PHYSICAL CHEMISTRY-II

M.Sc. Chemistry
First Year, Semester-II, Paper-I

Lesson Writers

Prof. R. Ramesh Raju
Dept. of Chemistry
University College of Sciences
Acharya Nagarjuna University

Dr. Ch. Subramanyam
Dept. of Chemistry
Bapatla Engineering College
Bapatla

Prof. K. Rambabu
Dept. of Chemistry
University College of Sciences
Acharya Nagarjuna University

Dr. Ch. Naga Sesha Sai Pavan Kumar
Dept. of Chemistry
Vignan University
Vadlamudi

Editor

Prof. R. Ramesh Raju
Dept. of Chemistry
University College of Sciences
Acharya Nagarjuna University

Academic Advisor

Prof. M. Subba rao
Department of Chemistry
Acharya Nagarjuna University

DIRECTOR, I/c.
Prof. V. Venkateswarlu
M.A., M.P.S., M.S.W., M.Phil., Ph.D.
CENTRE FOR DISTANCE EDUCATION
ACHARYA NAGARJUNA UNIVERSITY
NAGARJUNA NAGAR 522 510
Ph: 0863-2346222, 2346208
0863- 2346259 (Study Material)
Website www.anucde.info
E-mail: anucdedirector@gmail.com

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Prof. V. VENKATESWARLU
Director, I/c
Centre for Distance Education,
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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
M.Tech., Ph.D.,
Vice-Chancellor I/c
Acharya Nagarjuna University.

M.Sc. Chemistry 1 Year 2nd Sem- 201CH24-Physical Chemistry-II

PHYSICAL CHEMISTRY-II

CODE: 201CH24

Course Outcomes:

- Knowledge on Third law of thermodynamics, Maxwell-Boltzmann distribution law and Sackur - Tetrode equation and their derivations.
- Understand the Free radical, ionic and Zeigler -Natta Polymerisation, Techniques and method for polymer weight determinations.
- Understand the Butler - Volmer equation and Ilkovic equation, Half wave potential, polarography.
- Understand the Branching Chain Reactions, Enzyme catalysis and Photochemical Equilibrium.
- Understand the free energy change in biochemical reactions, exergonic and endergonic reactions, DNA and RNA in living systems in biopolymer interactions.

UNIT-I:

Thermodynamics II: Third law and Statistical thermodynamics-Nernst Heat theorem -Third law of thermodynamics - Its limitations - Determination of absolute entropy -Concept of distribution - Thermodynamic probability and most probable distribution -Ensemble-ensemble averaging - Maxwell- Boltzmann distribution law – Partition function - Fermi-Dirac statistics - Bose Einstein statistics - Entropy and probability -Boltzmann-Plank equation - Calculation of thermodynamic properties in terms of partition function - Application of partition function - Chemical equilibrium and partition function - Translational, rotational and electronic partition function - Entropy of Monoatomic gases (Sackur - Tetrode equation).

UNIT-II:

Polymer Chemistry: Classification of polymers - Free radical, ionic and Zeigler –Natta Polymerisation - kinetics of free radical polymerisation - Techniques of polymerisation - Glass transition temperature - Factors influencing the glass transition temperature -Number average and Weight average, Molecular weights - molecular weights determination - End group analysis - Osmometry - Light scattering and ultra centrifugation methods.

UNIT-III:

Electro Chemistry II: Electrode potentials - Double layer at the interface - rate of charge transfer - Decomposition potential - Over potential - Tafel plots - Derivation of Butler - Volmer equation for one electron transfer - electro chemical potential. Electro catalysis -Fuel cells-Theory of polarography - Diffusion current - Ilkovic equation - Equation for half- wave potential – Applications of polarography - Amperometric titrations -Corrosion- Forms of corrosion - prevention methods.

UNIT-IV:

Chemical Kinetics: Branching Chain Reactions - Hydrogen-oxygen reaction - lower and upper explosionlimits - Fast reactions - Study of kinetics by flow methods – Relaxation methods - Flash photolysis - Acid base catalysis - protolytic and prototropic mechanism - Enzyme catalysis.

Photo Chemistry: Quantum yield and its determination - Actinometry - Reactions with low and high quantum yields - Photo sensitisation - Exciplexes and Excimers -Photochemical equilibrium – Chemieluminescence - Kinetics of collisional quenchingStern - Volmer equation - Photo Galvanic cells.

UNIT-V:

Biophysical Chemistry: Standard free energy change in biochemical reactions, exergonic and endergonic reactions, hydrolysis of ATP, thermodynamics of biopolymer solutions, chain configuration of bio polymers, calculation of average dimensions. Membrane equilibrium, ion transport through cell membrance, dialosis and its function. Structure and functions of proteins, enzymes, DNA and RNA in living systems, forces involved in bio polymer interactions, electrostatic forces, hydrophobic forces, molecular expansion and dispersion forces.

Reference Books:

1) Physical chemistry, G.K. Vemulapalli (Prentice Hall of India).
2) Physical chemistry, P.W. Atkins. ELBS
3) Chemical kinetics - K.J. Laidler, McGraw Hill Pub.
4) Text book of Physical Chemistry, Samuel Glasstone, Macmillan pub.
5) Statistical Thermodynamics - M.C. Gupta.
6) Polymer Science, Gowriker, Viswanadham, Sreedhar
7) Elements of Nuclear Science, H.J. Arniker, Wiley Eastern Limited.
8) Quantitative Analysis, A.I. Vogel, Addison Wesley Longmann Inc.
9) Physical Chemistry-G.W. Castellan, Narosa Publishing House, Prentice Hall
10) Physical Chemistry, W.J. Moore, Prentice Hall
11) Polymer Chemistry – Billmayer.
12) Fundamentals of Physical Chemistry, K K Rohatgi-Mukherjee. Wiley Eastern Limited Publications.
13) Statistical Thermodynamics - M.Dole.
14) M.N. Hughes, The Inorganic chemistry of Biological Processes, John Wiley and Sons, New York 2nd Edition, 1981.
15) A text book of Biochemistry, AV.S.S. Rama Rao.
16) Physical Chemistry by Atkenes.

ACHARYA NAGARJUNA UNIVERSITY
M.Sc. DEGREE EXAMINATION – FIRST YEAR
ORGANIC CHEMISTRY – R22 Regulations – Semester II

Paper – 201CH24: PHYSICAL CHEMISTRY – II

Time: 3 Hours Maximum Marks: 70

Answer all questions

1. (a) State and explain the Third Law of Thermodynamics. Discuss its limitations. 4M

OR

1. (b) Explain Nernst heat theorem and describe its thermodynamic significance. 4M

2. (a) Derive the Sackur–Tetrode equation for the entropy of a monoatomic ideal gas. Discuss its physical significance. 10M

OR

2. (b) Explain Maxwell–Boltzmann distribution law and derive the expression for the most probable velocity. 10M

3. (a) Write short notes on Bose–Einstein and Fermi–Dirac statistics. Compare their applications. 4M

OR

3. (b) Define partition function. Derive expressions for translational and rotational partition functions. 4M

4. (a) Discuss the relationship between partition function and thermodynamic properties. Explain its application to equilibrium. 10M

OR

4. (b) Explain ensemble and ensemble averaging in statistical thermodynamics with suitable examples. 10M

5. (a) Describe the mechanism of free radical polymerization and derive its rate expression. 4M

OR

5. (b) Write short notes on ionic polymerization and Ziegler–Natta polymerization. 4M

6. (a) Explain the techniques of polymerization and the factors influencing glass transition temperature (T_g). 10M

OR

6. (b) Discuss the methods of molecular weight determination of polymers using osmometry and light scattering techniques. 10M

7. (a) Define electrode potential. Explain how it depends on the nature of the metal and electrolyte concentration. 4M

OR

7. (b) Explain the concept of the electrical double layer at the electrode–electrolyte interface. 4M

8. (a) Derive the Butler–Volmer equation for a one-electron transfer reaction and explain the significance of each term. 10M

OR

8. (b) Describe the theory of polarography and derive the Ilkovic equation. Explain the determination of half-wave potential and its applications. 10M

9. (a) Explain branching chain reactions with reference to the hydrogen–oxygen system. 4M

OR

9. (b) Write short notes on enzyme catalysis and its kinetic mechanism. 4M

10. (a) Discuss photochemical equilibrium and explain the terms quantum yield and Stern–Volmer equation with applications. 10M

OR

10. (b) Describe photo-sensitization, chemiluminescence, and the working principle of a photo-galvanic cell. 10M

CONTENTS

LESSON-1
STATISTICAL THERMODYNAMICS

Third law and Statistical thermodynamics-Nernst Heat theorem -Third law of thermodynamics - Its limitations

OBJECTIVES:

After studying this lesson, you should be able to:

- To know about the Thermodynamics.
- To study about Nernst Heat Theorem.
- To study about Third Law of Thermodynamics.
- To know about the Applications, Consequences and limitations of Third Law of Thermodynamics.

1.1 INTRODUCTION

The classical thermodynamics is not concerned constituent (i.e Molecules, Atoms, neutrons, Protons, Electrons etc.) of the matter the classical thermodynamics is applied to microscopic system.

Boltzmann's provided the molecules bases to the chemical thermodynamics. This is the new approach and is called statistical thermodynamics. It deals with application of statistical mechanic to the chemical thermodynamics. It has been applied successfully to relate the microscopic properties of the individual molecules (Moment of Inertia, dipole moment etc) of system having large no of molecules.

1.2 DISTINCTION BETWEEN QUANTUM MECHANICS, STATISTICAL MECHANICS AND STATISTICAL THERMODYNAMICS.

Statistical mechanics act as bridge b/w thermodynamics and quantum mechanics. Quantum mechanics provide information about the energy of the molecular system. Statistical thermodynamics tells us about the possible arrangement of energy among various molecules of the system and introduce the concept of probability and partition function. Statistical thermodynamics deals with relationship between probability of partition function and thermodynamic properties.

The following are the important probability theorem and which are commonly used in statistical thermodynamics.

1. The no of ways in which 'n' distinguishable particles can be arranged in order will be equal to N!.
2. The no of different ways in which 'n' particles can be selected from N distinguishable particles irrespective of the order of selection will be equal to

$$\frac{N!}{(N-n)!\,n!}$$

3. The no of different ways in which 'n' indistinguishable particles can be arranged in 'g' distinguishable states with not more than one particle in each state will be equal to

$$\frac{g!}{n!\,(g-n)!}$$

1.3 NERNST HEAT THEOREM

Statement

The value of is approaches $\partial\left(\frac{\Delta G}{\partial t}\right)$ zero gradually as temperature is lowered towards the absolute zero.

According to Gibbs – Helmholtz equation.

$$\Delta G - \Delta H = T\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta H = \Delta G - T\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta H = \Delta G + T\Delta S \qquad \left[\left(\frac{\partial}{\partial T}\Delta G\right)_P = -\Delta S\right]$$

Differentiate with respect to 'T' at constant Pressure 'P' We Get

$$\left(\frac{\partial}{\partial T}\Delta H\right)_P = \left(\frac{\partial}{\partial T}\Delta G\right)_P + \Delta S\left(\frac{\partial}{\partial T}T\right)_P + T\left(\frac{\partial}{\partial T}\Delta S\right)_P \qquad \text{(UV formula)}$$

$$\left(\frac{\partial}{\partial T}\Delta H\right)_P = \left(\frac{\partial}{\partial T}\Delta G\right)_P + \Delta S + T\left(\frac{\partial}{\partial T}\Delta S\right)_P \qquad \left(\frac{\partial}{\partial T}T\right)_P = 1$$

$$\Delta C_p = -\Delta S + \Delta S + T\left(\frac{\partial}{\partial T}\Delta S\right)_P \qquad \left[\left(\frac{\partial}{\partial T}\Delta G\right)_P = -\Delta S\right]$$

$$\Delta C_p = T\left(\frac{\partial}{\partial T}\Delta S\right)_P \longrightarrow (1)$$

$$\Delta H = \Delta G + T\Delta S$$

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

Differentiate with respect to 'T' at constant Pressure 'P' We Get

$$\left(\frac{\partial}{\partial T}\Delta G\right)_P = \left(\frac{\partial}{\partial T}\Delta H\right)_P - \Delta S\left(\frac{\partial}{\partial T}T\right)_P - T\left(\frac{\partial}{\partial T}\Delta S\right)_P$$

$$\left(\frac{\partial}{\partial T}\Delta G\right)_P = \left(\frac{\partial}{\partial T}\Delta H\right)_P - \Delta S - T\left(\frac{\partial}{\partial T}\Delta S\right)_P \qquad \left(\frac{\partial}{\partial T}T\right)_P = 1$$

$$-\Delta S = \left(\frac{\partial}{\partial T}\Delta H\right)_P - \Delta S - T\left(\frac{\partial}{\partial T}\Delta S\right)_P \qquad \left[\left(\frac{\partial}{\partial T}\Delta G\right)_P = -\Delta S\right]$$

$$-\left(\frac{\partial}{\partial T}\Delta H\right)_P = \Delta S - \Delta S - T\left(\frac{\partial}{\partial T}\Delta S\right)_P$$

$$-\left(\frac{\partial}{\partial T}\Delta H\right)_P = -T\left(\frac{\partial}{\partial T}\Delta S\right)_P$$

$$\left(\frac{\partial}{\partial T}\Delta H\right)_P = T\left(\frac{\partial}{\partial T}\Delta S\right)_P \longrightarrow (2)$$

From equation (1) and (2) We get

$$\left(\frac{\partial}{\partial T}\Delta H\right)_P = \Delta C_p \longrightarrow (I)$$

Fro Gibbs Equation

$$\Delta G = \Delta H - T\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta G - \Delta H = T\left(\frac{\partial}{\partial T}\Delta G\right)_P \longrightarrow (3)$$

If temperature increases then ΔG is increase & ΔH is decreases

We know that

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

We also know that

$$\Delta G - \Delta H = -T\Delta S \longrightarrow (4)$$

From equation (3) and (4) We get

$$T\left(\frac{\partial}{\partial T}\Delta G\right)_P = -T\Delta S$$

$$\left(\frac{\partial}{\partial T}\Delta G\right)_P = -\Delta S \longrightarrow (II)$$

By measuring EMF of the cells at different temperature the va $\partial\left(\frac{\Delta G}{\partial t}\right)$ decreases in temperature

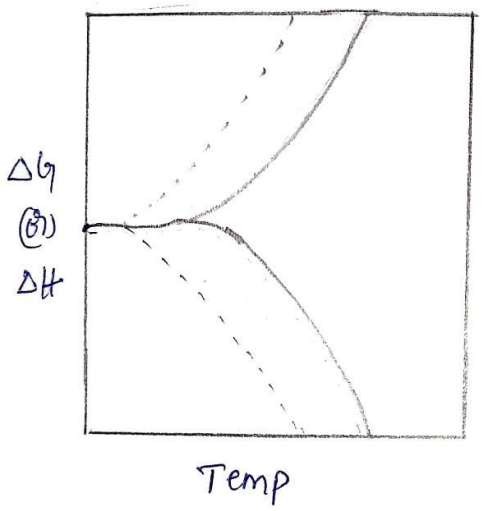
If T=0 then ΔG = ΔH

Case – 1 :

$$\lim_{T \to 0} \Delta G = \lim_{T \to 0} \Delta H = 0$$

$$\lim_{T \to 0} \left(\frac{\partial}{\partial T} \Delta G \right)_P = \lim_{T \to 0} \left(\frac{\partial}{\partial T} \Delta H \right)_P = 0$$

$$\lim_{T \to 0} \Delta G = 0 \quad \& \quad \lim_{T \to 0} \Delta H = 0$$



Case – 2 :

If Temperature decreases then

$$\lim_{T \to 0} \Delta G = 0 \quad \& \quad \Delta C_p = 0$$

Significance:

1. The entropy changes of reaction approaches to zero.
2. The difference between heat capacity of product and reactant are approaches to zero.
3. This theorem holds in case of solids.

1.4 THIRD LAW OF THERMODYNAMICS

According to this law, when a system reaches absolute zero, its entropy approaches a constant minimum value. In an ideal system (such as a perfect crystal), this value is zero. This is because at 0 K, the system is in its ground state, with no thermal motion or additional configurations generating entropy.

1. The third law of thermodynamics deals with the entropy of pure crystalline substances at the absolute zero of temperature.
2. This law can be state in two ways.

Planks statement:

According to Nernst heat theorem the basic for third law as

$$\lim_{T \to 0} \Delta C_p = \lim_{T \to 0} \left[(C_P)_{Product} - (C_P)_{Reactant} \right]$$

From the above equation it follows that ΔC_p decreases very rapidly to zero as the absolute temperature is zero approached. It implies that the heat capacity of products and reactants become identical at absolute zero. Hence plank extended this concept and postulated that heat capacity of substances tend to become zero at absolute zero. Hence extended form of the Ernst heat theorem may be follows.

$$\lim_{T \to 0} C_p = 0$$

We Know that

$$\lim_{T \to 0} \Delta S = \left[S_{Product} - S_{Reactant} \right]$$

Again this equation reveals that all substance in the solid state must have the same entropy at the absolute zero of temperature. Then third law of thermodynamics may be stated as entropy of solid or a liquid approaches zero at the absolute zero of the temperature.

$$\text{i.e.} \quad \lim_{T \to 0} S = 0$$

Lewis and Raudall's Statement:

The third law of thermodynamics is used for calculating the absolute entropies of solid, liquids and gases of at different temperatures.

Applications of Third law of Thermodynamics:

The third law has been found to be useful to calculating the absolute entropies of the pure substance at different temperatures by using thermal data.

We know that

$$dS = \Delta C_p \cdot \frac{dT}{T}$$

$$dS = \Delta C_p \cdot \frac{dT}{T}$$

Now Integrating between temperature limits '0' to 'T' We get.

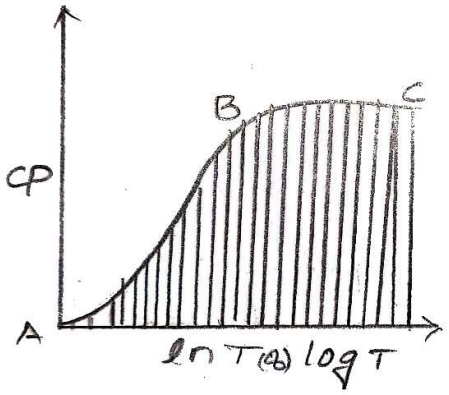
$$S_T - S_0 = \int_0^T C_p \cdot \frac{dT}{T}$$

$$S_T - S_0 = C_p \ln T$$

According to third law of thermodynamics as that $S_0 = 0$ at T= 0, then we get

$$S_T = \int_0^T C_p \cdot \frac{dT}{T}$$

$$S_T = C_p \ln T$$



Consequences of the Third Law of Thermodynamics

1. Impossibility of reaching absolute zero temperatures

It follows from the third law of thermodynamics that absolute zero temperature cannot be achieved in any final process associated with a change in entropy. It can only be approached asymptotically.

Therefore, the third law of thermodynamics is sometimes formulated as the principle of the impossibility of reaching absolute zero temperature.

2. The behaviour of thermodynamic coefficients

A number of thermodynamic consequences follow from the third law of thermodynamics: as $T \rightarrow 0$, it must also tend to zero:

- Heat capacity at constant pressure and constant volume
- coefficients of thermal expansion and some similar values.

The validity of the third law of thermodynamics was questioned at one time, but it was later discovered that all apparent contradictions are associated with metastable states of matter that cannot be considered to be in thermodynamic equilibrium.

Limitations of the third law of thermodynamics

1. Impossibility of reaching absolute zero

One of the main limitations of the third law is that **absolute zero is not reachable** in a finite number of steps.

This principle, known as the absolute zero inaccessibility theorem, implies that any attempt to cool a system to 0 K will only succeed in asymptotically approaching this temperature.

Consequently, there will always be a small remnant of thermal motion and hence a residual entropy.

2. Limitations in real systems

Another significant limitation is found in **real systems**, such as crystals.

Although the theory assumes perfect crystals with no structural defects, real crystals contain imperfections that generate additional configurations and increase entropy, even at temperatures close to absolute zero. These defects are unavoidable, since crystals form at temperatures above 0 K.

3. Incompatibility with metastable states

The third law cannot describe systems in **metastable** states or outside thermodynamic equilibrium, such as glasses or amorphous polymers.

In these cases, the residual entropy is not uniquely defined, which complicates the application of the law.

SUMMARY

- To know about the Thermodynamics.
- To study about Nernst Heat Theorem.
- To study about Third Law of Thermodynamics.
- To know about the Applications, Consequences and limitations of Third Law of Thermodynamics.

SELF ASSESSMENT QUESTIONS

1. Derive Nernest equation.
2. Define Third Law of Thermodynamics.
3. Write about Third Law of Thermodynamics.

Prof. K. Rambabu

LESSON-2
DETERMINATION OF ABSOLUTE ENTROPY -CONCEPT OF DISTRIBUTION - THERMODYNAMIC PROBABILITY AND MOST PROBABLE DISTRIBUTION -ENSEMBLE- ENSEMBLE AVERAGING

OBJECTIVES:

After studying this lesson, you should be able to:

- To know about the absolute entropy of Liquids and Gases.
- To study about Distribution.
- To study about Difference of M-B, B-E and F-D Statistics.
- Thermodynamic probability and most probable distribution:
- To know System – Assemble and Ensemble
- To study about on Ensemble Average.

