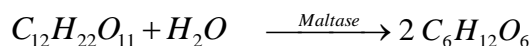
6. ENZYME CATALYSIS

Characteristics of Enzyme Catalysts

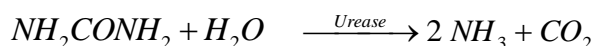
- ⇒ Biological catalysts or enzyme catalysts are protein catalysts produced in living cells.
- ⇒ Enzymes are extremely specific in their catalytic function. For example, the enzyme *urease* will catalyze the hydrolysis of urea and no other reactions.
- ⇒ The activity of enzyme depends on the temperature. All enzymes are effective at room temperature. Since many of them are so sensitive, they become inactive at about 50°C.
- ⇒ The enzyme activity also depends on the pH.

Some important examples are:

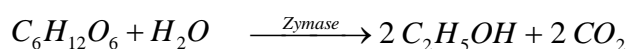
1. *Maltase*, an enzyme converts maltose into glucose



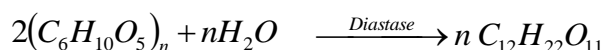
2. *Urease*, an enzyme converts urea into ammonia.



3. *Zymase*, an enzyme converts glucose into ethanol.



4. *Diastase*, an enzyme converts starch into maltose sugar

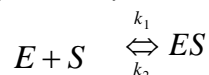


Kinetics of Enzyme Catalysis (Michaelis – Menten Equation)

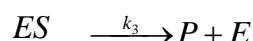
⇒ The general mechanism for the kinetics of enzyme-catalysed reaction was first proposed by L. Michaelis and Mary Menten in 1913.

⇒ The mode of action of an enzyme in Michaelis-Menten mechanism is as follows:

(i) *Formation of the Enzyme-substrate complex.*



(ii) *Decomposition of the complex.*



where E is the enzyme, S is the substrate, ES is the enzyme-substrate complex, (intermediate activated complex) and P is the end product.

⇒ The rate of formation of the product is given by:

$$\frac{d[P]}{dt} = r = k_3[ES] \quad \dots(1)$$

⇒ In order to solve the equation (1), it is necessary to know the concentration of ES . This can be calculated through steady-state principle.

⇒ According to this “when a short-lived reaction intermediate exists at low concentration in a system, the rate of formation of intermediate can be considered to be equal to its rate of disappearance”.

⇒ Applying steady-state principle,

$$\begin{aligned} k_1[E][S] &= k_2[ES] + k_3[ES] \\ k_1[E][S] &= [ES](k_2 + k_3) \\ [ES] &= \frac{k_1[E][S]}{(k_2 + k_3)} \quad \dots(2) \end{aligned}$$

⇒ Since the enzyme exists either in free form E , or the combined form ES , the total concentration of the enzyme, E_o originally added can be obtained from the material balance equation.

$$\begin{aligned} [E_o] &= [E] + [ES] \\ [E] &= [E_o] - [ES] \quad \dots(3) \end{aligned}$$

⇒ Inserting the value $[E]$ in equation (2), we get

$$[ES] = \frac{k_1\{[E_o] - [ES]\}[S]}{(k_2 + k_3)}$$

$$\begin{aligned}
(k_2 + k_3)[ES] &= k_1[E_0][S] - k_1[ES][S] \\
(k_2 + k_3)[ES] + k_1[ES][S] &= k_1[E_0][S] \\
[ES]\{(k_2 + k_3) + k_1[S]\} &= k_1[E_0][S] \\
[ES] &= \frac{k_1[E_0][S]}{k_1[S] + (k_2 + k_3)} \quad \dots(4)
\end{aligned}$$

⇒ Substituting $[ES]$ in equation (1), we get:

$$\frac{d[P]}{dt} = r = \frac{k_3 k_1 [E_0][S]}{k_1[S] + (k_2 + k_3)} \quad \dots(5)$$

⇒ Dividing the numerator and denominator of equation (5) by k_1 gives:

$$\begin{aligned}
\frac{d[P]}{dt} &= r = \frac{k_3[E_0][S]}{[S] + \left(\frac{k_2 + k_3}{k_1}\right)} \\
r &= \frac{k_3[E_0][S]}{[S] + k_m} \quad \dots(6)
\end{aligned}$$

where $k_m = \left(\frac{k_2 + k_3}{k_1}\right)$

⇒ k_m is called Michaelis constant and *equation (6) is known as Michaelis-Menten equation.*

Significance of k_m (Michaelis Constant)

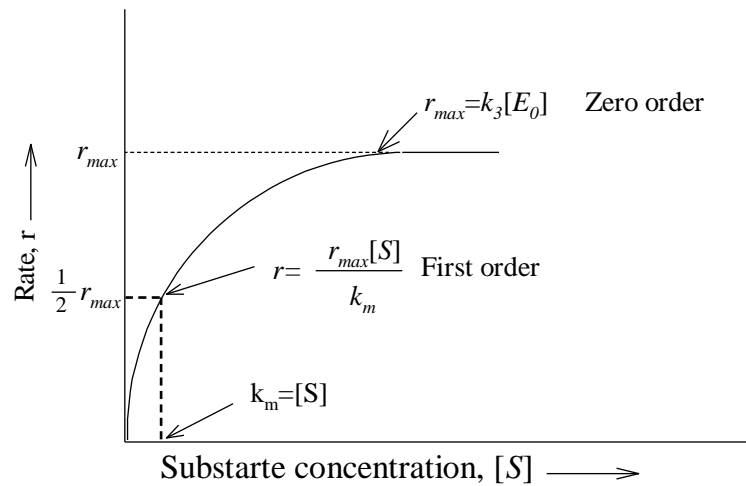
⇒ When all the enzyme has reacted with substrate at high concentration, the reaction will be going at maximum rate. No free enzyme will remain, so that $[E_0] = [ES]$. Hence from equation (1), we have

$$\frac{d[P]}{dt} = r_{\max} = k_3[E_0] \quad \dots(7)$$

where r_{\max} is the maximum rate.