2.1 EVOLUTION OF ABSOLUTE ENTROPIES OF LIQUIDS AND GASES:

In all these easy the given substances at the crystalline state of the give substance at the absolute zero and then the supplying heat to this solid at 0 K. It can be converted into the required state of the substance at a given temperature. The sum of the entropy changes involving these conversions will give the value of absolute. Entropy of the specific substances at the given temperature. In these calculations the absolute entropy at 0'K has been taken to be zero.

When we must calculate the absolute entropy of liquid, the following steps are involved.

First of all, measurements are made on the solid from at the melting point. The entropy of the solid at this temperature (ΔS_1) is given by

$$\Delta S_1 = \int_0^{T_m} \left(C_p\right)_s \frac{dT}{T}$$

T_m - Melting point temperature.

In order to obtain the entropy of the melting point becomes necessary to add the entropy of fusion (ΔS_2) which as follows.

$$\Delta S_2 = \frac{\Delta H_f}{T_m}$$

Where ΔH_f is molar heat fusion

So to evaluate the entropy of liquid at any higher temperature to increase in entropy can be calculated by area under the curves between melting point and any particular temperature.

$$\Delta S_3 = \int_{T_m}^{T_L} \left(C_p\right)_L \frac{dT}{T}$$

Hence the total absolute entropy of (S_T) equal to sum of all the above steps.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$S_T = \int_0^{T_m} (C_p)_s \frac{dT}{T} + \frac{\Delta H_f}{T_m} + \int_{T_m}^{T_L} (C_p)_L \frac{dT}{T}$$

Total absolute entropy of liquid is calculated as above then to evaluate the absolute entropy of gasses the following steps are used.

The liquid is converted to vapor's at its boiling point

$$\Delta S_4 = \frac{\Delta H_V}{T_b}$$

Here ΔH_V is molar heat of vaporization.

T_b is boiling point of temperature.

The entropy involved in heating the gas from temperature T_b to the given temperature T is given as follows

$$\Delta S = \int_{T_b}^{T} (C_p)_g \frac{dT}{T}$$

$(C_P)_g$ is heat capacity of substance in the gaseous state.

The absolute entropy (ST) of the gas at temperature 'T' is given by

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

$$S_T = \int_0^{T_m} (C_p)_s \frac{dT}{T} + \frac{\Delta H_f}{T_m} + \int_{T_m}^{T_L} (C_p)_L \frac{dT}{T} + \frac{\Delta H_V}{T_b} + \int_{T_b}^{T} (C_p)_g \frac{dT}{T}$$

Limitations:

1. The absolute entropy of some substances is calculated by graphical integration of heat capacity. The agreement between the calculating spectroscopy and colorimetric entropies of the substances like O_2, N_2, …… etc are calculated.
2. The other substance is CO, NO, H_2O, N_2O, etc has colorimetric entropies less than spectroscopic entropies is calculated.

2.2 DISTRIBUTION:

The set of occupation number is called Distribution.

Micro State:

Micro state to which each molecule of the system belongs to temporary.

Macro state

It may be defined as the specification of the number of molecules or phase points in each cell of phase space, such as n_1 molecules in cell, n_2 molecules in cell and so on…….

2.3 TYPES OF DISTRIBUTION OR STATISTICS:

There are three types of statistics depending on different physical situations in nature.

1. Maxwell-Boltzmann (or M-B) Distribution: In M-B statistics the particles are assumed to be distinguishable and any number of particles may occupy the same energy level.

2. **Bose-Einstein (or B-E) Statistics:** In B-E statistics the particles are assumed to be indistinguishable and any number of particles may occupy the same energy level. This statistic is obeyed by particles having integral (I= 1, 2, 3, 4 etc) spins. E.g. ^4He, N_2, H_2, D_2, photons, etc. The B-E statistics is applicable to those particles whose wave functions are symmetric in nature.

3. Fermi-Dirac (F-D) Statistics: In F-D statistics the particles are assumed to be indistinguishable but only one particle may occupy in a given energy level. This statistic is obeyed by particles having half-integral (I=1/2, 3/2, 5/2, 7/2 etc) spins. E.g. ^3He, NO, protons, electrons etc. The F-D statistics is applicable to those particles whose wave functions are antisymmetric in nature.

The differences among the three types of statistics are summarizes in **table 2.1.**

Table 2.1: Difference of M-B, B-E and F-D Statistics

M-B Statistics	B-E Statistics	F-D Statistics
The laws of classical mechanics are applicable according to which individual molecules/atoms have definite positions and momenta.	The laws of quantum mechanics are applicable according to which individual molecules/atoms have only quantized values of energy.	The laws of quantum mechanics are applicable.
Particles are distinguishable	Particles are indistinguishable	Particles are indistinguishable
Any number of particles may occupy the same energy level.	Any number of particles may occupy the same energy level.	Only one particle may occupy in each energy level.
Does not depend on the internal structure of the particles.	This statistic is obeyed by particles having integral nuclear spin whose wave functions are symmetric in nature.	This statistic is obeyed by particles having half-integral spin whose wave functions are antisymmetric in nature
The particles obeying the M-B statistics are called maxwellons or boltzmannons.	The particles obeying the B-E statistics are called bosons.	The particles obeying the F-D statistics are called Fermions.

2.4 THERMODYNAMIC PROBABILITY AND MOST PROBABLE DISTRIBUTION:

1. Thermodynamic probability of macro state of a system is defined as the total no of different ways total no of micro states by which the given micro state may be realized.
2. It is denoted by ‘P’ or ‘W’
3. Probability if Macro state = Number of micro states corresponding to that macro state.
4. The thermodynamic probability is proportional to the mathematical probability.

5. Suppose the volume of the molecular system (V) contains 'n' particles and the distinguishable particles are very large.
6. Then the total energy of the system E at the temp T.
7. All the particles will not have the same energy.
8. Each particle may exists in no of allowable energy levels.
9. Suppose n_o is the no of particles in the energy level with energy E_o, n_1 particles with energy E_1, n_2 particles having energy E_2 etc. then total no of particles is

   b. $N = \sum_{i=0}^{i} n_i E_i$

   c. $= n_0 + n_1 + n_2 + n_3 + \ldots\ldots\ldots + n_i$

   d. Total energy $E = \sum_{i=0}^{i} n_i E_i$

10. Hence the total number, if possible, distribution can be determined by statistical method.
11. According to classical statistics the no of ways in which 'n' particles can be arranged in these energy levels equal to the no of permutations of 'n' things in group $n_0 + n_1 + n_2 + \ldots\ldots\ldots + n_i$
12. The total no of distributions

    a. $$\frac{n!}{n_0!\, n_1!\, n_2!\, \ldots\ldots\ldots n_i!}$$

13. Thermodynamic probability

14. $$P = \frac{n!}{n_0!\, n_1!\, n_2!\, \ldots\ldots\ldots n!}$$

15. Taking the log on both sides to the above equation

    i. $\ln P = \ln n! - (\ln n_0! + \ln n_1! + \ldots\ldots\ldots + \ln n_i!$

    ii. $\Rightarrow \quad \ln P = \ln n! - \sum_{i=0}^{i} \ln n_i!$ ----------(2)

16. According to sterling formula is that

    i. $\ln n! = n \ln n - n$ ----------(3)

    ii. $\sum \ln n_i! = \sum n_i \ln n_i - \sum n_i$ ----------(4)

    b. Substituting Equation (3) and (4) in equation (2) we get

       i. $\ln P = n \ln n - n - \sum n_i \ln n_i + n$

       2. $\ln P = n \ln n - \sum n_i \ln n_i$

       ii. Differentiating the above equation

       1. $d \ln P = - d \sum n_i \ln n_i$

Modifications:

1. Certain states are energetically close to each other that they cannot be distinguish from one another, i.e. degeneracy of energy level.
2. Regarding this correction a factor 'g' is called statistical energy weight factor for each state is introduced.
3. A given energy level is said to be g-degenerated.
4. If they are 'g' number of possible distributions of energy in that energy level.
5. It is due to fact that the molecules are indistinguishable.
6. Hence we had divide the total expressive for 'P' by n! then the probability.

a. $$P = \frac{g_0^{n_0}}{n_0!} \frac{g_1^{n_1}}{n_1!} \frac{g_2^{n_2}}{n_2!} \ldots\ldots\ldots \frac{g_i^{n_i}}{n_i!}$$

7. This equation is result that the classical statistical treatment modified by the quantum statistics.

2.5 SYSTEM – ASSEMBLE AND ENSEMBLE:

Suppose we have a collection of particles then each particle is known as system and collection of particles as whole is called assemble.

An ensemble is defined as the collection of large number of assembles which are independent of each other, but which have been made macroscopically has identical as possible.

Different types of ensembles

i) Uniform ensemble:

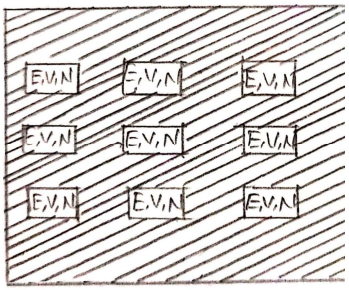
In a uniform ensemble the density in phase space is constant.

$$\lim_{\Delta V \to 0} \frac{1}{\Delta V} = \lim_{N \to \infty} \frac{\Delta N}{N} = \text{Constant}$$

Where ΔN is number of system in an element of volume. ΔV and N denotes the total number of systems in example.

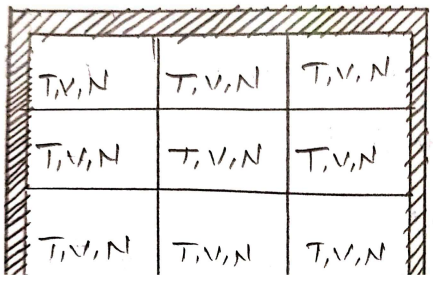
ii) Micro Canonical Ensemble:

1. An ensemble consisting of large collection of identical
   a. independent assembles.
2. Which has the same energy E, Volume V, and number
   a. of system N.
3. Each Assembles is separated from its neighbours
   a. by means of rigid impermeable adiabatic walls wit
   b. of particles and energy.



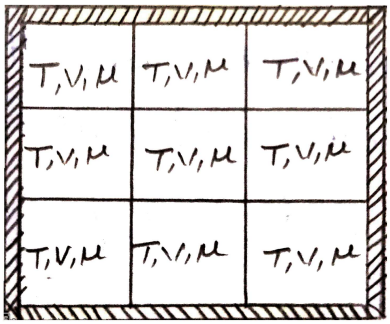
iii) Canonical Ensemble:

1. It is collection of large number of identical but distingui assemblies (System)
2. Having the same temperature T, Volume V and number identical system.
3. As the temperature of all assemblies is same follows tha thermal contact or energy exchange is allowed b the system of the ensembles but not exchanges o particles.
4. In this ensembles are separated by rigid and impermeabl



iv) Grand canonical Ensemble:

1. It is collection of large number of independent assembli
   a. having the same temperature T, Volume V and Ch
   b. potential μ of each species.
2. It follows that individual assembles are separated by rigid
   a. permeable and conducting walls with exchange bc



b. and energy.

Uses of Ensembles:

Although there is infinite no of ensembles. We have considered only four type of which are useful for two reasons.

1. All the four types correspond approximately to the type of thermodynamic measurements which are frequently met in practice.
2. We have considered four types in which the values of thermodynamic quantity are not very sensitive to the method of measurements.

2.6 ENSEMBLE AVERAGE:

The average value of any properties 'm' of a system takes over all the systems that are members the ensemble called ensemble average m of the properties, so that

$$\overline{m} = \sum \frac{mJ}{n}$$

There are two basic postulates required to relate concept of the ensemble to practical calculations of average properties.

1. The average of any mechanical variable 'm' over a long time in the actual system is equal to the ensemble average 'm' provide that the system of ensemble replicate thermodynamic state and surroundings of the actual system.
2. In an ensemble of isolated thermodynamics system, the members are distributed with equal probability over the possible quantity states consists with specified values N,V,E. This is the principle of equal priori probabilities.

SUMMARY:

- To know about the absolute entropy of Liquids and Gases.
- To study about Distribution.
- To study about Difference of M-B, B-E and F-D Statistics.
- Thermodynamic probability and most probable distribution:
- To know System – Assemble and Ensemble
- To study about on Ensemble Average.

SELF ASSESSMENT QUESTIONS

1. Write about different types of Ensembles.
2. discuss about distribution.
3. write a note on ensemble average.

Prof. K. Rambabu

LESSON-3
MAXWELL- BOLTZMANN DISTRIBUTION LAW – PARTITION FUNCTION - FERMI-DIRAC STATISTICS - BOSE EINSTEIN STATISTICS - ENTROPY AND PROBABILITY -BOLTZMANN-PLANK EQUATION

OBJECTIVES:

After studying this lesson, you should be able to:

- To know about different types of statistics.
- To study about Derivation of Maxwell Boltzmann Statistics.
- To study about derivation of Bose – Einstein Statistics.
- To study about derivation of Fermi – Dirac Statistics.
- To know about Entropy and Probability – Boltzmann – Plank's equation.

3.1 TYPES OF STATISTICS:

There are three types of statistics.

1. Maxwell Boltzmann Statistics
2. Bose – Einstein Statistics.
3. Fermi – Dirac Statistics.

Maxwell Boltzmann Statistics:

In these particles are assumed to be distinguishable and any number of particles may occupy the same energy level. Particles obeying m-B statistic are called Boltzmann's or Maxwellians.

Bose – Einstein Statistics:

In these particles are indistinguishable and any number of particle may be occupy a given energy level particles obeying Bose- Einstein Statistic are called Bassons.

Ex: H_2, D_2, N_2, $^4He^+$ and Photons.

Fermi – Dirac Statistics:

In these particles are indistinguishable but only one particle may be occupy a given energy level.

Particles obeying F-D statistics are called Fermions

Ex: NO, He^3, Protons, Electrons.

3.2 MAXWELL – BOLTZMANN DISTRIBUTION LAW:

Assumptions:

1. Each particle of the molecular system (microstate) is distinguishable from the other.
2. Intramolecular forces are absent
3. No restriction on assigning various energy level to the particle is being imposed.
4. The particles are localized.

Derivation

1. Consider the distribution of total energy E among the various energy level E_0, E_1, E_2,…….. E_i, of 'n' particles.
2. Each particle may exist in a number of allowable energy levels.
3. The no of particles 'n' may be assigned to the energy levels.
4. In such way that n_2 particles to be present in the level with energy E_2.
5. Irrespective of the distribution the total number of particles and energy of the system remains constant.

Now system contain number of particles

$$N = \sum_{i=1}^{i} n_i \qquad \text{----------(1)}$$

Total energy of the particles 'E' is

$$E = \sum_{i=1}^{n_i} E_i\, n_i \qquad \text{----------(2)}$$

Then Probability 'P'

$$P = \frac{n!}{n_0!\ n_1!\ n_2!\ \ldots\ldots n!} \qquad \text{---------- (3)}$$

Taking 'ln' on both sides

$$\ln P = \ln n! - \sum \ln n_i ! \qquad \text{----------(4)}$$

Applying sterling formula

$$\ln n! = n \ln n - n \qquad \text{----------(5)}$$

$$\ln n_i! = n_i \ln n_i - n_i$$

$$\sum \ln n_i! = \sum n_i \ln n_i - \sum n_i \qquad \text{----------(6)}$$

Substitute equation (5) and (6) in equation (4) we get.

$$\ln P = n \ln n - n - \sum_{i=0}^{i} n_i \ln n_i + \sum n_i$$

$$\ln P = n \ln n - n - \sum n_i \ln n_i + n$$

$$\ln P = n \ln n - \sum n_i \ln n_i \qquad \text{----------(7)}$$

6. The most probable distribution of particles or molecules in the system s one for which P or W is maximum.
7. Hence for these conditions and d ln P will have to be zero.

$$d \ln P = dP = 0 \qquad \text{----------(8)}$$

Differentiate equation (7) we get

$$d \ln P = dn [\ln n] - d \sum n_i \ln n_i$$

$$d \ln P = 0 - \sum [n_i\ (1/n_i)\, dn_i + \ln n_i\, d n_i]$$

$$d \ln P = - \sum [1 + \ln n_i]\, dn_i$$

$$\sum [1 + \ln n_i]\, dn_i = 0 \qquad \text{----------(9)}$$

8. For this maximum total number of particles and total energy of the system must remaining constant with time.
9. The variation of dn and dE must be equal to zero so that from equation (1) we get

$$dn = \sum_{i=0}^{i} d\, n_i = 0 \qquad \text{----------(10)}$$

i

Similarly $dE = \sum_{i=0} E_i\, dn_i = 0$ ----------(11)

Multiply equation (10) and (11) by orbitary constant $\propto^I$ and β adding equation (9).We get

$$\sum [\ln n_i + (1+ \propto^I) + \beta E_i\ ]\ dn_i = 0$$
$$\Rightarrow [\ln n_i + (1+ \propto^I) + \beta E_i\ ]\ dn_i = 0$$
$$\Rightarrow \ln n_i + (1+ \propto^I) + \beta E_i = 0$$
$$\Rightarrow \ln n_i = -\ [\ (1+ \propto') + \beta E_i\ ]$$
$$\Rightarrow n_i = e^{-(1+\propto')}\, e^{\beta E_i} \qquad \text{----------(12)}$$

Deriving eq (12) are made that each level said to be non degenerate. It is possible that there may be no of quantum levels almost identical energies for this introduced 'g_i' for energy level 'E_i' then

$$\Rightarrow n_i = g_i\, e^{-(1+\propto')}\, e^{-\beta E_i} \qquad \text{----------(13)}$$
$$\Rightarrow \sum n_i = \sum g_i\, e^{-(1+\propto')}\, e^{-\beta E_i}$$
$$n = \sum g_i\, e^{-(1+\propto')}\, e^{-\beta E_i} \qquad \text{----------(14)}$$

Then n_i / n

$$\frac{n_i}{n} = \frac{g_i\, e^{-(1+\propto')}\, e^{-\beta E_i}}{\sum g_i\, e^{-(1+\propto')}\, e^{-\beta E_i}}$$

$$\frac{n_i}{n} = \frac{g_i\, e^{-\propto}\, e^{-\beta E_i}}{\sum g_i\, e^{-\propto}\, e^{-\beta E_i}} \qquad \because \propto = (1+\propto')$$

$$\frac{n_i}{n} = \frac{g_i\, e^{-\beta E_i}}{\sum g_i\, e^{-\beta E_i}}$$

3.3 BOSE – EINSTEIN STATISTICS:

Consider a system of 'N' indistinguishable particles such as n_i particles are in energy levels E_i with degeneracy g_i then n_i particles have distribute among 'g_i' states.

Suppose there are n_i particles with energy 'E_i' in which there are 'g' state of energy we shall need g-1 position to place in n_i particle in 'g' sections. Each section corresponds to degeneracy level 'g' and permutation of n_i particles and g-1 particles occurs simultaneously. We will be given $(n_i + g_i - 1)!$ Also include n_i particles among themselves. Hence we must divide $(n_i + g_i - 1)!$ By the number of permutations of (g_i-1) partitions. i.e. $(g_i-1)!$ and the number of permutations of n_i particles viz $n_i!$ to obtain the no of possible arrangements of the n_i particles in the energy level 'E_i'.

Thus the total number of arrangements

$$\frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \longrightarrow (1)$$

The thermodynamic probability will given by

$$W = \sum \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \longrightarrow (2)$$

Apply ln both sides we get

$$\ln W = \sum \ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)!$$

Applying sterling formula we get

i.e. $\sum \ln n_i = n \ln n - n \longrightarrow$ (3)

$\ln W = \sum [(n_i + g_i - 1) \ln (n_i + g_i - 1) - (n_i + g_i - 1)] - [n_i \ln n_i - n_i] - [(g_i - 1) \ln (g_i - 1) - (g_i - 1)]$

Here $(g_i - 1) \cong g_i$

$\Rightarrow \ln W = \sum [(n_i + g_i) \ln (n_i + g_i) - (n_i + g_i)] - [n_i \ln n_i - n_i] - [g_i \ln g_i - g_i]$

$\Rightarrow \ln W = \sum [(n_i \ln (n_i + g_i) + g_i \ln (n_i + g_i) - n_i - g_i - n_i \ln n_i + n_i - g_i \ln g_i + g_i]$

$\Rightarrow \ln W = \sum [(n_i \ln (n_i + g_i) + g_i \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i]$

$$\Rightarrow \ln W = \sum n_i \ln \left(\frac{n_i + g_i}{n_i}\right) + g_i \ln \left(\frac{n_i + g_i}{g_i}\right)$$

Differentiate the above equation we get

$$d \ln W = \sum n_i \left(\frac{n_i + g_i}{n_i}\right) d\left(\frac{n_i + g_i}{n_i}\right) + \ln \left(\frac{n_i + g_i}{n_i}\right) d n_i + g_i \left(\frac{n_i + g_i}{g_i}\right) d\left(\frac{n_i + g_i}{g_i}\right) + \ln \left(\frac{n_i + g_i}{g_i}\right) d g_i$$

$$d \ln W = \sum n_i \left(\frac{n_i + g_i}{n_i}\right) d\left(1 + \frac{g_i}{n_i}\right) + \ln \left(1 + \frac{g_i}{n_i}\right) d n_i + g_i \left(\frac{n_i + g_i}{g_i}\right) d\left(\frac{n_i}{g_i} + 1\right) + \ln \left(\frac{n_i}{g_i} + 1\right) d g_i$$

$$d \ln W = \sum n_i \left(\frac{n_i}{n_i + g_i}\right) d\left(1 + \frac{g_i}{n_i}\right) + \ln \left(1 + \frac{g_i}{n_i}\right) d n_i + g_i \left(\frac{g_i}{n_i + g_i}\right) d\left(\frac{n_i}{g_i} + 1\right)$$

$$d \ln W = \sum n_i \left(\frac{n_i}{n_i + g_i}\right) \left(-\frac{1}{n_i^2}\right) g_i d n_i + \ln \left(1 + \frac{g_i}{n_i}\right) d n_i + g_i \left(\frac{g_i}{n_i + g_i}\right) \left(\frac{1}{g_i}\right) d n_i$$

$$d \ln W = \sum \left(\frac{n_i^2}{n_i + g_i}\right) \left(-\frac{g_i}{n_i^2}\right) d n_i + \ln \left(1 + \frac{g_i}{n_i}\right) d n_i + g_i \left(\frac{g_i}{n_i + g_i}\right) \left(\frac{1}{g_i}\right) d n_i$$

$$d \ln W = \sum -\left(\frac{g_i}{n_i + g_i}\right) d n_i + \ln \left(1 + \frac{g_i}{n_i}\right) d n_i + \left(\frac{g_i}{n_i + g_i}\right) d n_i$$

$$d \ln W = \sum \ln \left(1 + \frac{g_i}{n_i}\right) d n_i \longrightarrow (4)$$

'N' the maximum, ln W is zero

$$d \ln W = \sum \ln \left(1 + \frac{g_i}{n_i}\right) d n_i = 0$$

We know that $\sum d n_i = 0 \longrightarrow (5)$

$\sum E_i d n_i = 0 \longrightarrow (6)$

Multiply equation (5) with $\propto$ and equation (6) with β substitute equation (4)

$$\sum \left[\propto + \beta E_i - \ln \left(1 + \frac{g_i}{n_i}\right)\right] d n_i = 0$$

$$\propto + \beta E_i = \ln \left(1 + \frac{g_i}{n_i}\right)$$

$$e^{\propto + \beta E_i} = \left(1 + \frac{g_i}{n_i}\right)$$

$$\frac{g_i}{n_i} = e^{\propto + \beta E_i} - 1$$

$$n_i = \frac{g_i}{e^{\propto + \beta E_i} - 1}$$

This equation is called Bose – Einstein statistics equation.

3.4 FERMI DIRAC STATISTICS:

In Bose – Einstein statistics no restriction's was made to the number of particles present in any energy state.

1. But in Fermi Dirac statistics to particles (electrons) the Poulis exclusion principle is also taken into consideration.
2. Two particles in an atom cannot posses the same energy state.
3. Suppose, if there are n_i particles of energy E_i with degeneracy g_i.
4. Hence all the particles are identical and one state can posses only on state.
5. The number of ways in which g_i is replaced by $(g_i - n_i)$.
6. According to Fermi Dirac, the n_i particles can be distinguished in g – states in that group is given by

$$\frac{g_i}{n_i!\,(g_i - n_i)!}$$

7. Then thermodynamics probability will be

$$W = \sum \frac{g_i}{n_i!\,(g_i - n_i)!}$$

Apply ln both sides we get

$\ln W = \sum \ln g_i - \ln n_i ! - \ln (g_i - n_i)!$

Applying sterling formula we get

i.e. $\sum \ln n_i = n \ln n - n$

$\ln W = \sum [(g_i \ln g_i - g_i) - [n_i \ln n_i - n_i] - [(g_i - n_i) \ln (g_i - n_i) - (g_i - n_i)]$

$\ln W = \sum [(g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i - n_i) \ln (g_i - n_i) + g_i - n_i)]$

$\ln W = \sum [(g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i))]$

At 'g' is constant

$$\ln W = \sum g_i \ln \left(\frac{g_i}{g_i - n_i}\right) - n_i \ln \left(\frac{g_i}{g_i - n_i}\right)$$

$$d \ln W = \sum \ln \left(\frac{g_i - n_i}{n_i}\right) d n_i$$

at the maximum, $d\ln W = 0$

$$\sum \ln \left(\frac{g_i}{n_i} - 1\right) d n_i = 0 \longrightarrow (1)$$

We know that $\sum d n_i = 0 \longrightarrow (2)$

$\sum E_i \, d n_i = 0 \longrightarrow (3)$

Multiply equation (2) with $\propto$ and equation (3) with β subtracting equation (1)

$$\sum \left[\propto + \beta E_i - \ln \left(\frac{g_i}{n_i} - 1\right) \right] d n_i = 0 \qquad [\because d n_i \neq 0]$$

$$\propto + \beta E_i - \ln \left(\frac{g_i}{n_i} - 1\right) = 0$$

$$\propto + \beta E_i = \ln \left(\frac{g_i}{n_i} - 1\right)$$

$$e^{\propto + \beta E_i} = \left(\frac{g_i}{n_i} - 1\right)$$

$$e^{\alpha+\beta E_i} + 1 = \left(\frac{g_i}{n_i}\right)$$

$$n_i = \frac{g_i}{e^{\alpha+\beta E_i} + 1}$$

This equation is known as Fermi – Dirac Statistics equation.

3.5 ENTROPY AND PROBABILITY – BOLTZMANN – PLANK'S EQUATION:

According to Boltzmann, entropy is a function of the probability of thermodynamics state

$S = f(w)$

Where 's' is the entropy and 'w' is probability of particular state.

The nature of this function can be determined by considering two study states having entropies S_1 and S_2 and their probabilities W_1 and W_2. we know that entropy is an additives. So the entropy of composite state is given by $S = S_1 + S_2$

We also know that probabilities is multiplicative, so the probability of composite state is

$W = W_1 + W_2$

$\therefore S = S_1 + S_2 = f(W_1 + W_2)$

As $S_1 = f(W_1)$ and $S_2 = f(W_2)$ then it follows that on

$f(W_1) + f(W_2) = f(W_1 \times W_2)$ ⟶ (1)

on differentiating equation (1) with respect to W_1 and W_2 kept constant

$W_2 f'(W_1 \times W_2) = f'(W_1)$

Now differentiating equation (1) with W_2 kept W_1 is constant

$f'(W_1 \times W_2) + W_1 W_2 f''(W_1 \times W_2) = 0$

$f'(W) + W f''(W) = 0 \quad (\because W = W_1 \times W_2)$

But putting $p = f'(W)$ and $dp / dw = f''(W)$ then

$$P + W\frac{dP}{dW} = 0$$

$PdW + WdP = 0$

$D(PW) = 0$

On integration, we get $WP=K$

Where 'K' is integration constant

$$W\frac{d}{dW}f(W) = K \qquad \left[\because P = f'(W) = \frac{d}{dW}f(W)\right]$$

$$\frac{d}{dW}f(W) = \frac{K}{W}$$

$$d\,f(W) = K\,\frac{dW}{W}$$

Now integrating the above expression we get

$$\int d\,f(W) = K\int \frac{dW}{W}$$

$f(W) = K \ln W + C$

$S = K \ln W + C$

This equation is known as Boltzmann – plank equation.

SUMMARY:

- To know about different types of statistics.
- To study about Derivation of Maxwell Boltzmann Statistics.
- To study about derivation of Bose – Einstein Statistics.
- To study about derivation of Fermi – Dirac Statistics.
- To know about Entropy and Probability – Boltzmann – Plank's equation.

SELF ASSESSMENT QUESTIONS

1. Derive Maxwell Boltzmann Statistics.
2. Write the de derivation of Bose – Einstein Statistics.
3. Derive Fermi – Dirac Statistics.
4. Explain the Boltzmann – Plank's equation for Entropy and Probability.

Prof. K. Rambabu

LESSON-4

CALCULATION OF THERMODYNAMIC PROPERTIES IN TERMS OF PARTITION FUNCTION - APPLICATION OF PARTITION FUNCTION - CHEMICAL EQUILIBRIUM AND PARTITION FUNCTION - TRANSLATIONAL, ROTATIONAL AND ELECTRONIC PARTITION FUNCTION

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the partition function.
- To study about derivation of Translation Partition Function.
- To know about the Rotational Partition Function.
- To learn about Electronic Partition Function.
- To know about Calculation of thermodynamic properties.

4.1 PARTITION FUNCTION

The partition function may be defined as the sum of the probability factors for different energy states.

According to Boltzmann distribution law

$$\frac{n_i}{n} = \frac{g_i \; e^{-E_i/KT}}{\sum g_i \; e^{-E_i/KT}}$$

Here the denominator on the right hand side of the above function is known as partition function. It is represented by Q.

$$Q = \sum g_i \; e^{-E_i/KT}$$

$$Q = g_0 \, e^{-E_0/KT} + g_1 e^{-E_1/KT} + g_2 e^{-E_2/KT} + \qquad + g_i \; e^{-E_i/KT}$$

Where g_i is the statistical weight factor and is equal to the degree of degeneracy. i.e. number of super imposed energy levels K is Boltzmann constant.

i.e K = R / N

E_i the energy if the quantum state in excess of lowest possible value & T is temperature on Kelvin scale.

For general purpose it may be written as

$$Q = \sum_{i=0}^{\infty} g_i \; e^{-E_i/KT}$$

Physical significance: -

1. Partition function is dimensioning less quantity. Its value depends up to the molecular weight, the temperature, the molecular volume, the inter nuclear distance, the molecular motion and the inter molecular forces.
2. It is used in the microscopic properties of individual molecules (Such as momentum of inertia, dipole moment) with the macroscopic (Such as molar hem entropy and polarization).

Form Maxwell Boltzmann law

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-E_i/KT}$$

Where $E_0 = 0$ and $g_0 = 1$

$$n_i = n_0 g_i e^{-E_i/KT}$$

$$\sum n_i = \sum n_0 g_i e^{-E_i/KT}$$

$$\sum n_i = n_0 \sum g_i e^{-E_i/KT}$$

$$\sum n_i = n_0 Q \qquad \because Q = \sum g_i e^{-E_i/KT}$$

$$n = n_0 Q \qquad \because \sum n_i = n$$

$$Q = \frac{n}{n_0}$$

The partition function is defined as the ratio of number o particles in the i^{th} level to the zero level.

4.2 TRANSLATION PARTITION FUNCTION

- The partition function (Q_t) for translation motion is in one direction given by

$$Q_t(x) = \sum g_t e^{-E_i/KT} \longrightarrow (1)$$

Where E_t = Translational energy of molecule in 'X' direction.
K = Boltzmann constant
g_t = Statistical weight factor in each level.

- As the statistical weight of each level is unity ($g_t = 1$)
- The partition function $Q_t(x)$ becomes as

$$Q_t(x) = \sum e^{-E_i/KT} \longrightarrow (2)$$

- We shall now proceed to calculate the value of E_t
- According to Broglie's Principle

$$\lambda = \frac{h}{m\mu}$$

$$\lambda_x = \frac{h}{m\mu}$$

$$m\mu = \frac{h}{\lambda_x} = Px \longrightarrow (3)$$

- Here Px is pressure (or) momentum of moving particle.
- The energy of such particle is given by

$$E_t = \frac{P_x^2}{2m} \longrightarrow (4)$$

Substitute equation (3) in equation (4) we get

$$E_t = \frac{h^2}{2m\lambda_x^2} \longrightarrow (5)$$

- For stationary wave function l_x must b equal to $n\lambda_x / 2$

$$l_x = \frac{n\lambda_x}{2} \longrightarrow (6)$$

$$\lambda_x = \frac{2l_x}{n} \longrightarrow (7)$$

Substitute equation (7) in equation (5)

$$E_t = \frac{h^2}{2m\left(\frac{2l_x}{n}\right)^2}$$

$$E_t = \frac{n^2h^2}{8ml_x^2} \longrightarrow (8)$$

Now substitute equation (8) 8n equation (2) we get.

$$Q_t(x) = \sum e^{-E_i/KT}$$

$$Q_t(x) = \sum e^{-\left(\frac{n^2h^2}{8ml_x^2}\right)\Big/KT}$$

$$Q_t(x) = \sum e^{-n^2a} \qquad \because a = \left(\frac{h^2}{8ml_x^2}\right)\Big/KT$$

Integrating the above equation we get

$$Q_t(x) = \int_0^\infty e^{-n^2a}\, dn$$

$$= \frac{1}{2}\sqrt{\frac{\Pi}{a}}$$

$$Q_t(x) = \frac{1}{2}\sqrt{\frac{\Pi}{\left(\frac{h^2}{8ml_x^2}\right)\Big/KT}}$$

$$Q_t(x) = \frac{1}{2}\sqrt{\frac{\Pi\, 8m\lambda_x^2}{h^2\, KT}}$$

$$Q_t\ (x) = \frac{1}{2}\ \frac{2\,(2m\pi KT)^{\frac{1}{2}}}{h}\ l_x$$

$$Q_t\ (x) = \frac{(2m\pi KT)^{\frac{1}{2}}}{h}\ l_x$$

Similarly Q_t (y) and Q_t (z)

$$Q_t\ (y) = \frac{(2m\pi KT)^{\frac{1}{2}}}{h}\ l_y$$

$$Q_t\ (z) = \frac{(2m\pi KT)^{\frac{1}{2}}}{h}\ l_z$$

$Q_t = Q_x$ (x) x Q_t (y) x Q_t (z)

$$Q_t = \frac{(2m\pi KT)^{\frac{3}{2}}}{h^3}\ l_x l_y l_z$$

$$Q_t = \frac{(2m\pi KT)^{\frac{3}{2}}}{h^3}\ V$$

Where 'V' is Volume assemble to molecule.

4.3 ROTATIONAL PARTITION FUNCTION

- The partition function of rotational energy of diatomic molecule is given by

$$Q_r = \sum g_r\ e^{-E_r / KT} \longrightarrow (1)$$

- From quantum mechanics the rotational of diatomic molecule in the I^{th} state

$$E_r = \frac{J(J+1)h^2}{8\pi^2 I} \longrightarrow (2)$$

Where J = 0, 1, 2,3……..J, I is the momentum of Inertia.

We know that rotational energy at the J^{th} level is degenerate as (2J+1) states

$$Q_r = \sum (2J+1)\, e^{-\left(\frac{J(J+1)h^2}{8\pi^2 I}\right)\Big/ KT}$$

$$Q_r = \sum (2J+1)\, e^{-\left(\frac{J(J+1)h^2}{8\pi^2 I\, KT}\right)} \longrightarrow (3)$$

Now integrate the above equation(3) we get

$$Q_r = \int_0^{\infty} (2J+1)\, e^{-\left(\frac{J(J+1)h^2}{8\pi^2 I\, KT}\right)}\, dJ$$

$$Q_r = \int_0^{\infty} (2J+1)\, e^{-J(J+1)\beta}\, dJ \longrightarrow (4) \quad \because \beta = \frac{h^2}{8\pi^2 I\, KT}$$

Again put $Z = J(J+1) \longrightarrow (5)$

$dZ = 2J(J+1) \longrightarrow (6)$

Substitute equation (5) & (6) in equation (4) we get

$$Q_r = \int_0^{\infty} (2J+1)\, e^{-z\beta}\, dZ = \frac{1}{\beta}$$

$$Q_r = \frac{8\Pi^2 IKT}{h^2} \longrightarrow (7)$$

In order to overcome this complication of symmetry number 'σ' is introduced.
Hence equation (7) becomes.

$$Q_r = \frac{8\Pi^2 IKT}{\sigma h^2}$$

This equation is called Rotational partition function.

The value of σ is two for symmetrical diatomic molecule and is unity for unsymmetrical molecule.

This Rotational partition function for poly atomic molecule is given by

$$Q_r = \frac{1}{n\sigma} \left(\frac{8\Pi^2 \left(I_A^{\,a} \times I_B^{\,b} \ldots\ldots\right)^{1/n} KT}{h^2} \right)^{n/2}$$

Where $I_A{}^a$, $I_B{}^b$,….. are the momentum of Inertia of various atoms of the molecule and 'σ' is symmetrical number.

Assuming the molecule to behave like a rigid rotator, the rotational partition function excluding the nuclear spin factor for a non – linear Molecule may be given by

$$Q_r = \frac{8\Pi^2 \left(8\Pi^3 A B C\right)^{1/2} (KT)^{3/2}}{\sigma h^3}$$

Where A,B,C are Momentum of Inertia of the molecule with respect to three perpendicular axes.

4.4 ELECTRONIC PARTITION FUNCTION

Many mono atomic molecules as well as a few poly atomic molecules such as Oxygen, NO, N_2O_2 etc posses multiple electronic ground state. In most of these in their normal state, there are two or more different electronic levels whose energies are so close that be assigned a single level with a statistical weight factor greater than unity. In addition such levels, there be exited electronic states whose energies may be much greater than that of the ground state. If we increase the temperature such exited states become more and more occupied. In such cases are electronic partition function is greater than unity and various with temperature.

The electronic partition function is given by.

$$Q_e = \sum g_e\, e^{-E_e/KT}$$

Where g_e is statistical weight factor of each electronic level and equal to (2J+1). Here J is resultant quantum number of the atom in given state and E_e is the energy of the electronic state in excess of lowest state (ground state)

$$\text{i.e. } Q_e = \sum (2J + 1)\, e^{-E_e/KT}$$

In ground state, the energy is zero i.e $E_e = 0$

$$\therefore Q_e = \sum (2J + 1)\, e^{o}$$
$$= \sum (2J + 1)\,.\,1 \qquad (\because e^{o} = 1)$$
$$\therefore Q_e = \sum (2J + 1)$$

It follows that the contribution of state to the electronic partition function is thus (2J+1). For Helium, Neon, Mercury etc the value of J found to be unity for lowest energy state and they above equation becomes as Q_e=1.

This electronic partition function is unity and so can be disregarded even if 2J+1 were not unity the effect on the energy and heat capacity would still be zero. Because the quantity are dependent on the derivatives of logarithm of partition function with temperature.

In some atom there are one or more electronic states above the ground state are appreciably occupied even in at moderate temperature. It means that some appropriate terms must be included in the partition function. For eg there are two states of the chlorine atoms in the ground state i.e. for E_o , J= 3/2 and for E_1, J=1/2. Thus, the electronic partition function for atomic chlorine a ordinary temperature is therefore given by equation as

$$Q_e = (2 \times 3/2 + 1)\, e^{-0/KT} + (2 \times 1/2 + 1)\, e^{-E_1/KT}$$

$$Q_e = 4 + 2\, e^{-E_1/KT}$$

4.5 CALCULATION OF THERMODYNAMIC PROPERTIES IN TERMS OF PARTITION FUNCTION

1) Internal Energy:

The internal energy of molecular system is given by expression

$$E = n_0E_0 + n_1E_1 + n_2E_2 + \ldots\ldots\ldots\ldots + n_iE_i \longrightarrow (1)$$

Where $n_0, n_1, n_2, \ldots\ldots\ldots\ldots n_i$ are the number of molecules in the system possessing energies respectively $E_0, E_1, E_2, \ldots\ldots\ldots\ldots E_i$.

We know that

$$Q = g_0\, e^{-E_0/KT} + g_1\, e^{-E_1/KT} + g_2\, e^{-E_2/KT} + \qquad + g_i\, e^{-E_i/KT}$$

Differentiate above equation with respect to 'T' at constant volume

$$\left(\frac{\partial Q}{\partial T}\right)_V = \frac{g_0E_0}{KT^2} e^{-E_0/KT} + \frac{g_1E_1}{KT^2} e^{-E_1/KT} + \frac{g_2E_2}{KT^2} e^{-E_2/KT} + \qquad + \frac{g_iE_i}{KT^2} e^{-E_i/KT} \longrightarrow (2)$$

$$\left(\frac{\partial Q}{\partial T}\right)_V = \frac{1}{KT^2}\left[\, g_0E_0\, e^{-E_0/KT} + g_1E_1\, e^{-E_1/KT} + g_2E_2\, e^{-E_2/KT} + \qquad + g_iE_i\, e^{-E_i/KT}\,\right]$$

$$KT^2\left(\frac{\partial Q}{\partial T}\right)_V = \left[\, g_0E_0\, e^{-E_0/KT} + g_1E_1\, e^{-E_1/KT} + \qquad + g_iE_i\, e^{-E_i/KT}\,\right]$$

Dividing this equation by 'Q' we get

$$\frac{KT^2}{Q}\left(\frac{\partial Q}{\partial T}\right)_V = \left[\frac{g_0E_0}{Q} e^{-E_0/KT} + \frac{g_1E_1}{Q} e^{-E_1/KT} + \qquad + \frac{g_iE_i}{Q} e^{-E_i/KT}\right] \longrightarrow (3)$$

We know that

$$\frac{n_i}{n} = \frac{g_i}{Q} e^{-E_i/KT}$$

Equation (3) becomes

$$\frac{KT^2}{Q}\left(\frac{\partial Q}{\partial T}\right)_V = \frac{n_0E_0}{n} + \frac{n_1E_1}{n} + \quad + \frac{n_iE_i}{n}$$

$$KT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V = \frac{n_0E_0}{n} + \frac{n_1E_1}{n} + \quad + \frac{n_iE_i}{n}$$

$$KT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V = \frac{1}{n}\left[\, n_0E_0 + n_1E_1 + \quad + n_iE_i \,\right]$$

$$nKT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V = \left[\, n_0E_0 + n_1E_1 + \quad + n_iE_i \,\right]$$

$$nKT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V = \sum n_iE_i$$

$$E = nKT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V$$

If system certain one mole of the gas 'n' can be equal to 'N'

$$E = NKT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V$$

$$E = RT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V \qquad \because K = \frac{R}{N}$$

2) Heat Capacity:

We Know that

$$E = RT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V$$

Differentiate above equation with respect to 'T' at constant volume

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(RT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V\right)$$

$$C_V = \frac{\partial}{\partial T}\left(RT^2\left(\frac{\partial}{\partial T}\ln Q\right)\right)_V \qquad \because \left(\frac{\partial E}{\partial T}\right)_V = C_V$$

This is molar heat capacity of an ideal gas at constant volume in terms of partition function.