⇒ The Michaelis-Menten equation can now be written as:

$$r = \frac{r_{\max}[S]}{k_m + [S]} \quad \because r_{\max} = k_3[E_0]$$



⇒ **Case 1:** If Michaelis constant, k_m is equal to substrate concentration, $[S]$ i.e.: $k_m = [S]$, then

$$r = \frac{r_{\max} [S]}{[S] + [S]}$$

$$r = \frac{1}{2} r_{\max} \quad \dots(8)$$

⇒ The Michaelis constant is a measure of enzyme activity and can be shown to be equal to $(k_2 + k_3) / k_1$. It is also equal to the substrate concentration at one half the maximum rate.

⇒ **Case 2:** At low concentration of substrate, when $[S] \ll k_m$, then

$$r = \frac{k_3 [E_0] [S]}{k_m}$$

$$r = \frac{r_{\max} [S]}{k_m} \quad \dots(9)$$

⇒ So, the rate of the reaction will be of first order with respect to the substrate and enzyme.

⇒ **Case 3:** At high concentration of substrate, when $[S] \gg k_m$, then

$$r = \frac{k_3 [E_0] [S]}{[S]}$$

$$r = k_3 [E_0]$$

$$r = r_{\max} \quad \dots(10)$$

⇒ So, the rate of the reaction will be zero order with respect to substrate for a given amount of enzyme.

⇒ It is clearly understand that the reaction of an enzyme catalyzed reaction changes from first order to zero order as the substance concentration is increased. This is because each enzyme molecule has one or more active sites at which the substrate must be bound in order that the catalytic action may occur.

⇒ At low substrate concentration, most of these active sites remain unoccupied at any time. As the substrate concentration is increased, the number of active sites which are occupied increases and hence the reaction rate also increases.

❖ Lineweaver-Burke Plots (Determination of k_m)

⇒ Lineweaver-Burk Equation (Reciprocal form of Michaelis-Menten equation) is used to calculate Michaelis constant.

$$\begin{aligned}\frac{1}{r} &= \frac{k_m + [S]}{r_{\max} [S]} \\ \frac{1}{r} &= \frac{1}{r_{\max}} + \frac{k_m}{r_{\max} [S]}\end{aligned}\quad \dots(11)$$

⇒ A plot of $\frac{1}{r}$ vs $\frac{1}{[S]}$ gives a straight line whose intercept is $1/r_{\max}$ and whose slope is k_m/r_{\max} . Hence Michaelis constant which is characteristic for an enzyme with a substrate can be determined (Fig. 5.6).

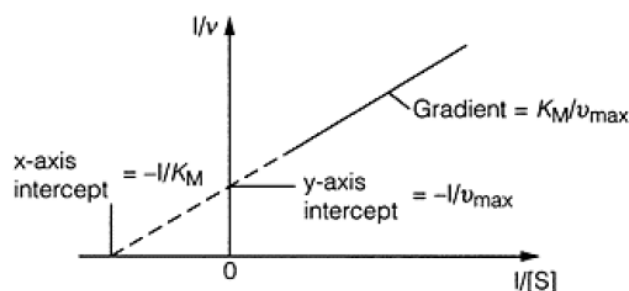


Fig. 5.6: The Lineweaver-Burke plot for enzyme kinetics:
The reciprocal of reaction rate, v , is plotted against the reciprocal of substrate concentrations $[S]$ for experiments using the same total enzyme concentration

Turnover Number: The constant k_3 is called the turnover number of the enzyme. It is defined as “the ability of one molecule of enzyme to form the complex with number of molecules of substrate and to convert it into products”.

References

1. Julian R.H. Ross, Heterogeneous Catalysis: Fundamentals and Applications, Elsevier, 1st Edition, 2011.
2. G.C. Bond, Heterogeneous Catalysis: Principles and Application. Oxford University Press, USA, 1987.
3. B. Vishwanathan, S. Sivasankar and A.V. Ramaswamy, Catalysis: Principles and Applications, Narosa Publishing House, New Delhi, 2004.
4. R. Aveyard and D.A Haydon, An Introduction to the Principles of Surface Chemistry, Cambridge University Press, 1973.

REVIEW QUESTIONS

1. Explain the characteristics of catalysis.
2. Explain homogeneous catalysis.
3. Explain the application of photocatalysis in water remediation.
4. Explain the application of photocatalysis in air purification.
5. Explain heterogeneous catalysis.
6. Justify the graphite intercalation compounds as model compounds in catalysis research.
7. Explain the interstitial compounds of graphite.
8. Discuss Lineweaver-Burke plot for the determination of k_m .
9. Explain the characteristics of enzyme catalysts?
10. Discuss the concept of Langmuir-Hinshelwood mechanism for heterogeneous catalysis.
11. Explain the basic principle and mechanism of photocatalysis.
12. Explain staging sequence according to Rüdorff and Schulze & Daumas and Herold models for graphite intercalation compounds.
13. Discuss the structural aspects of molecular-graphite intercalation.
14. Explain catalytic reactions catalyzed by metal-graphite intercalation compounds.
15. Discuss the kinetics of Michaelis-Menten equation.
16. Explain homogeneous catalysis and heterogeneous catalysis with suitable examples.