3) Entropy:

The mathematical probability is defined as

$$W = \frac{n!}{n_0!\, n_1!\, n_2! \ldots\ldots n!} \longrightarrow (1)$$

This equation requires modification in two respects.

a) First correction involves the insertion of statistics weight corresponding to each cell.

∴ equation (1) becomes

$$W = n! \frac{g_0^{n_0}}{n_0!} \frac{g_1^{n_1}}{n_1!} \frac{g_2^{n_2}}{n_2!} \ldots\ldots\ldots \frac{g_i^{n_i}}{n_i!} \longrightarrow (2)$$

b) Second correction involves the quantum statistical recognition about the identical particles as indistinguishable ones. To apply this correction, it is required to divide equation (2) by 'n!' so that the result is

$$W = \frac{g_0^{n_0}}{n_0!} \frac{g_1^{n_1}}{n_1!} \frac{g_2^{n_2}}{n_2!} \ldots\ldots\ldots \frac{g_i^{n_i}}{n_i!} \longrightarrow (3)$$

Taking log on both sides

$\ln W = (n_o \ln g_o - \ln n_o!) + (n_1 \ln g_1 - \ln n_1!) + (n_2 \ln g_2 - \ln n_2!) + \ldots\ldots\ldots\ldots + (n_i \ln g_i - \ln n_i!)$

$= \sum n_i \ln g_i - \sum \ln n_i! \longrightarrow (4)$

By using sterling approximation, we have

$\ln n_i! = n_i \ln n_i - n_i$

∴ equation (4) becomes

$\ln W = \sum n_i \ln g_i - \sum (n_i \ln n_i - n_i)$

$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + \sum n_i$

$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + n \longrightarrow (5) \quad [\because \sum n_i = n]$

We know that

$$\frac{n_i}{n} = \frac{g_i}{Q} e^{-E_i / KT}$$

On taking log on both sides

$\ln n_i - \ln n = \ln g_i - E_i / KT - \ln Q$

Multiplying above equation with n_i, we get

$n_i \ln n_i - n_i \ln n = n_i \ln g_i - n_i \ln Q - n_i E_i / KT$

$n_i \ln n_i = n_i \ln n + n_i \ln g_i - n_i \ln Q - n_i E_i / KT$

$n_i \ln n_i = n_i \ln n - n_i \ln Q + n_i \ln g_i - n_i E_i / KT$

$n_i \ln n_i = n_i \ln (n / Q) + n_i \ln g_i - n_i E_i / KT$

By taking summation overall the quantum statistics

$\sum n_i \ln n_i = -\sum n_i \ln (Q / n) + \sum n_i \ln g_i - \sum n_i E_i / KT \longrightarrow (6)$

Substituting Equation (6) in equation (5) we get

$\ln W = \sum n_i \ln g_i - [-\sum n_i \ln (Q / n) + \sum n_i \ln g_i - \sum n_i E_i / KT] + n$

$\ln W = \sum n_i \ln g_i + \sum n_i \ln (Q / n) - \sum n_i \ln g_i + \sum n_i E_i / KT + n$

$\ln W = n \ln (Q / n) + \sum n_i E_i / KT + n$

But $$\sum E_i n_i = nKT^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V$$

$$\therefore \ln W = n \ln (Q / n) + nT \left(\frac{\partial}{\partial T} \ln Q \right)_V + n$$

From Boltzmann planks equation we know that

$S = K \ln W$

$$S = K \left[n \ln (Q / n) + nT \left(\frac{\partial}{\partial T} \ln Q \right)_V + n \right]$$

$$S = nK \left[\ln (Q / n) + T \left(\frac{\partial}{\partial T} \ln Q \right)_V + 1 \right]$$

For one mole of perfect gas

$$S = NK \left[\ln (Q/n) + T\left(\frac{\partial}{\partial T} \ln Q\right)_V + 1 \right]$$

$$S = R \left[\ln (Q/n) + T\left(\frac{\partial}{\partial T} \ln Q\right)_V + 1 \right] \qquad \because K = R/N$$

$$S = R \left[\ln \left(\frac{Q}{N}\right) + T\left(\frac{\partial}{\partial T} \ln Q\right)_V + 1 \right]$$

4) Work function:

We know that

$$A = E - TS$$

$$\therefore A = RT^2\left(\frac{\partial}{\partial T} \ln Q\right)_V - RT \left[\ln (Q/n) + T\left(\frac{\partial}{\partial T} \ln Q\right)_V + 1 \right]$$

$$A = RT^2\left(\frac{\partial}{\partial T} \ln Q\right)_V - RT \ln (Q/n) - RT^2 \left(\frac{\partial}{\partial T} \ln Q\right)_V - RT$$

$$A = -RT \ln (Q/n) - RT$$

$$A = -RT (\ln (Q/n) + 1)$$

5) Pressure:

We have

$$A = -RT \ln (Q/N) - RT$$

$$A = -RT \ln Q + RT \ln N - RT$$

Differentiate the above equation with respect to 'v' at constant temperature.

$$\left(\frac{\partial A}{\partial V}\right)_T = -RT \left(\frac{\partial}{\partial V} \ln Q\right)_T$$

But we know that

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$-P = -RT \left(\frac{\partial}{\partial V} \ln Q\right)_T$$

$$\therefore P = RT \left(\frac{\partial}{\partial V} \ln Q\right)_T$$

6) Heat Content:

$$H = E + PV$$

$$H = RT^2\left(\frac{\partial}{\partial T} \ln Q\right)_V + VRT \left(\frac{\partial}{\partial V} \ln Q\right)_T$$

$$H = RT \left[T\left(\frac{\partial}{\partial T} \ln Q\right)_V + V \left(\frac{\partial}{\partial V} \ln Q\right)_T \right]$$

7) Gibbs Free Energy:

$$G = A + PV$$

$$G = -RT\,(\ln (Q/n) + 1) + VRT \left(\frac{\partial}{\partial V} \ln Q\right)_T$$

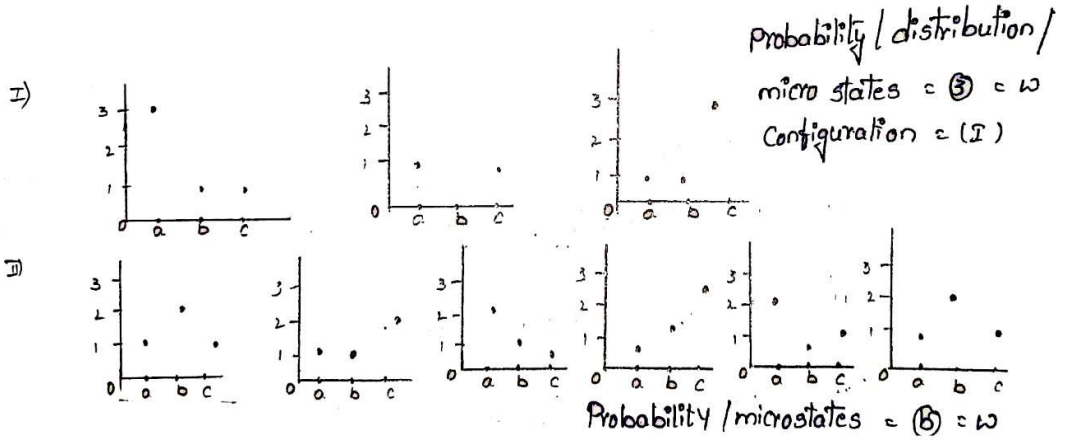
$$G = -RT \left[\ln (Q/n) + 1 - V\left(\frac{\partial}{\partial V} \ln Q\right)_T\right]$$

$$G = -RT \left[\ln (Q/n) + 1 - \left(\frac{\partial \ln Q}{\partial \ln V}\right)_T\right]$$

4.6 CONCEPT OF DISTRIBUTION:

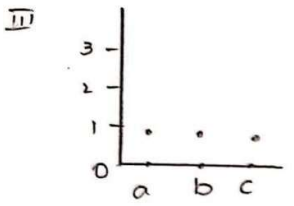
In system consisting of 'N' individual and independent particles and there are various energy states occupied by these particles " the number of particles in a given energy state is the occupation number.

A distribution can be defined as "set of occupation number in different energy the particles can occupy any energy state, but the total energy must have a constant value.



Let us begin with simple can of three particles which share three quanta of energy. There are ten possible distribution of three distinguishable particles to share three quanta of energy.

In which the dots are so placed that the particle concerned is indicated by the letter a/b/c marking along the absicissca and the number of energy quanta assigned to it can be read from the ordinate.



Micro states distribution = ① = ω

$$W = \frac{N!}{n_1!\, n_2! \ldots\ldots n_3!}$$

The configuration which has maximum number of micro states is called most probable distribution.

SUMMARY:

- To learn about the partition function.
- To study about derivation of Translation Partition Function.
- To know about the Rotational Partition Function.
- To learn about Electronic Partition Function.
- To know about Calculation of thermodynamic properties.

SELF ASSESSMENT QUESTIONS

1. Derive expressions for translational partition functions.
2. Derive Rotational Partition Functions.
3. Explain derivation of Electronic Partition Function.
4. Write the calculation of thermodynamic properties.

Prof. K. Rambabu

LESSON-5
APPLICATIONS OF PARTITION FUNCTION- ENTROPY OF MONOATOMIC GASES (SACKUR - TETRODE EQUATION).

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the applications of Partition Function for Entropy of Monoatomic gases and diatomic gases.
- To study about Chemical equilibrium and Equilibrium partition function.
- To study about the derivation of Entropy of Mono atomic gases (or) Sackur – Tetrode equation.

5.1 TO MONO ATOMIC GASES:

1) Internal Energy:

If the rotational and vibrational energy absent then the individual energy of Mono atomic molecules will be only due to

$$E_t = RT^2 \left(\frac{\partial}{\partial T} \ln Q_t\right)_V \longrightarrow (1)$$

Where Q_t is translational partition function for mono atomic molecule and its value given by.

$$Q_t = \frac{(2m\pi KT)^{\frac{3}{2}}}{h^3} V$$

Taking log on both sides

$$\ln Q_t = \frac{3}{2} \ln T + \ln \frac{(2m\pi K)^{\frac{3}{2}}}{h^3} V$$

Differentiate with respect to temperature

$$\frac{\partial}{\partial T} \ln Q_t = \frac{3}{2} \frac{\partial}{\partial T} \ln T$$

$$\frac{\partial}{\partial T} \ln Q_t = \frac{3}{2T}$$

Substitute above value in equation in equation (1)

$$E_t = \frac{3}{2} RT$$

2) Entropy of Mono atomic gases (or) Sackur – Tetrode equation:

- We know that the entropy of ideal mono atomic gas is given by

$$S = R\left[\ln\left(\frac{Q}{N}\right) + T\left(\frac{\partial}{\partial T} \ln Q\right)_V + 1\right]$$

- For mono atomic gases

$$S = R\left[\ln\left(\frac{Q_t}{N}\right) + T\left(\frac{\partial}{\partial T} \ln Q_t\right)_V + 1\right]$$

$$S = R\left[\ln\left(\frac{Q_t}{N}\right) + T\,\frac{3}{2T} + 1\right] \qquad \because \left(\frac{\partial}{\partial T}\ln Q_t\right)_V = \frac{3}{2T}$$

$$S = R\left[\ln\left(\frac{Q_t}{N}\right) + \frac{5}{2}\right]$$

We know that

$$Q_t = \frac{(2m\pi KT)^{\frac{3}{2}}}{h^3}\,V$$

$$S = R\left[\ln\frac{(2m\pi KT)^{\frac{3}{2}}}{Nh^3}\,V + \frac{5}{2}\right]$$

$$S = R\left[\ln\frac{(2m\pi KT)^{\frac{3}{2}}}{Nh^3}\,\frac{RT}{P} + \frac{5}{2}\right] \qquad \because PV = RT$$

The above equation is alternative form of Sockur – Tetrode equation on simplification we get

$$S = 2.303\,R\left[\frac{3}{2}\log m + \frac{5}{2}\log T - \log P - 0.505\right]$$

5.2 TO DIATOMIC MOLECULES:

1) Rotational Internal Energy:

We know that

$$E = RT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V$$

If the rotational partition function is independent of the volume of the system then the above equation changes to

$$E_r = RT^2\left(\frac{\partial}{\partial T}\ln Q_r\right)_V \longrightarrow (1)$$

We Know that

$$Q_r = \frac{8\pi^2 IKT}{\sigma h^2}$$

Taking log on both sides

$$\ln Q_r = \ln\frac{8\pi^2 IK}{\sigma h^2} + \ln T$$

On differentiating we get

$$\frac{\partial}{\partial T}(\ln Q_r) = \frac{\partial}{\partial T}(\ln T)$$

$$\frac{\partial}{\partial T}(\ln Q_r) = \frac{1}{T}$$

Equation (1) becomes

$$E_r = RT^2 \frac{1}{T}$$

$$E_r = RT$$

2) Rotational Entropy:

We know that

$$S = \frac{E}{T} + R \ln Q$$

For rotational entropy

$$S_r = \frac{E_r}{T} + R \ln Q_r$$

Substitute the values of E_r and Q_r we get

$$S_r = \frac{RT}{T} + R \ln \frac{8\Pi^2 IKT}{\sigma h^2}$$

$$S_r = R \left[1 + \ln \frac{8\Pi^2 IKT}{\sigma h^2} \right]$$

By substituting the values of Π, K, h & R we get

$S_r = 4.576$ [log I + log T - log σ + 38.32] cal deg^{-1} $mole^{-1}$

5.3 CHEMICAL EQUILIBRIUM AND EQUILIBRIUM PARTITION FUNCTION (OR) STATISTICAL EXPRESSION FOR EQUILIBRIUM CONSTANT:

We will know express the equilibrium constant of free energy function. Firstly, we will derive the value of free energy function of the substance

$$E - E^o = RT^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V \longrightarrow (1)$$

Where E is total energy of 'N' molecules and E_o is zero point energy of same molecule.

We know that the total internal energy of an ideal gas is independent of pressure at a given temperature, the value E and E^0 can be replaced their standard states E^0 and E_o^0 respectively.

$$E^o - E_o^o = RT^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V$$

$$E^o = E_o^o + RT^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V \longrightarrow (2)$$

According to Gibbs Free Energy

$G = H - TS$

$G = E + PV - TS$

$G = E + RT - TS \longrightarrow (3)$ (∵ PV = RT)

We Know that

$$S = R \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial}{\partial T} \ln Q \right)_V + 1 \right]$$

Substitute 'S' value in equation (3)

$$G = E^{\circ} + RT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V + RT - RT\left[\ln\left(\frac{Q}{N}\right) + T\left(\frac{\partial}{\partial T}\ln Q\right)_V + 1\right]$$

$$G = E^{\circ} - RT\ln\left(\frac{Q}{N}\right)$$

Now the given system taken standard state as

$$G^{\circ} = E^{\circ} - RT\ln\left(\frac{Q^{\circ}}{N}\right)$$

$$\Rightarrow RT\ln\left(\frac{Q^{\circ}}{N}\right) = -(G^{\circ} - E^{\circ})$$

$$\Rightarrow R\ln\left(\frac{Q^{\circ}}{N}\right) = \frac{-(G^{\circ} - E^{\circ})}{T} \longrightarrow (4)$$

This term is known as free energy function But we know that

$$H = E + PV$$

$$H = E + RT$$

When the substance is in this standard state (1 atm pressure)

The above equation at 0^0 K becomes as

$$H_o^0 = E_o^0 \qquad [\because T=0]$$

By substituting E_o0 Value in equation (4)

$$R\ln\left(\frac{Q^{\circ}}{N}\right) = \frac{-(G^{\circ} - H^{\circ})}{T}$$

$$G^{\circ} = H^{\circ} - RT\ln\left(\frac{Q^{\circ}}{N}\right)$$

Consider a Gaseous equation

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

In which $\Delta G = (c\,G_C + dG_D) - (aG_A + bG_B)$

$\Delta G^0 = (c\,G^0_C + dG^0_D) - (aG^0_A + bG^0_B)$

We know that

$$G^{\circ} = H^{\circ} - RT\ln\left(\frac{Q^{\circ}}{N}\right)$$

$$G^{\circ}_C = H^{\circ}_C - RT\ln\left(\frac{Q^{\circ}_C}{N}\right)$$

$$G^{\circ}_D = H^{\circ}_D - RT\ln\left(\frac{Q^{\circ}_D}{N}\right)$$

$$G^{\circ}_B = H^{\circ}_B - RT\ln\left(\frac{Q^{\circ}_B}{N}\right)$$

$$G^{\circ}_A = H^{\circ}_A - RT\ln\left(\frac{Q^{\circ}_A}{N}\right)$$

$$\Delta G^{\circ} = \left[c\left(H^{\circ}_C - RT\ln\left(\frac{Q^{\circ}_C}{N}\right)\right) + d\left(H^{\circ}_D - RT\ln\left(\frac{Q^{\circ}_D}{N}\right)\right)\right] - \left[b\left(H^{\circ}_B - RT\ln\left(\frac{Q^{\circ}_B}{N}\right)\right) + a\left(H^{\circ}_A - RT\ln\left(\frac{Q^{\circ}_A}{N}\right)\right)\right]$$

$$\Delta G^{\circ} = \left[\left(c\,H^{\circ}_C + d\,H^{\circ}_D\right) - \left(bH^{\circ}_B + aH^{\circ}_A\right)\right] - cRT\ln\left(\frac{Q^{\circ}_C}{N}\right) - dRT\ln\left(\frac{Q^{\circ}_D}{N}\right) + bRT\ln\left(\frac{Q^{\circ}_B}{N}\right) + aRT\ln\left(\frac{Q^{\circ}_A}{N}\right)$$

$$\Delta G^{o} = \Delta H^{o} - RT \ln \frac{\left(\frac{Q_C^{o}}{N}\right)^{c}\left(\frac{Q_D^{o}}{N}\right)^{d}}{\left(\frac{Q_B^{o}}{N}\right)^{b}\left(\frac{Q_A^{o}}{N}\right)^{a}}$$

The given substance is taken in standard state then that standard change in enthalpy of a system is unitiy.

$$\Delta H^{0} = 1$$

$$\Delta G^{o} = 1 - RT \ln K_p \qquad \because K_p = \frac{\left(\frac{Q_C^{o}}{N}\right)^{c}\left(\frac{Q_D^{o}}{N}\right)^{d}}{\left(\frac{Q_B^{o}}{N}\right)^{b}\left(\frac{Q_A^{o}}{N}\right)^{a}}$$

Finally the change in free energy function in that right hand side of the result is known as equilibrium constant of given substance

$$\ln K_p = -\frac{1}{RT}\Delta G^{o}$$

$$\ln K_p = -\frac{1}{RT}\left(\Delta H^{o} - RT \ln K_p\right)$$

$$\ln K_p = -\frac{\Delta H^{o}}{RT} + \ln K_p$$

$$K_p = e^{-\frac{\Delta H^{o}}{RT}} + \ln \frac{\left(\frac{Q_C^{o}}{N}\right)^{c}\left(\frac{Q_D^{o}}{N}\right)^{d}}{\left(\frac{Q_B^{o}}{N}\right)^{b}\left(\frac{Q_A^{o}}{N}\right)^{a}}$$

The value of K_P can be calculated by provided ΔH^0 is known. This can be calculated from spectroscopic date.

5.4 ENTROPY OF MONO ATOMIC GASES (OR) SACKUR – TETRODE EQUATION:

The mathematical probability is defined as

$$W = \frac{n!}{n_0!\, n_1!\, n_2! \ldots\ldots n!} \longrightarrow (1)$$

This equation requires modification in two respects.

a) First correction involves the insertion of statistics weight corresponding to each cell.

$\therefore$ equation (1) becomes

$$W = n! \frac{g_0^{n_0}}{n_0!} \frac{g_1^{n_1}}{n_1!} \frac{g_2^{n_2}}{n_2!} \ldots\ldots\ldots \frac{g_i^{n_i}}{n_i!} \longrightarrow (2)$$

b) Second correction involves the quantum statistical recognition about the identical particles as indistinguishable ones. To apply this correction, it is required to divide equation (2) by 'n!' so that the result is

$$W = \frac{g_0^{n_0}}{n_0!} \frac{g_1^{n_1}}{n_1!} \frac{g_2^{n_2}}{n_2!} \ldots\ldots\ldots \frac{g_i^{n_i}}{n_i!} \longrightarrow (3)$$

Taking log on both sides

$\ln W = (n_o \ln g_o - \ln n_o!) + (n_1 \ln g_1 - \ln n_1!) + (n_2 \ln g_2 - \ln n_2!) + \ldots\ldots\ldots\ldots + (n_i \ln g_i - \ln n_i!)$

$\ln W = (n_o \ln g_o + n_1 \ln g_1 + n_2 \ln g_2 + \ldots\ldots + n_i \ln g_i) - (\ln n_o! + \ln n_1! + \ln n_2!) + \ldots\ldots + \ln n_i!)$

$= \sum n_i \ln g_i - \sum \ln n_i! \longrightarrow (4)$

By using sterling approximation, we have

$\ln n_i! = n_i \ln n_i - n_i$

$\therefore$ equation (4) becomes

$\ln W = \sum n_i \ln g_i - \sum (n_i \ln n_i - n_i)$

$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + \sum n_i$

$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + n \longrightarrow (5) \quad [\because \sum n_i = n]$

We know that

$$\frac{n_i}{n} = \frac{g_i}{Q} e^{-E_i / KT}$$

On taking log on both sides

$\ln n_i - \ln n = \ln g_i - E_i / KT - \ln Q$

Multiplying above equation with n_i, we get

$n_i \ln n_i - n_i \ln n = n_i \ln g_i - n_i \ln Q - n_i E_i / KT$

$n_i \ln n_i = n_i \ln n + n_i \ln g_i - n_i \ln Q - n_i E_i / KT$

$n_i \ln n_i = n_i \ln n - n_i \ln Q + n_i \ln g_i - n_i E_i / KT$

$n_i \ln n_i = n_i \ln (n / Q) + n_i \ln g_i - n_i E_i / KT$

By taking summation overall the quantum statistics

$\sum n_i \ln n_i = -\sum n_i \ln (Q / n) + \sum n_i \ln g_i - \sum n_i E_i / KT \longrightarrow (6)$

Substituting Equation (6) in equation (5) we get

$\ln W = \sum n_i \ln g_i - [-\sum n_i \ln (Q / n) + \sum n_i \ln g_i - \sum n_i E_i / KT] + n$

$\ln W = \sum n_i \ln g_i + \sum n_i \ln (Q / n) - \sum n_i \ln g_i + \sum n_i E_i / KT + n$

$\ln W = n \ln (Q / n) + \sum n_i E_i / KT + n$

But $$\sum E_i n_i = nKT^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V$$

$$\therefore \ln W = n \ln (Q / n) + nT \left(\frac{\partial}{\partial T} \ln Q \right)_V + n$$

From Boltzmann planks equation we know that

$S = K \ln W$

$$S = K \left[n \ln (Q / n) + nT \left(\frac{\partial}{\partial T} \ln Q \right)_V + n \right]$$

$$S = nK \left[\ln (Q / n) + T \left(\frac{\partial}{\partial T} \ln Q \right)_V + 1 \right]$$

For one mole of perfect gas

$$S = NK \left[\ln (Q / n) + T \left(\frac{\partial}{\partial T} \ln Q \right)_V + 1 \right]$$

$$S = R \left[\ln (Q / n) + T \left(\frac{\partial}{\partial T} \ln Q \right)_V + 1 \right] \quad \because K = R/N$$

$$S = R \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial}{\partial T} \ln Q \right)_V + 1 \right]$$

Where 'N' is the Avogadro's number

A mono atomic molecule has no vibrational or rotational energy and so the only contributions to the partition function are those for translational energy.

$$E_t = RT^2 \left(\frac{\partial}{\partial T} \ln Q_t\right)_V$$

Where Q_t is the translational partition function and its value is given by

$$Q_t = \frac{(2m\pi KT)^{\frac{3}{2}}}{h^3} V$$

On taking logarithm on both sides

$$\ln Q_t = \frac{3}{2} \ln T + \ln \frac{(2m\pi K)^{\frac{3}{2}}}{h^3} V$$

Differentiate with respect to temperature at constant volume

$$\left(\frac{\partial}{\partial T} \ln Q_t\right)_V = \frac{3}{2} \frac{\partial}{\partial T} \ln T$$

$$\left(\frac{\partial}{\partial T} \ln Q_t\right)_V = \frac{3}{2T}$$

- Again, the molar entropy of an ideal mono atomic gas is given by

$$S = R\left[\ln\left(\frac{Q}{N}\right) + T\left(\frac{\partial}{\partial T} \ln Q\right)_V + 1\right]$$

- For mono atomic gases

$$S = R\left[\ln\left(\frac{Q_t}{N}\right) + T\left(\frac{\partial}{\partial T} \ln Q_t\right)_V + 1\right]$$

$$S = R\left[\ln\left(\frac{Q_t}{N}\right) + T\,\frac{3}{2T} + 1\right] \qquad \because \left(\frac{\partial}{\partial T} \ln Q_t\right)_V = \frac{3}{2T}$$

$$S = R\left[\ln\left(\frac{Q_t}{N}\right) + \frac{5}{2}\right]$$

We know that

$$Q_t = \frac{(2m\pi KT)^{\frac{3}{2}}}{h^3} V$$

$$S = R\left[\ln \frac{(2m\pi KT)^{\frac{3}{2}}}{Nh^3} V + \frac{5}{2}\right]$$

$$S = R\left[\ln \frac{(2m\pi KT)^{\frac{3}{2}}}{Nh^3} \frac{RT}{P} + \frac{5}{2}\right] \qquad \because PV = RT$$

The above equation is alternative form of Sockur – Tetrode equation, deroved in a somewhat different manner by O.Sackur (1911-13) and H.Tetrode (1712)

The above equation can be simplified as

$$S = R\left[\frac{3}{2}\ln m + \frac{5}{2} \ln T - \ln P + \ln \frac{R}{N}\left(\frac{2\pi K}{h^2}\right)^{\frac{3}{2}} + \frac{5}{2}\right]$$

$$S= 2.303\ R\left[\frac{3}{2}\ln m+\frac{5}{2}\ln T-\ln P+\ln\frac{R}{N}\left(\frac{2\pi K}{h^2}\right)^{\frac{3}{2}}+\frac{5}{2}\right]$$

$$S= 2.303\ R\left[\frac{3}{2}\ln m-\frac{3}{2}\ln N+\frac{5}{2}\ln T-\ln P+\ln R\left(\frac{2\pi K}{h^2}\right)^{\frac{3}{2}}+\frac{5}{2}\right]$$

$$S= 2.303\ R\left[\frac{3}{2}\ln m+\frac{5}{2}\ln T-\ln P+C_1\right]$$

$$\text{Where}\quad C_1=\frac{5}{2}-\frac{3}{2}\ln N+\ln R\left(\frac{2\pi K}{h^2}\right)^{\frac{3}{2}}$$

The Value of C_1 can be calculated by putting the values of R, N, K & h and its value is -0.505.

The above equation becomes

$$S = 2.303\,R\left[\frac{3}{2}\log m+\frac{5}{2}\log T-\log P-0.505\right]$$

SUMMARY:

- To learn about the applications of Partition Function for Entropy of Monoatomic gases and diatomic gases.
- To study about Chemical equilibrium and Equilibrium partition function.
- To study about the derivation of Entropy of Mono atomic gases (or) Sackur – Tetrode equation.

SELF ASSESSMENT QUESTIONS

1. Derive Entropy of Mono atomic gases.
2. Derive Sackur – Tetrode equation.

References Books

1. Physical chemistry, G.K. Vemulapalli (Prentice Hall of India).
2) Physical chemistry, P.W. Atkins. ELBS.
3) Text book of Physical Chemistry, Samuel Glasstone, Macmillan pub.
4) Statistical Thermodynamics - M.C. Gupta.
5) Statistical Thermodynamics - M.Dole.

Prof. K. Rambabu

LESSON-6
POLYMER CHEMISTRY: CLASSIFICATION OF POLYMERS; TYPES OF POLYMERIZATIONS; FREE RADICAL, IONIC AND ZIEGLER – NATTA POLYMERIZATION MECHANISMS

OBJECTIVES:

After studying this lesson, you should be able to:

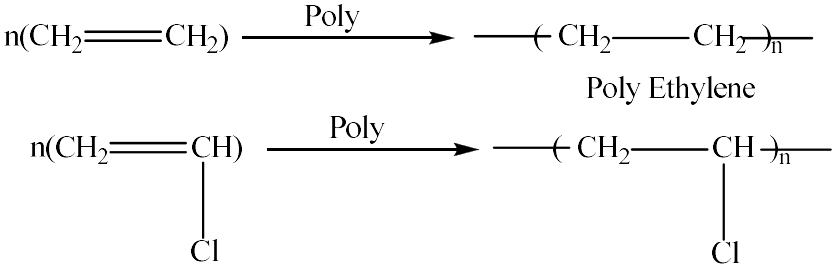
- To know about the Classification of polymers
- To study about Types of Polymerizations with mechanism
- To study about Free radical, Ionic and Ziegler – Natta Polymerization with their mechanism

6.1 INTRODUCTION

A polymer is a macromolecule consisting of repeat small units is called "Mers". Hence the name is called 'Polyer' the word polymer has been derived from the Greek word. i.e. poly means many and mers means *units*.

A polymer can be defined as a large molecule built by repeating structural units joint by covalent bond.

Ex:



The small molecule which combines with each other to form polymer molecule is known as monomer two monomers combine to form dimer, likewise trimer, tetramer etc., and the process of forming a big molecule (or) polymer is known as "Polymerization".

Difference between Polymer and Macromer:

A Macromolecule means a large molecule consists of many small molecules.
Example: Diamond, Graphite etc.

The Polymer is composed of number of repeating units. Whereas macro molecule does not contain repeating unit. i.e. polymer is macro molecule but a macro molecule is not polymer.

6.2 CLASSIFICATION OF POLYMERS:

Polymers have different chemical structures, physical properties, mechanical behavior, thermal characteristic etc., Hence they can be classified in different ways.

1) Depending upon their origin polymers can be divided into two ways.

a) Natural Polymers

Polymers which are isolated from natural materials are called natural products (or) natural polymers.

Ex: Cotton, Silk, Wool and Rubber, etc.,

b) Synthetic Polymers:

Polymers are synthesized from low molecular weight compounds are called "Synthetic polymers".

Ex: Poly Ethylene, Poly Vinyl Chloride, Nylon and Terylene.

2) Depending on the presence of carbon atom or not in the back bone chain of polymer.

a) Organic Polymer:

A polymer whose back bone chain is made up of carbon are called "Organic Polymers"

Ex : PVC, Nylon

b) Inorganic Polymer:

Polymer contain no carbon atoms in their back bone chain is called "Inorganic Polymers".

Ex: Glass, Silicone, Rubber.

3) On the basis of action of heat they are classified into two types:

a) Thermoplastic Polymers:

The polymers are soften on heating and becomes hard on cooling are called "Thermo Plastic".

Ex: Poly Ethylenes, PVC, Nylon.

b) Thermosettings Polymers:

These polymers which are in soft in solid o viscous state on heating indigo extensive cross linking in moulds and become irreversibly hard moulds and become irreversibly hard as well as insoluble products.

4) Depending on its ultimate form and use they can be classified into four types.

a) Fibers:

If polymers are drawn into long filament are called "Fibers"

Ex: Nylon, Terylene.

b) Elastomers:

Polymers exhibiting good strength and elongation are called "Elastomers"

Ex: Synthetic Rubbers, Natural Rubber, etc.,

c) Plastics:

A polymer changes into hard and tuff utility articles by the application of heat and pressure called 'Plastics'

Ex: PVC, Polystyrene.

d) Liquid Resins:

These are used as adhesives and paintly compounds in liquid form are called "Liquid Resins"

Ex: Polysulphide, Sealients.

5) On the basic of mechanism of formation of polymer they can be classified into three types.

a) Addition Polymers:

They are formed by the addition of small molecules without leaving any molecule.

Ex: Poly Ethylene, PVC.

b) Condensation Polymers:

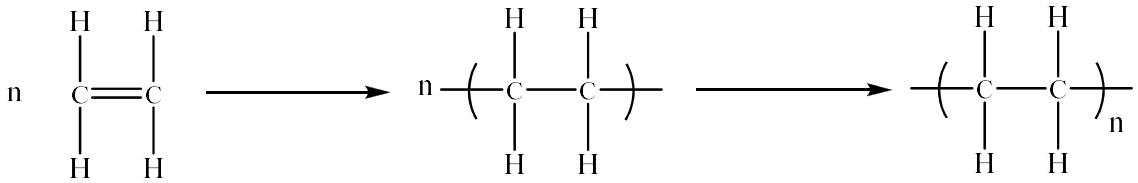
These are formed by the addition of small molecules with the elimination of simple molecules like H_2O, HCl etc.

Ex: Poly Esters, Poly amides.

c) Homo Polymers and Co-Polymers:

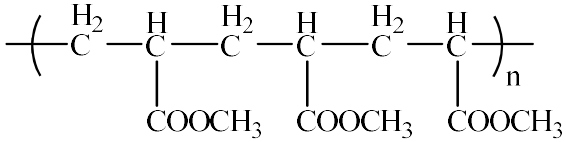
A Polymer containing similar type of monomers are called "Homo Polymer"

Ex: Ethylene combines to form poly ethylene.



A Polymer contain different type of monomers is called co-polymers (or) Hetero polymer.

EX: Poly Vinyl, Acetate.



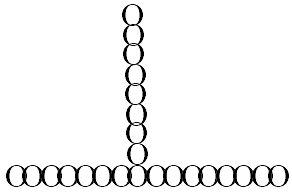
6) Depending on the chemical structure of polymers can classify into three types:

a) Linear Chain Polymers:

In these monomers is attached side by side each other in straight line.

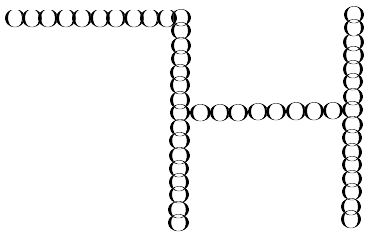
b) Branched Chain Polymers:

In this type of monomer are attached in a branched monomer.



c) Cross Linked Polymers:

In this type monomers are crosses to the many monomer molecules.



6.3 TYPES OF POLYMERIZATIONS:

Basing in the reaction mechanism polymerization process is classified into two (steps) types.

1) Step polymerization (or) Condensation polymerization.
2) Chain polymerization (or) Addition polymerization.

1) Step Polymerization:

The polymerization in which a polymer is formed by the addition of monomer of same or different with the elimination of small molecules such as H_2O, HCl etc… called "Step wise polymerization"

It is very slow process and makes used of condensation addition and ring opening reaction. So this polymerization can derive into three types.

i) Poly condensation
ii) Poly addition
iii) Ring opening

2) Chain Polymerization:

This polymerization is characterized by self addition of monomer molecules to each other by a chain reaction is known as chain polymerization containing relative double bonds can undergoes chain polymerization. In this reaction the products ormed in an exact multiple of the original monomeric molecule.

The addition polymerization must be investigated by the application of heat, light, pressure or catalyst for breaking down the double covalent bonds of monomers. This reaction also takes place in presence of peroxides. This addition polymerization involves chain reaction in which the chain carries may be an ion or a free radical.

6.4 MECHANISM OF ADDITION POLYMERIZATION:

Addition polymerization consists of three major steps namely initiation, propagation and termination and the process can be brought about by Free radical, Ionic Mechanism.

6.4.1 Free Radical Mechanism:

The process in which polymerization is carried out by free radical to make a polymer. This type of polymerization is called "Free radical polymerization" It involves three steps.

i) Initiation:

In which the step is considered to involve two reactions. The first is the production of free radicals by the hemolytic dissociation of an initiator.

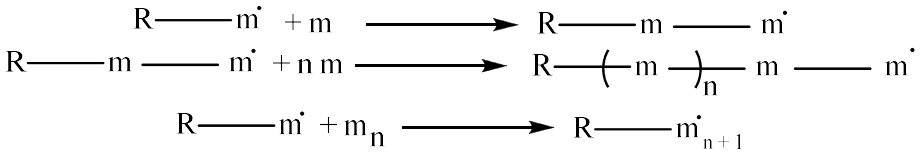
$$R{-}R \longrightarrow R^{\bullet} + R^{\bullet}$$

The second step of initiator involves the addition of this radical to the first monomer molecule (m) to produce the chain initiating species.

$$R^{\bullet} + m \longrightarrow R{-}m$$

ii) Propagation:

This step consists of growth of R-m by successive addition of large number of monomer molecules.



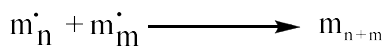
iii) Termination:

At some point the propagating polymer chain stops and growing terminate

i) By Combination
ii) By Disproportion

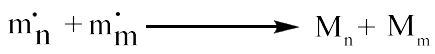
i) By Coupling (or) Combination:

By combining the two radicals, the chain reaction can be terminated and the forward polymer is called dead polymer.



ii) By Disproportiation:

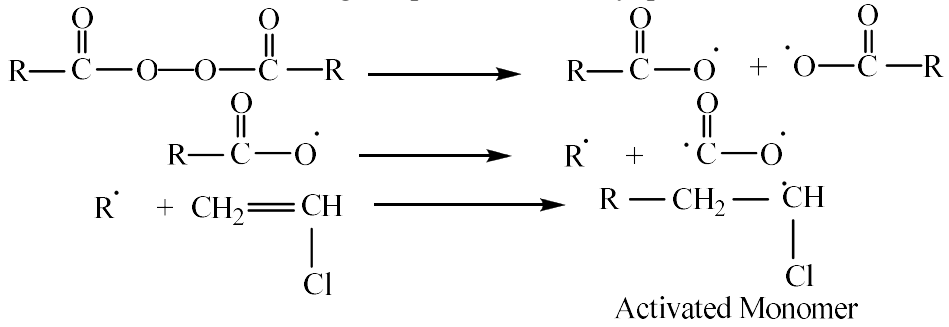
In this reaction hydrogen atom of one free radical centre is transferred into another radical centre forming two polymer molecules in which one is saturated and the other one is unsaturated compound.



Example:

i) Chain Initiation:

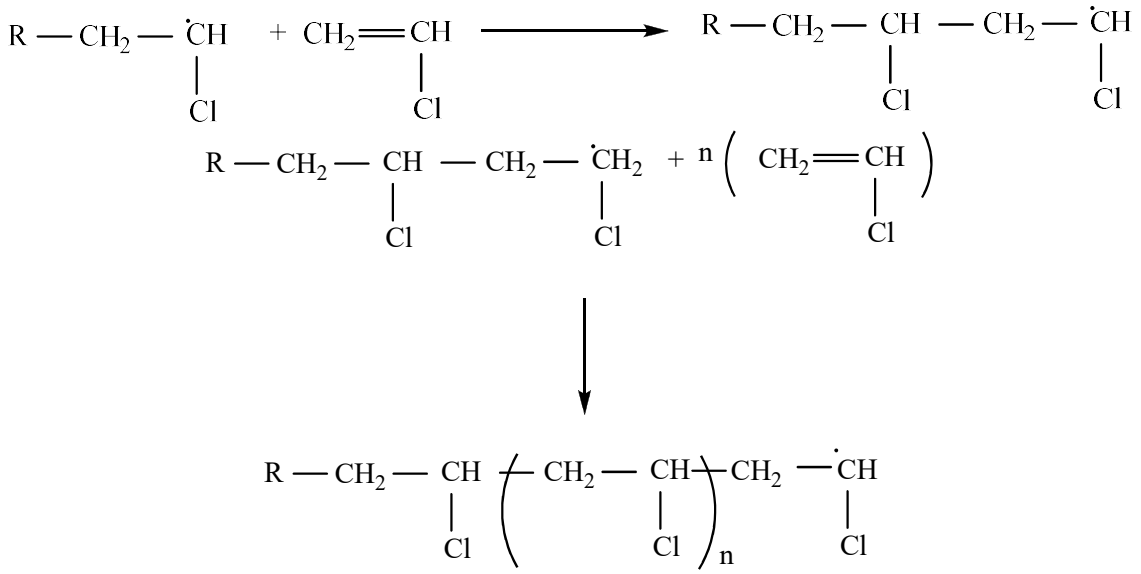
Initiators used are organic peroxides as acetyl peroxides.



ii) Chain Propagation:

iii)

The radical site at the first monomer attacks the double bond of fresh monomer molecule. This continuous propagation of chain takes place.

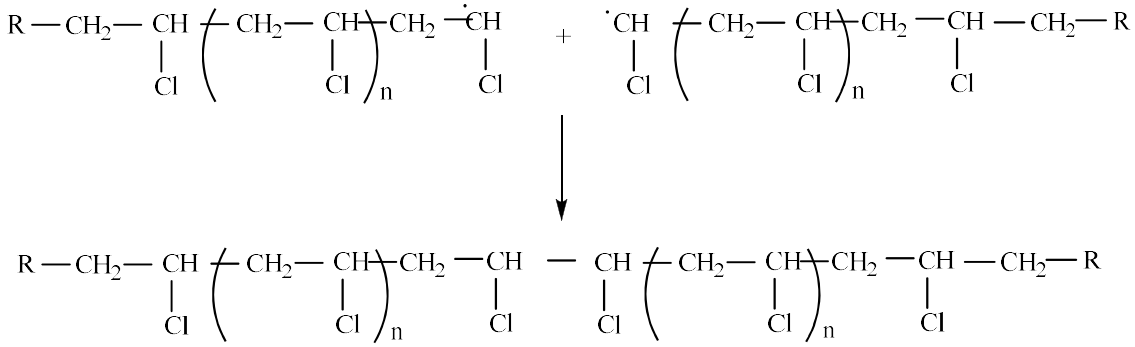


Growing Radical Chain

iv) Chain Termination:

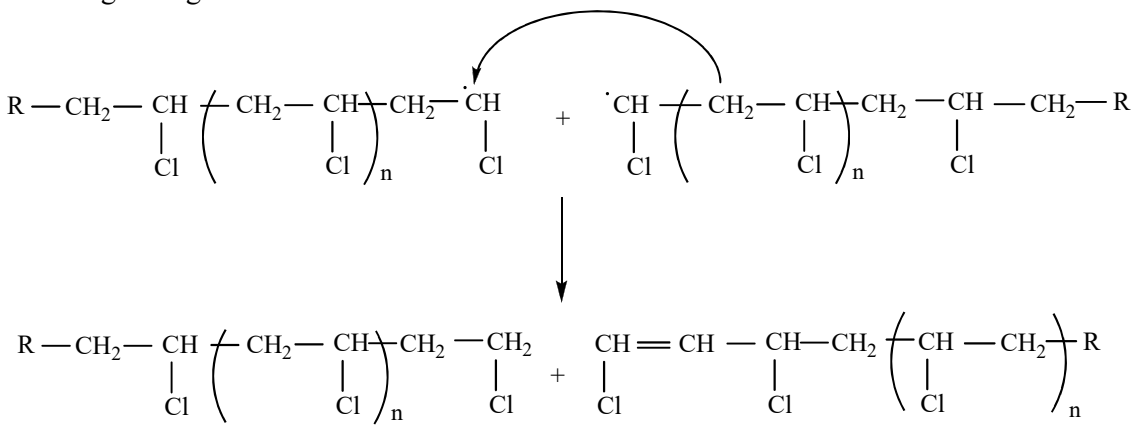
This may occurs in two steps.

i) By combination of two growing radical chains:



ii) By Disproportion:

This process involves transfer of hydrogen atom from one growing chain to another growing chain.



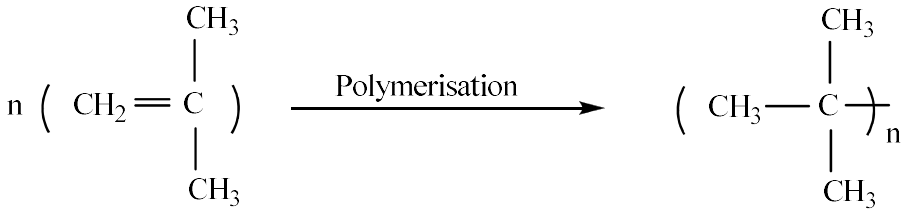
Saturated Compound Unsaturated Compound

6.4.2 Ionic Polymerization:

Ionic polymerization is classified as cationic and anionic depending upon the nature of the ions used for Initiation of polymerization.

1) Cationic polymerization:

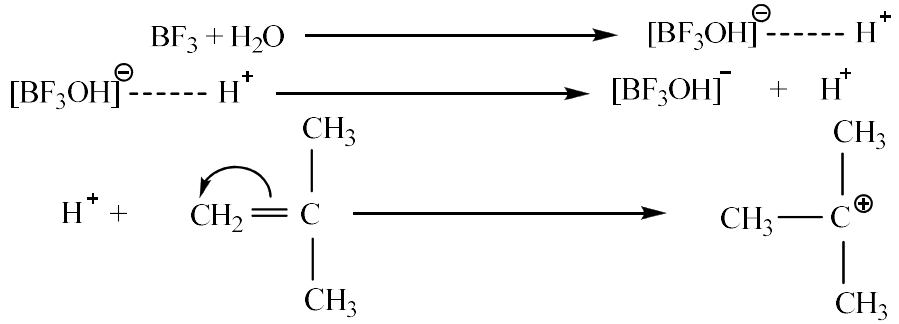
The polymerization is carried out by cat ion is called "Cationic Polymerization"
Ex: Polymerization of Isobutene



i) Chain Initiation:

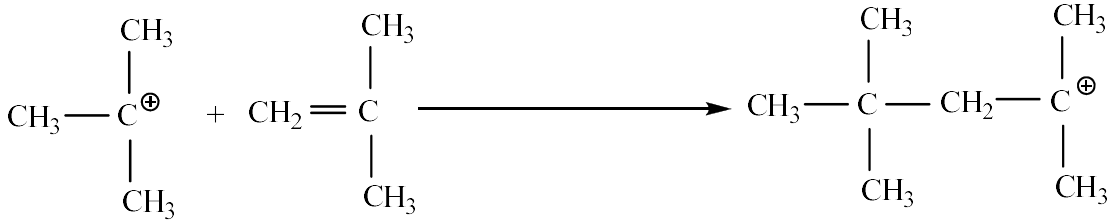
This polymerization is carried out by Lewis acids such as BF_3, $AlCl_3$, etc…

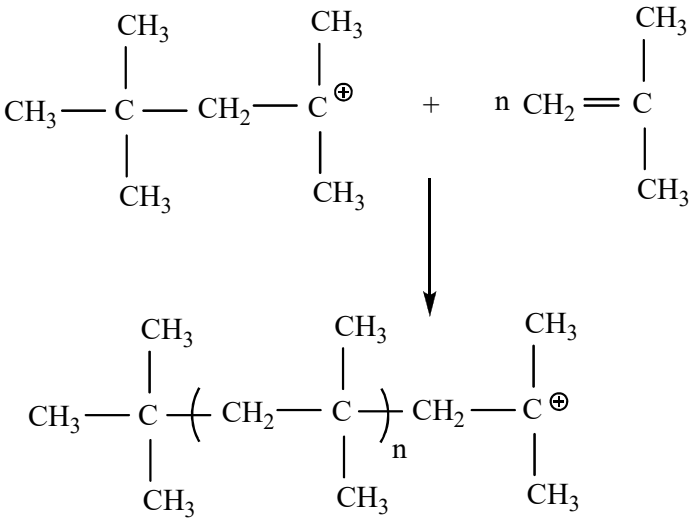
In this step initiator react with water molecule to produce protons.



ii) Chain Propagation:

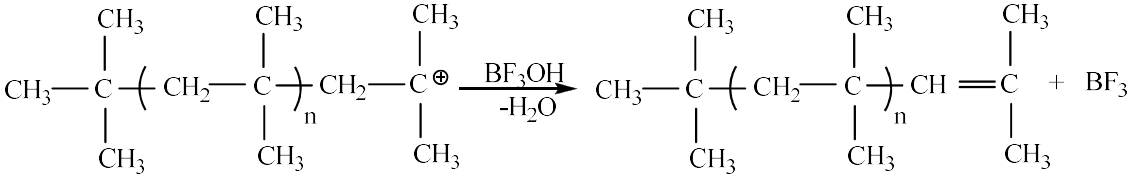
The carbonium ion attacks to another monomer forming another carbonium ion. The addition of continuous and chain propagation takes place





iii) Chain Termination:

It occurs when collision between activated polymer carbonium ion and an ion



Ex: Polymerization of Ethylene.
Polymerization of Vinyl Cyanide.

2) An ionic Polymerization:

In this polymerization initiated by an anion. This type of polymerization caused anionic polymerization.

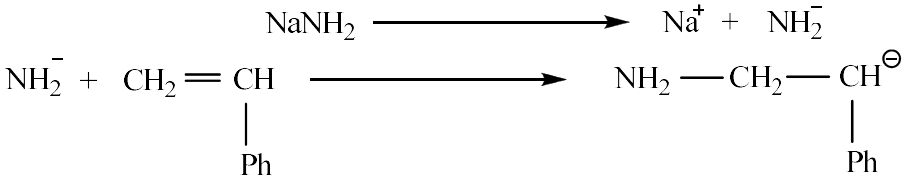
In this polymerization initiators are base such as $NaNH_2$, $LiNH_2$

Ex: Polymerization of Styrene.

Mechanism:

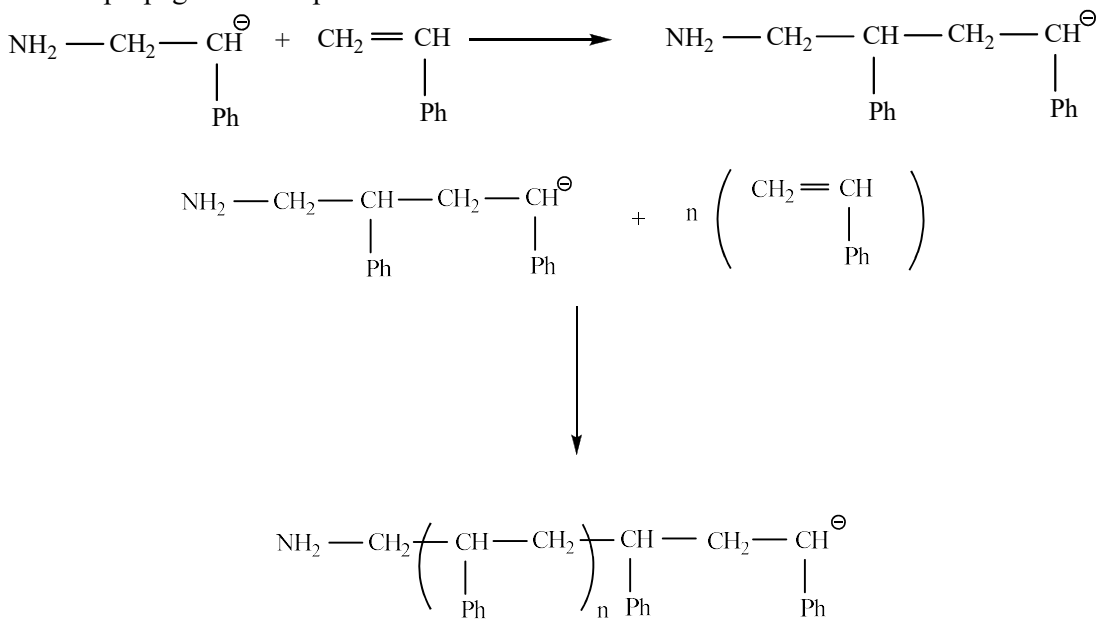
i) Chain initiation:

This polymerization carried out by base like $NaNH_2$, $LiNH_2$ ionizes to cation and anion.



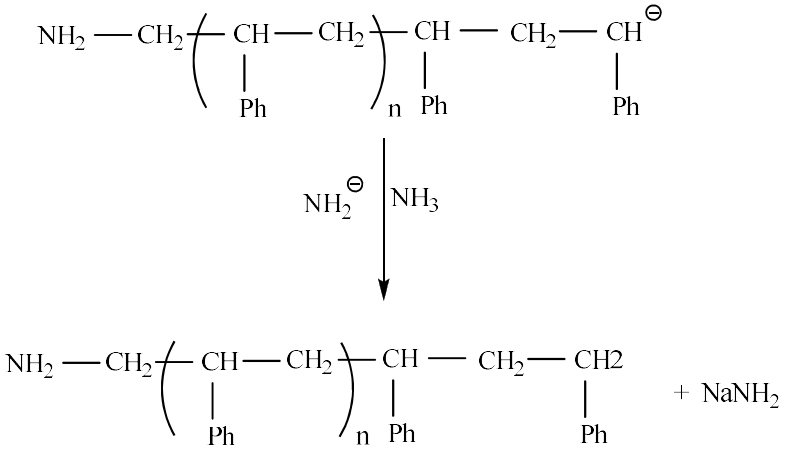
ii) Chain Propagation:

The carbonium attacks to monomer forming another carbanion. The addition continuous and the chain propagation take place.



iii) Chain Termination:

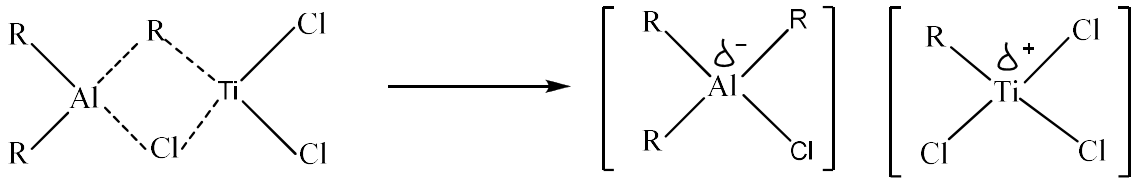
The activated polymer reacts with NH_3 and the chain is terminated.



6.4.3 Ziegler – Natta Polymerization:

These are the special type of co-ordination catalyst compared with two compounds. One is 'catalyst' and another one is 'co-catalyst'. Catalyst consists of hydrides of I to IV group elements. Other one is co-catalyst consists of hydrides of I to IV group metals.

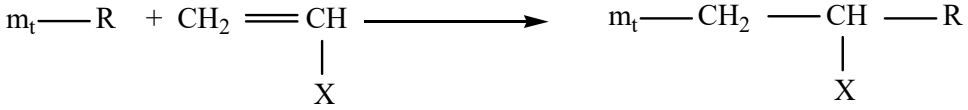
The most important catalyst and co-catalyst are based on Organo aluminum chloride and the other type of system is $TiCl_3$, $TiCl_4$. The above case 'Al' act as the electron acceptor and 'Ti' halide act as electro donor and forms as co- ordinated complexes.



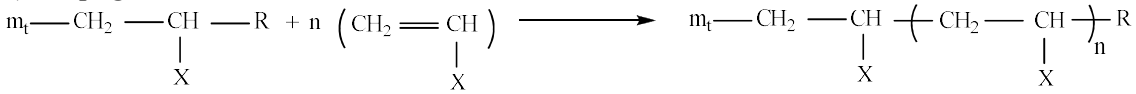
The complex is insoluble in the solvent and hetero generous in nature.

Mechanism:

i) Initiation

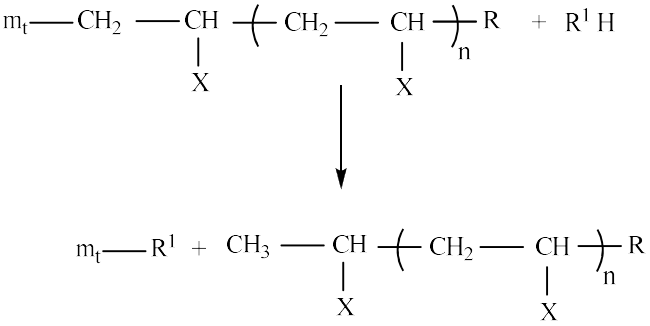


ii) Propagation

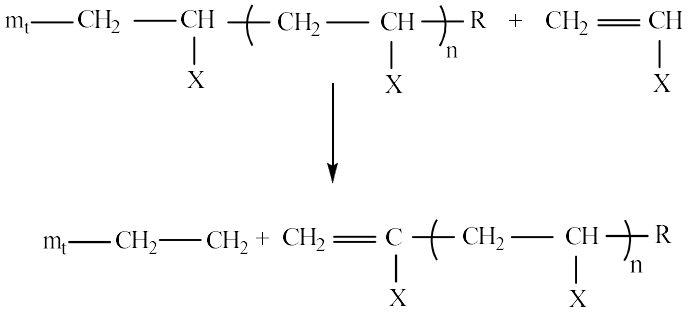


iii) Termination

a. By active hydrogen compound

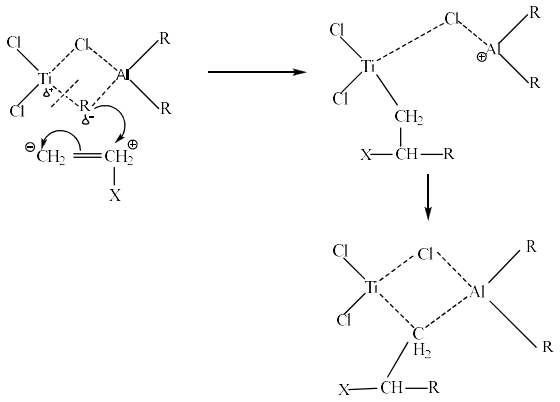


b. By transfer with monomer:

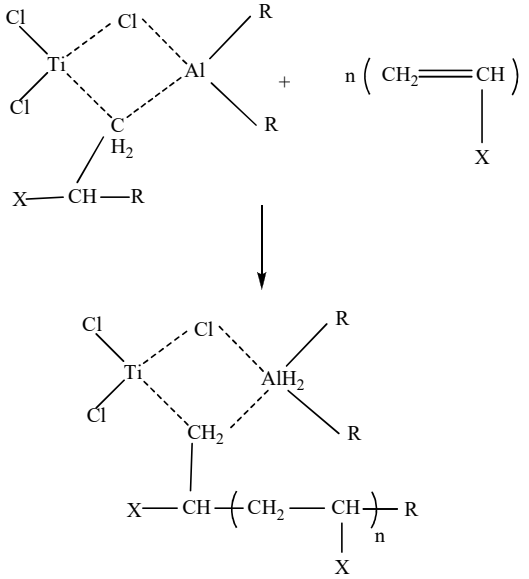


Example:

i) Initiation

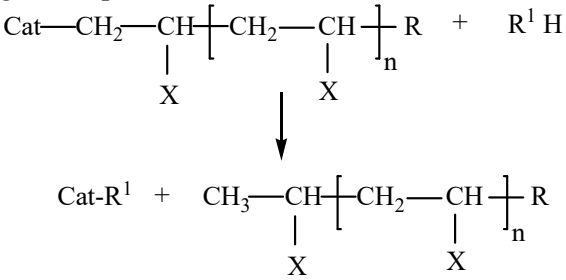


ii) Propagation:

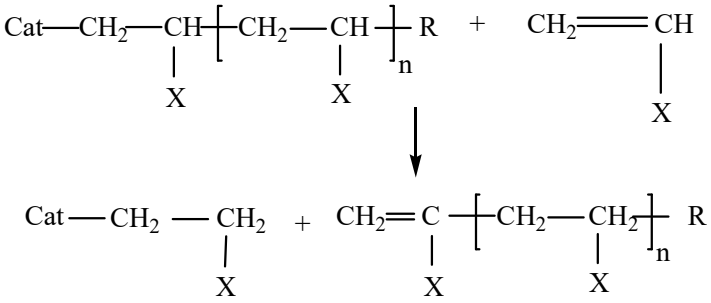


iii) Termination:

a) By active hydrogen compound



b) By transfer with monomer



Uses:

1. It is widely used for easily undergoes polymerization.
2. The Polymerization carried out by low temperature and low pressure.
3. Stereo specific and stereo regular polymer are preparing.

SUMMARY

- To know about the polymers.
- To study about Different Types of classifications of polymers.
- To study about Mechanism of Polymerizations.
- To study about free radical, Cationic and Anionic and Ziegler Natta polymerization mechanics.

SELF ASSESSMENT QUESTIONS

1. Define polymers and write their classification.
2. Write the various types of mechanism involved in Polymerization.
3. Discuss about mechanism involving free radical polymerization.
4. Write Zeigler-Natta Polymerization mechanism.

Prof. R. Ramesh Raju

LESSON-7
KINETICS OF FREE RADICAL POLYMERIZATION; TECHNIQUES OF POLYMERIZATION; GLASS TRANSITION TEMPERATURE; FACTORS INFLUENCING THE GLASS TRANSITION TEMPERATURE.

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the kinetics of Free radical polymerization.
- To study about various Techniques of Polymerization.
- To study about Glass Transition Temperature and their Factors influencing the glass transition temperature.

7.1 KINETICS OF FREE RADICAL POLYMERIZATION:

Free radical chain polymerization takes place in three steps

i) Initiation:

To initiate the reaction, we need free radicals which are generated by hemolytic decomposition o initiator.

$$I \xrightarrow{K_d} R^{\cdot} + R^{\cdot} \longrightarrow (1)$$

Here 'I' is initiator 'R' is free radical and K_d is initiator decomposition of rate constant.

But the rate of decomposition of initiator is related to concentration of initiator.

$$-\frac{d}{dt}[I] = R_d = Q K_d \longrightarrow (2)$$

The free radicals generated by the decomposition of initiator can attacks monomer to give new free radicals.

$$R^{\cdot} + m \xrightarrow{K_i} Rm^{\cdot} \longrightarrow (3)$$

Where K_i is initiation rate constant

The rate of initiation is denoted by "R_i"

$$-\frac{d}{dt}[m] = R_i = K_i [R^{\cdot}][m] \longrightarrow (4)$$

The rate of formation of free radicals from equation (3) and (4)

$$R_i = R_d$$

$$R_i = Q K_d [I] \longrightarrow (5)$$

This equation good when all free radicals produces are effective but some of the monomer initiate not effective since they lost as side products. Such as recombination of radicals. If 'f' is the fraction of free radicals produced that effective in the initiating the chin growth then "R_f" can be modified as

$$R_f = 2 f K_d [I] \longrightarrow (6)$$

ii) Propagation:

$$Rm^{\cdot} + m \xrightarrow{K_p} Rmm^{\cdot}$$

$$Rmm^{\cdot} + m \xrightarrow{K_p} Rmmm^{\cdot}$$

$$Rmmm^{\cdot} + nm \xrightarrow{K_p} Rm_n + 2m^{\cdot}$$

Where K_p is rate of propagation constant

$$R_p = K_p [m] [m^{\cdot}] \qquad ([m] = Rm^{\cdot} / Rmm^{\cdot} / Rmmm^{\cdot})$$

ii) Termination:

a) Combination of two growing chains

$$Rm_{n1}m^{\cdot} + Rm_{n2}m^{\cdot} \xrightarrow{K_t} Rm_{n1}mmm_{n2}R$$

$$-\frac{d}{dt}[m^{\cdot}] = R_t = 2K_t[m^{\cdot}]^2 \longrightarrow (7)$$

When number of chain growth initiated equal total number of chain growth arrested.

Rate of initiation = Rate of termination

$$R_i = R_t$$

$$R_i = R_t$$

$$2 f K_d [I] = 2 K_t [m^{\cdot}]^2$$

$$f K_d [I] = K_t [m]^2$$

$$[m^{\cdot}]^2 = \frac{f K_d [I]}{K_t}$$

$$[m^{\cdot}] = \left[\frac{f K_d [I]}{K_t}\right]^{1/2} \longrightarrow (8)$$

Substituting equation (8) in R_p then we get

$$R_p = K_p [m] [m^{\cdot}]$$

$$[m] = \frac{R_p}{K_p [m^{\cdot}]}$$

$$[m] = \frac{R_p}{K_p\left[\frac{f K_d [I]}{K_t}\right]^{1/2}}$$

$$R_p = K_p\left[\frac{K_d}{K_t} f[I]\right]^{1/2}[m]$$

Kinetic chain length:

It is defined as the average number of monomer molecules consumes by each effective free radical generated by initiator.

$$V = \frac{\text{Rate of Propogation}}{\text{Rate of initiator}} = \frac{R_p}{R_i}$$

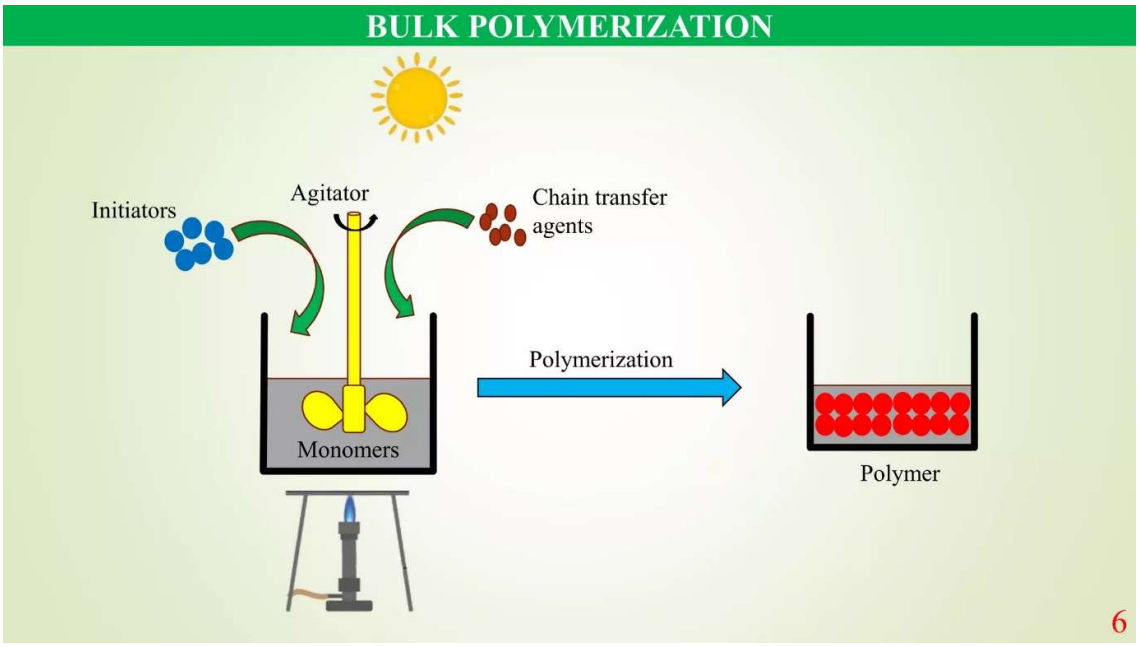
$$V = \frac{K_p\left[\frac{K_d}{K_t} f[I]\right]^{1/2}[m]}{2\,K_d\, f[\,I\,]}$$

7.2 TECHNIQUES OF POLYMERIZATION:

There are four types of general polymerization methods. Bulk, Solution, Suspension and Emulsion polymerization.

1) Bulk Polymerization:

- It is a simple polymerization technique in which polymer is isolated with high purity.
- First the monomer is in liquid phase and indicator is dissolved in monomer.
- Now the whole system is in Homogeneous phase.
- Now the reaction mass us exposed or heated to initiate the polymerization and kept under agitation for proper mass and heat transfer.
- Polymerization of monomer which is in the liquid state without solvent, called Bulk Polymerization.



Advantages:

- It is quite simple process.
- The product obtained as high purity.

Disadvantages:

- When the viscosity of the medium increases mixing becomes difficult and it leads to the products with very well.

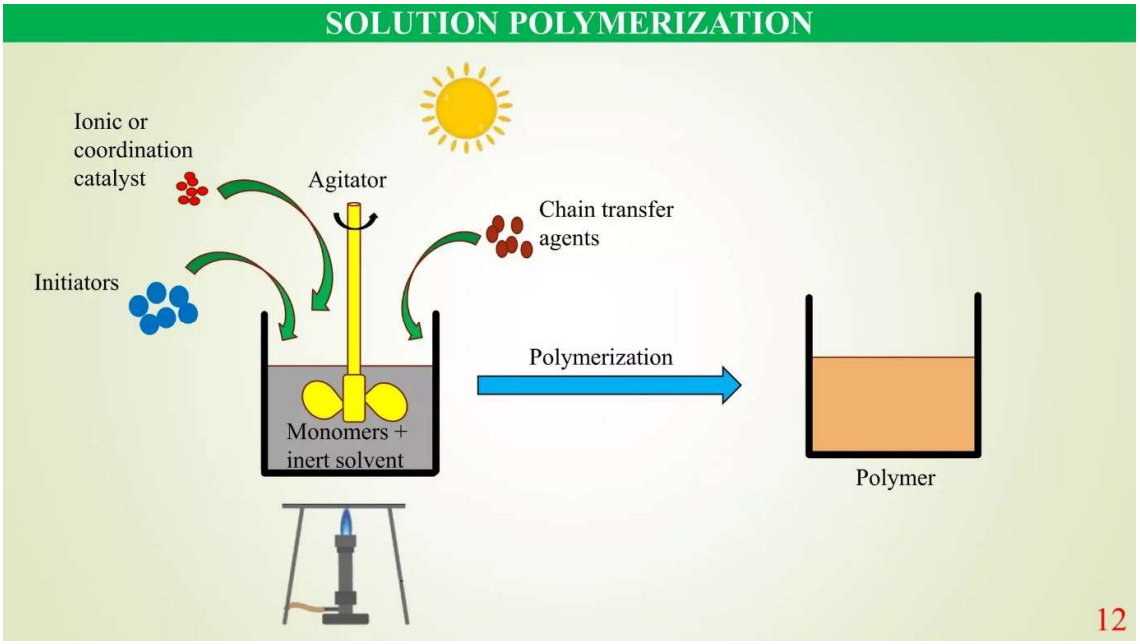
- ❖ When medium gets viscous diffusiability of growing polymer chain becomes restricted, termination become difficult.
- ❖ Sometimes uncontrolled "Exothermic reactions" leads to explosion.

Uses:

This method is used in free radical polymerization of methyl meta acrynate and styrene or also vinyl chloride.

2) Solution Polymerization:

- ❖ In this technique monomer dissolved in suitable inert solvent along with chain transparent agent and free radical initiator with ionic and co-ordination catalyst.
- ❖ Inert solvent medium helps to control increase in viscosity of medium and promote proper heat transfer.
- ❖ The polymer isolated from the solution either by evaporation of the solvent by precipitation.
- ❖ It is an advantage technique in which the polymer is formed as slurry.
- ❖ However the solvent is inert there is no proper chain transfer to the solvent to get very high molecular weight products.



Advantages:

- ❖ By using this technique block and co-polymer are prepared.
- ❖ Thermal control is possible by this technique with the help to inert solvent.
- ❖ The polymer is formed in this using pure state.

Disadvantages:

- ❖ It is difficult to remove the solvent.
- ❖ In this technique no degree of polymerization takes place.

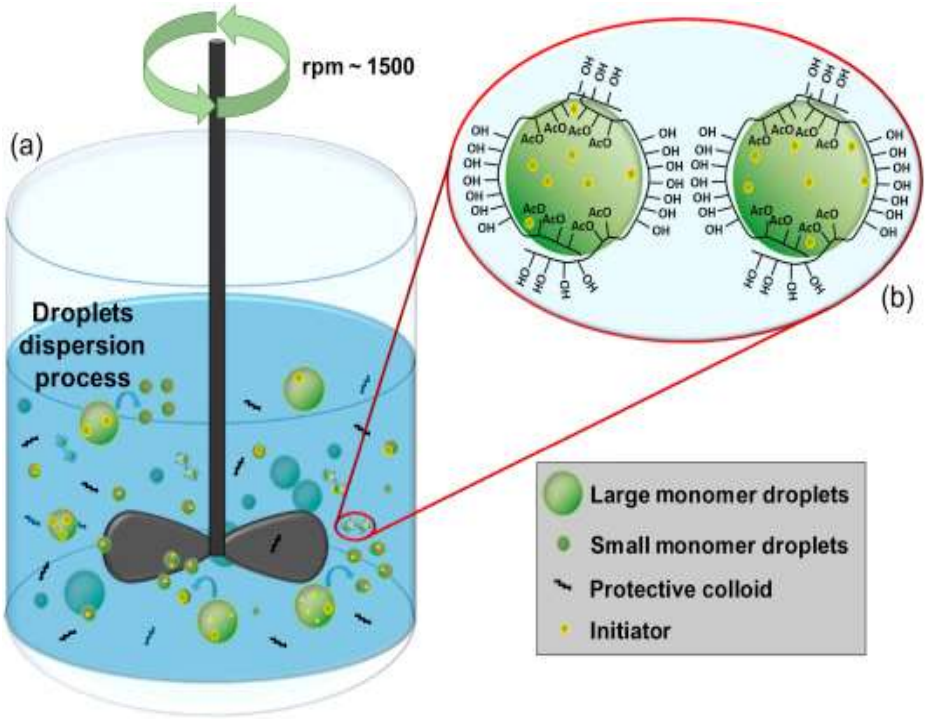
Uses:

- ❖ Industrial preparation of poly acrylo nitrile by the free radical polymerization.

- ❖ Poly isobutene by cationic polymerization.
- ❖ Industrial production of block copolymer.

3) Suspension Polymerization:

- ❖ This method is used for polymerize only water insoluble polymers.
- ❖ The monomer is suspended in water the form of tiny droplets. Droplets are pre rented from coalescing by water. Soluble protective colloids called surface active agents.
- ❖ Size of monomer droplets depends on monomer to water ratio.
- ❖ The initiators are monomers soluble and in which chain transparent agent are also placed.
- ❖ In this the polymer is formed as spherical beads or pearls. Hence this polymerization is called bead or pearl polymerization.
- ❖ The reaction sometimes carried out in presence of water soluble stabilizers such as finely divided organic or inorganic materials.



Advantages:

- ❖ This method is heat controlled process.
- ❖ This product is isolated by filtration method,
- ❖ The polymer prepared in this process is relatively free from contaminants.

Disadvantages:

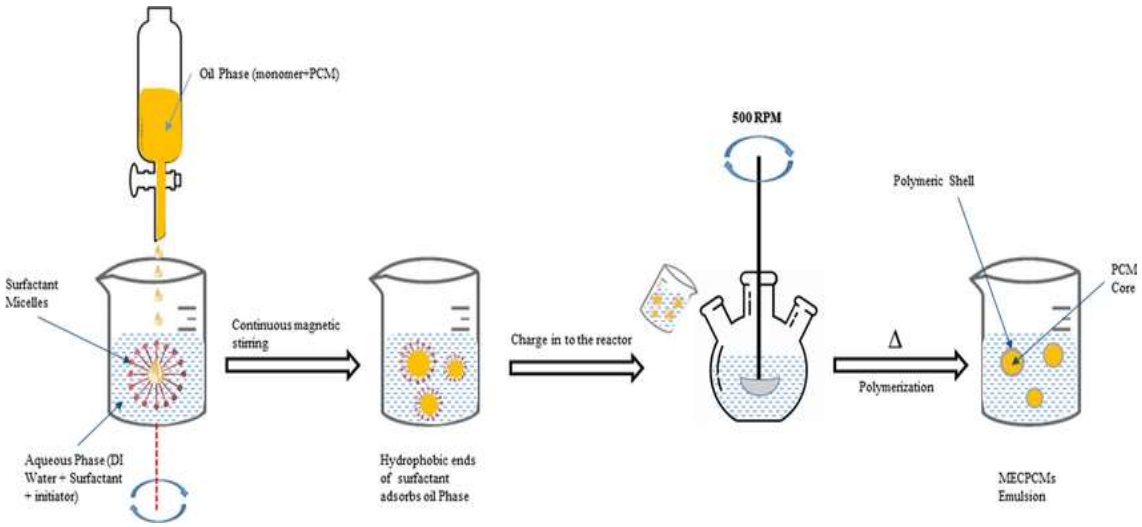
- ❖ The product from with much high particle size.

Uses:

- ❖ By this method PVC, Poly styrene can be prepared.
- ❖ Divinyl benzene copolymer beads are used in Ion exchange resins are produced by this method.

4) Emulsion Polymerization:

- ❖ In this method the monomer is dispersed in water and stabilized by the addition of soap or alkyl sulphates.
- ❖ As a result the monomers are formed as aggregates which are called as "Micelles".
- ❖ The initiator diffused into the micelle from water and starts the polymerization.
- ❖ Polymerization takes place in the core of Micelle.



Advantages:

- ❖ In this method temperature can be controlled.
- ❖ It used to prepare rubber namely BUNA-S, BUNA-N etc

Disadvantages:

- ❖ Polymerization is rapid but resulting polymer is very small.
- ❖ This is too expensive method.
- ❖ The observation of micelles formation is very difficult.

7.3 GLASS TRANSITION TEMPERATURE:

If an ordinary rubber ball is cooled below -70^{o}C becomes so hard and brittle and it will break into pieces like a glass ball falling on a hard surface. This is because there is a "Temperature Boundary" for almost all amorphous poly and many crystalline polymers. Only above which the substance remain soft, flexible and rubbery and below which it becomes brittle and glassy.

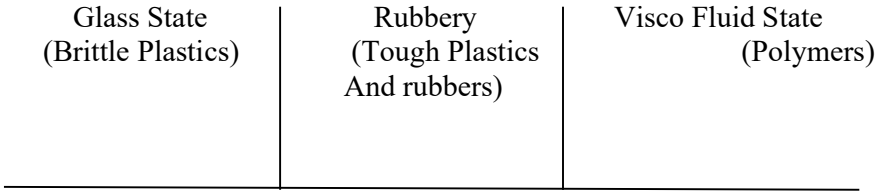
Definition:

In amorphous polymer the temperature below which is becomes hard and above it is soft called glass transition temperature. It is denoted by 'T_g'.

The hard brittle state is known as the glass state and soft, flexible state is rubbery state. On further heating the polymer becomes highly viscous liquid and state flowing, this is viscofluid state.

So the temperature at which the transition from glassy solid state to molten state in called glassy transition temperature.

The temperature at which are the polymer changes from rubbery state to liquid state called flow temperature.



Factors influencing the glass transition temperature:
The Glass transition temperature of polymer depends on the following parameters

i) Chain Geometry
ii) Chain Flexibility
iii) Molecular Aggregates

i) Chain Geometry:

If molecular geometry permits formation of a definite molecular orientation leading to long-range three-dimensional order such as a polymer has greater criticizability that why polymers with symmetrical (or) Stereo regular structure are crystalline.

Polymer with irregular chain back bone (or) randomly places side groups are non-crystalline. So segmental and side chain mobility are easier in non-crystallizable polymer than in crystalline polymer.

So highly crystalline polymers possessing a regular chain geometry shows high glass transition temperature.

ii) Chain flexibility:

Flexibility of the chain segments is determined by the degree of freedom with which different segment along the chain back bone can rotate around the covalent bonds.

Linear polymer chains made of C-C, C-O, or C-N single bonds have high degree of freedom for rotation. The presence of aromatic or cyclic structure in the chain back bone or of bulky side groups on the back bone carbon atoms hinders the freedom for rotation. The higher the freedom to rotate, the chain segments are more flexibility and hence higher their segmental mobility.

Bulky side groups increases the 'T_g' of polymer.
Example: Polyethylene has 'T_g' of -125° C. In this case 'T_g' quite low.
Because; i) Due to absent strong inter molecular cohesive forces.
ii) The substituent group on carbon atom 'C' is only hydrogen where as Nylon-6 has high glass transition temperature i.e. 50 °C.

iii) Molecular Aggregates:

Magnitude of the molecular aggregates is determined by inter molecular forces. In case of hydro carbon polymers only vanderwalls forces act as neighboring chain and hence molecular aggregates are not much strong. Chain segments can slip past each other easily.

In case polymer chains containing polar groups are held together more strongly by neighboring droplets as inter molecular hydrogen bonding and are unable to move easily.

SUMMARY:

- To know about the mechanism in kinetics of Free radical polymerization.
- To study about various Techniques involved for Polymerization.
- To study about Glass Transition Temperature and their Factors influencing the glass transition temperature

SELF ASSESSMENT QUESTIONS

1. Write the various techniques involved in polymerization.
2. Write the kinetic study for free radical Polymerization.
3. Discuss in detailed about glass transition temperature and their Factors influencing the glass transition temperature.

Prof. R. Ramesh Raju

LESSON-8
MOLECULAR WEIGHT OF POLYMERS; WEIGHT AVERAGE MOLECULAR WEIGHT; NUMBER AVERAGE MOLECULAR WEIGHT DETERMINATIONS

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the Molecular weight of polymers.
- To study about Weight Average Molecular Weight and Number Average Molecular Weight,
- To know about the Comparison of Number Average vs. Weight Average Molecular Weight.
-

8.1 MOLECULAR WEIGHT OF POLYMERS:

Molecular weight is an important property of any molecule a simple compound has fixed molecular weight.

For example, the molecule weight of acetone is 58. If molecular weight changes from 58 to 60 then the sample no longer acetone but it may be acetic acid. It is true for simple molecular weight compounds.

But in case of polymer, we use the term "Average Molecular Weight" because in polymers the molecular weight depends on the degrees of polymerization.

When ethylene is polymerized to form poly ethylene several polymers' chains start growing at any instant but all of them do not get terminated after growing to the same size. The chain termination is random process and hence each polymer molecule formed can have different number of monomer units and thus different molecular weight.

Ex: $R\text{+}CH_2-CH_2\text{+}_{500}R$ Mol.Wt $\cong$ 14,000

$R\text{+}CH_2-CH_2\text{+}_{600}R$ Mol.Wt $\cong$ 16,800

Two types of Average Molecular Weight have been defined.

1) Weight Average Molecular Weight.
2) Number Average Molecular Weight,

8.2 WEIGHT AVERAGE MOLECULAR WEIGHT:

Weight Average Molecular Weight (Mw) is a measure of the average molecular weight of a polymer sample, but it takes into account the relative abundance of different molecular weight fractions. It is calculated by summing the products of the number of molecules in each molecular weight fraction and their respective molecular weights, divided by the total number of molecules in the sample.

Mw provides information about the overall mass of the polymer sample, taking into consideration the contribution of each molecular weight fraction. It is particularly useful in characterizing polymers with a broad molecular weight distribution, where the presence of high molecular weight species can significantly impact the material's properties.

One advantage of Mw is its ability to capture the influence of high molecular weight species on the overall behavior of the polymer. It provides a more comprehensive representation of the sample, considering the relative abundance of different molecular weight fractions. Mw is often used in applications where the overall mass of the polymer is important, such as in the determination of mechanical properties or in the design of polymer blends.

However, the calculation of Mw is more complex compared to Mn. It requires the determination of both the number of molecules and their respective molecular weights in each molecular weight fraction. This can be achieved through advanced techniques like multi-angle light scattering (MALS) coupled with GPC or SEC. The presence of high molecular weight outliers can also have a significant impact on the accuracy of Mw, as they contribute more to the overall value compared to lower molecular weight species.

In summary, Mw provides a more comprehensive measure of the average molecular weight, considering the relative abundance of different molecular weight fractions. It is particularly useful for polymers with a broad molecular weight distribution, where the presence of high molecular weight species can significantly influence the material's properties. However, the calculation of Mw is more complex and requires advanced techniques to accurately determine the molecular weight distribution.

It depends upon the masses of the groups of molecules having particular weight. There force in average process the molecular weight of molecule is multiplied by the weight of that species and divided the figure obtained by total mass of an the species.

$$\overline{M_W} = \frac{m_1M_1 + m_2M_2 + m_3M_3 + ...}{m_1 + m_2 + m_3 + ...}$$

If n_1, n_2, n_3, …….etc are number of molecules havingSSS masses m_1, m_2, m_3, …….etc then

$m_1 = n_1m_1$, $m_2 = n_2m_2$, $m_3 = n_3m_3$,…….. etc

Now substitute the value of m_1, m_2, m_3, …….etc in above equation.

$$\overline{M_W} = \frac{n_1M_1 \times M_1 + n_2M_2 \times M_2 + n_3M_3 \times M_3 + ...}{n_1M_1 + n_2M_2 + n_3M_3 + ...}$$

$$\overline{M_W} = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2 + ...}{n_1M_1 + n_2M_2 + n_3M_3 + ...}$$

$$\overline{M_W} = \frac{\sum n_iM_i^2}{\sum n_iM_i}$$

8.3 NUMBER AVERAGE MOLECULAR WEIGHT (m_n):

Number Average Molecular Weight (Mn) is a measure of the average molecular weight of a polymer sample based on the number of molecules present. It is calculated by summing the products of the number of molecules in each molecular weight fraction and their respective molecular weights, divided by the total number of molecules in the sample.

Mn is particularly useful in characterizing polymers with a narrow molecular weight distribution. It provides information about the average size of the polymer chains and can be used to estimate the number of repeat units in a polymer. Mn is often used in quality control and research applications to ensure consistency and reproducibility of polymer samples.

One advantage of Mn is its simplicity in calculation. It only requires the determination of the number of molecules in each molecular weight fraction, which can be easily obtained through techniques such as gel permeation chromatography (GPC) or size exclusion chromatography (SEC). Mn is also less affected by the presence of high molecular weight outliers, making it a reliable measure for polymers with a well-defined molecular weight distribution.

However, Mn does not provide information about the relative abundance of different molecular weight fractions. It assumes that all molecules contribute equally to the overall properties of the polymer, regardless of their size. This assumption may not hold true for polymers with a broad molecular weight distribution, where a few high molecular weight species can significantly influence the overall behavior of the material.

Mn is a valuable measure for polymers with a narrow molecular weight distribution, providing information about the average size of the polymer chains. It is relatively simple to calculate and less affected by outliers, making it suitable for quality control and research applications.

It is defined as the weight of the sample of a macro molecule divided by the total number of molecules (n) present in the sample.

$$\overline{m_n} = \frac{\text{Weight of the Polymer}}{n}$$

If Polymer consists of 'n_1' molecules of molecular weight 'm_1' and 'n_2' molecules of molecular weight 'm_2' …….. then

$$\overline{m_n} = \frac{n_1m_1 + n_2m_2 + n_3m_3 + ...}{n_1 + n_2 + n_3 + ...}$$

$$\overline{m_n} = \frac{\sum n_i m_i}{\sum n_i}$$

Note: Weight average molecular weight always greater than that of number average molecular weight.

8.4 COMPARISON OF NUMBER AVERAGE vs. WEIGHT AVERAGE MOLECULAR WEIGHT

Attribute	Number Average	Weight Average Molecular Weight
Definition	The arithmetic mean of the molecular weights of a polymer sample.	The sum of the products of each molecular weight and its corresponding fraction in a polymer sample.
Calculation	Sum of all molecular weights divided by the number of molecules.	Sum of the product of each molecular weight and its corresponding fraction divided by the sum of all fractions.
Weighting	Each molecular weight is given equal weight.	Molecular weights are weighted by their respective fractions.

Significance	Provides an average molecular weight value for a polymer sample.	Reflects the distribution of molecular weights in a polymer sample.
Application	Useful for determining the average size of polymer chains.	Useful for characterizing the polydispersity of a polymer sample.

SUMMARY:

- To know about the Molecular weight of polymers.
- To study about Weight Average Molecular Weight and Number Average Molecular Weight,
- To know about the Comparison of Number Average vs. Weight Average Molecular Weight.

SELF ASSESSMENT QUESTIONS

1. Discuss briefly about the number average and weight average molecular mass of the polymer.
2. Differentiate number average and weight average molecular mass of the polymer.

Prof. R. Ramesh Raju

LESSON-9
MOLECULAR WEIGHT DETERMINATION METHODS; END – GROUP ANALYSIS; OSMOMETRY; LIGHT SCATTERING METHOD; ULTRA CENTRIFUGATION METHOD AND VISCOMETRY

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the hoe to determine Molecular weight of polymers.
- To study about End – Group Analysis and Osmometry methods for determination of Molecular Weight.
- To know about the Light Scattering Method Ultra Centrifugation Method and Viscometry methods for Molecular Weight determination.

9.1 MOLECULAR WEIGHT DETERMINATION METHODS:

Molecular weight of the polymer is determined by following methods.

1) End – Group Analysis
2) Osmometry
3) Light Scattering Method
4) Ultra Centrifugation Method
5) Viscometry

9.2 END – GROUP ANALYSIS:

The End group analysis is a chemical method. It is used for calculate the number average molecular weight of polymer sample whose molecules contain reactive functional groups at the one end or both ends of the molecule.

The number average molecular weight of linear polymer can be determined by estimation the number of end groups by chemical analysis. In this method the number and natural of end group per molecule should e reliably known. This method is applicable to linear condensation polymer and also to addition polymers.

a*) Condensation Polymer:*

Condensation polymers usually contain functional group which can lend them to chemical analysis. They are poly esters and poly amides containing carboxylic acid group can be estimated by titration with base in alcoholic (or) Phenolic solutions.

The amino group in poly amides can be estimated by titration against an acid under similar conditions, for the determination of hydroxyl groups in a polymer; it is reacted with titratable reagent.

b) Addition Polymer:

End group method can be applied to addition polymers also when the polymerization is initiated by initiators contain identifiable groups or ratio active labeled groups. The initiator fragment get attached to one or both ends of chain depending on the made of termination. If the mechanism of termination involves disproportions only one fragment get attached.

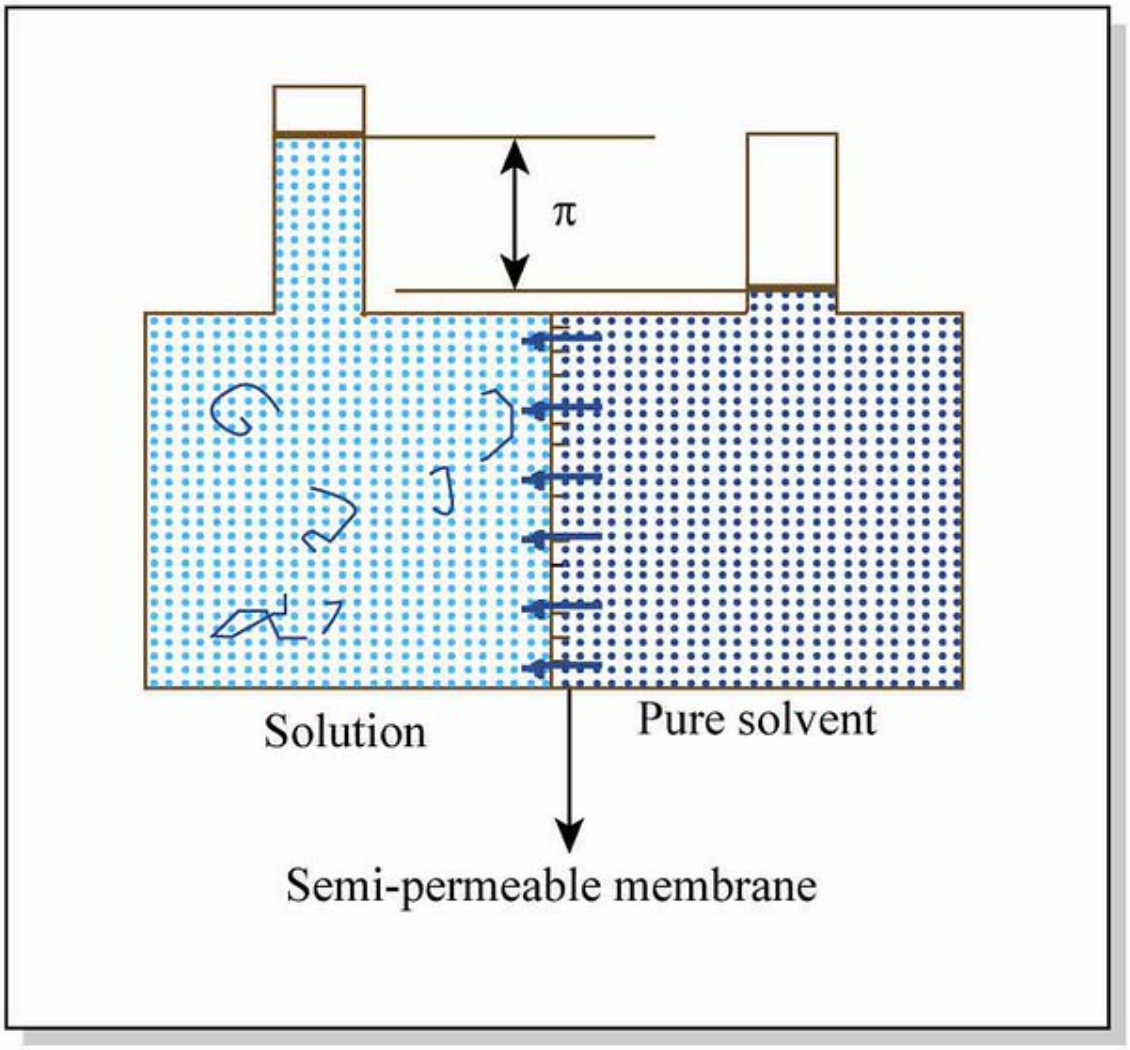
9.3 OSMOMETRY:

The number average molecular weight of many polymers can be measured by osmometry. It is based on the fact that certain semi - permeable membranes may be constructed which permit penetration by solvent molecule but which prevent the transparent of macro molecule.

Pure solvent possess through the membrane in order to lower the free energy of the system. If thermo stated cell is constructed and pure solvent in placed on the same solvent is placed on the other side of the membranes while a solution of the polymer in the same solvent is placed on the other side of membrane, a pressure gradient will develop.

The process will continue until an equilibrium reached in which the free energy change due to the pressure rise just equals the free energy change due to dilution of solution.

The equilibrium pressure developed is called the osmotic pressure. The principle of an osmotic pressure as shown in figure.



Application of elementary thermodynamics to the osmotic equilibrium gives the following relationship.

$$\frac{\Pi}{C} = RT\left[\frac{1}{\overline{M}_n} + A_2C + A_3C^2 + ...\right]$$

Where 'C' is the concentration of the solution in gm/cc. 'R' is gas constant and 'T' is absolute temperature.

In this derivation it is assumed that solutions are dilute and temperature is constant.

The above equation is power series in the concentration. In order to obtain the number average molecular (M_n) an extrapolation procedure yielding Π/C at the limit o infinite dilution is required.

As 'C' approaches zero, all inter molecular interactions vanish and the theory becomes exact.

Finally, the number average molecular weight is determined by using the following formula.

$$\overline{M}_n = \frac{1033 \times R \times T}{L \times d}$$

$$\overline{M}_n = \frac{1033 \times 0.0821 \times T}{L \times d}$$

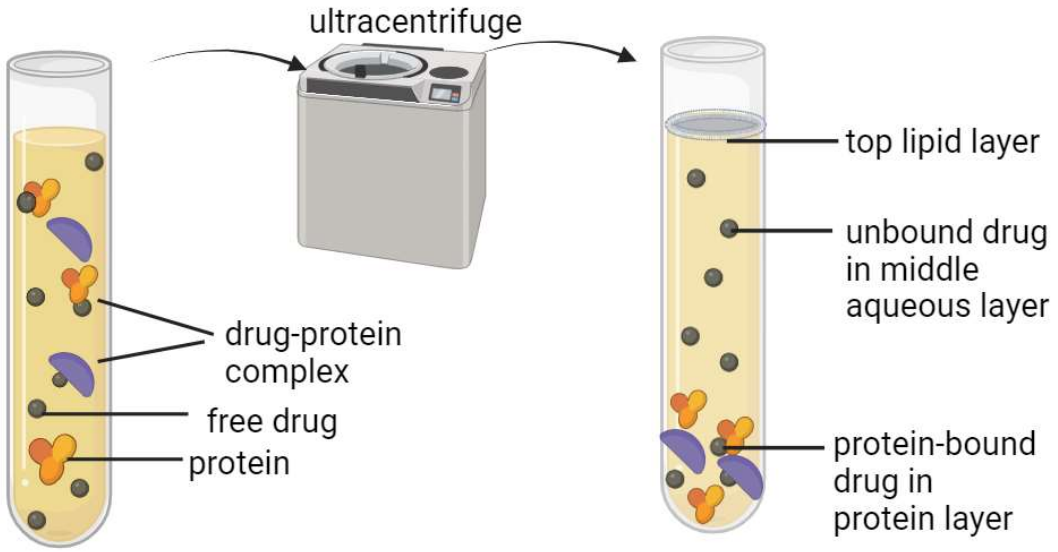
Where 'L' is limiting osmotic head.
'd' is density of solution.

9.4 ULTRA CENTRIFUGATION METHOD (OR) SEDIMENTATION:

Principle:

The sedimentation rate of polymer molecule setting down under the influence of constant centrifugal force is related to their molecular weight.

Making use if these principle two different methods are applied to determined molecular weight of polymer.



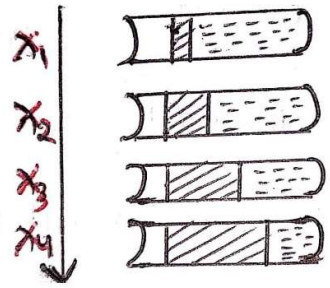
i) Sedimentation velocity method:

The earth gravitational force makes any particle in suspension settle down. Macro molecules in a polymer solution are also affected by gravity in similar way. The sedimentation velocity of polymer molecules depends on the molecular weight.

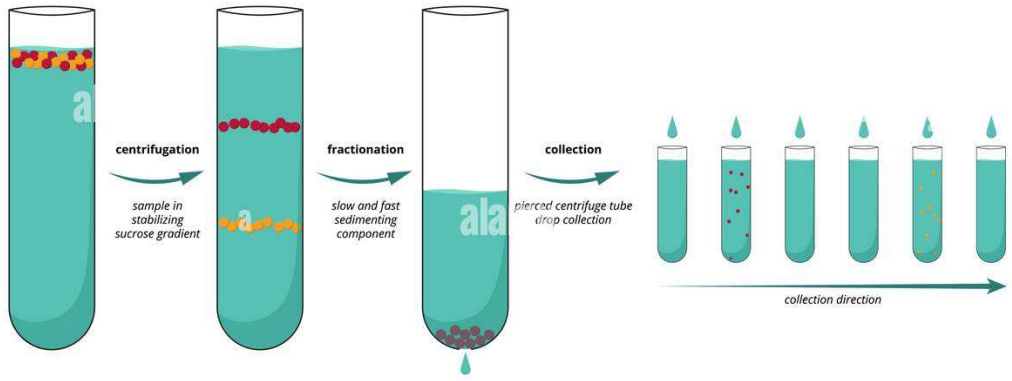
In this method the solution is subjected to very high gravitational fields. This process is affected by ultra centrifuge which can provide as high 65,000 revolutions per minute. Due to high

centrifugal forces, the polymer molecule starts sedimentation. By applying stokes law is possible that the sedimentation coefficient's' with molecular weight (m) by following expression.

$$\overline{m} = \frac{S_o RT}{D_o (1 - P\overline{V})}$$



Where 'S_o' and 'D_o' are sedimentation and diffusion constant. Respectively obtained by extrapolating the sedimentation and diffusion coefficient at different to zero concentrations.



'$\overline{V}$' is specific volume of polymer and 'P' is the density of solvent.

By substitute all these values we can determine molecular weight of polymer.

$$V = \frac{x_2 - x_1}{t_2 - t_1}$$

It is Sedimentation velocity.

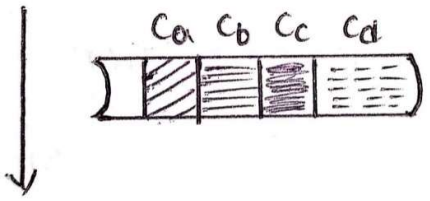
$$S = \frac{V}{W^2} \quad \frac{2}{x_2 - x_1}$$

ii) Sedimentation of Equilibrium Method:

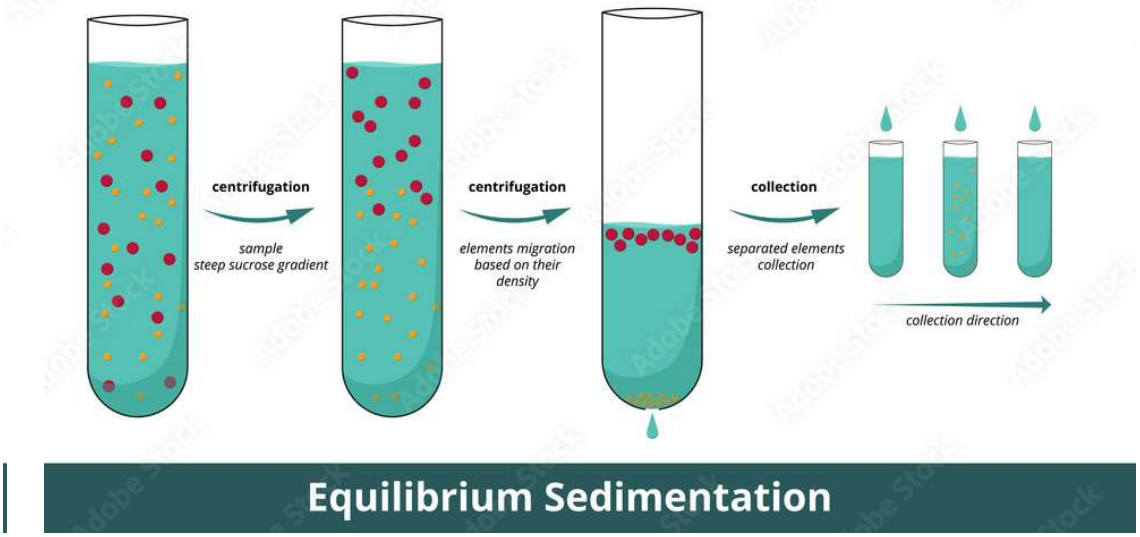
In this method the solution of macro molecule is taken in specially designed cell of the ultra-centrifuge and vigorously rotated in special rotators. The sedimentations are allowed to proceed until equilibrium. i.e. when the amount of particle sedimenting under the influence of centrifugal force is exactly balanced by amount diffused in opposite direction due to Brownian

and thermal motions. Then there is net flow of particles when equilibrium between sedimentation and diffusion is attained. The concentration of particle is measured in ultra centrifuge cell as a function of distance out from the centre of rotation by means of some optical methods.

$$\overline{M}_w = \frac{2\,RT \ln (C_a/C_b)}{(1-\overline{P}\overline{V})\, W^2 (x_1^2 - x_2^2)}$$

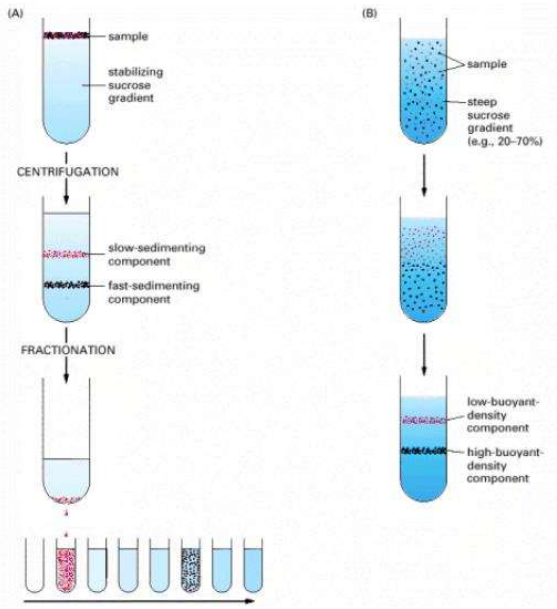


Where C_2/C_1 is concentration ratio and 'W' is angular velocity of polymer and X_2, X_1 are distance between the particles.



Where 'i_θ' is intensity of scattered light per unit volume 'V', 'R' is distance at angle 'θ' with reference to the incident beam and 'I_o' is intensity of incident light.

velocity sedimentation vs. equilibrium sedimentation



In equation "Ĩ" is turbidity of the medium which result from the scattering of light. 'K' and 'H' are light scattering calibrated constants and calculated by using formula.

$$K = \frac{2\Pi^2 n^2 (dn/dc)^2}{\lambda^4 NA}$$

$$H = \frac{32\Pi^3 n^2 (dn/dc)^2}{3\lambda^4 NA}$$

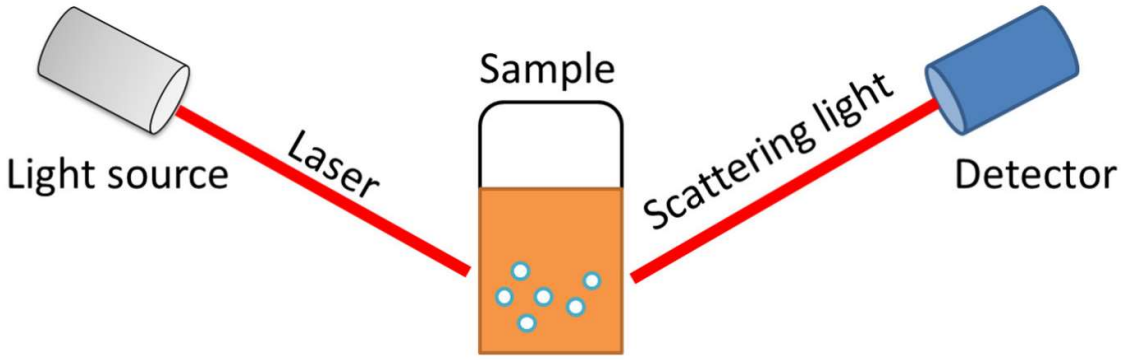
Where 'n' is refractive index of the solution.
dn / dc is change is refractive index with concentration
λ is wave length of incident light
NA is Avogadro's Number.

9.5 LIGHT SCATTERING METHOD:

This phenomenon used to measure the weight average molecular weight. M_w of polymer.

It has been recognized that in solutions and liquid mixtures, scattering of light occurs due to changes in density with the system arising from compositional vibration.

In all light scattering phenomena the amplitude of scattering found to be proportional to the mass of the particle 'm' which scatters the beam of light.



Debye arrived an expression to relate the molecular weight of solute particle to the intensity of scattered light.

This equation is known as Debye equation and holds good only for particle which are similar then the value length of light used for scattering experiment.

$$\frac{K_e}{R_{90}} = \frac{HC}{\tau} = \frac{1}{\overline{M}_w} + 2\,BC$$

Where 'B' is second virtal coefficient, 'C' is concentration of the solution 'R_{90}' is Rayleigh ratio at 90° angle.

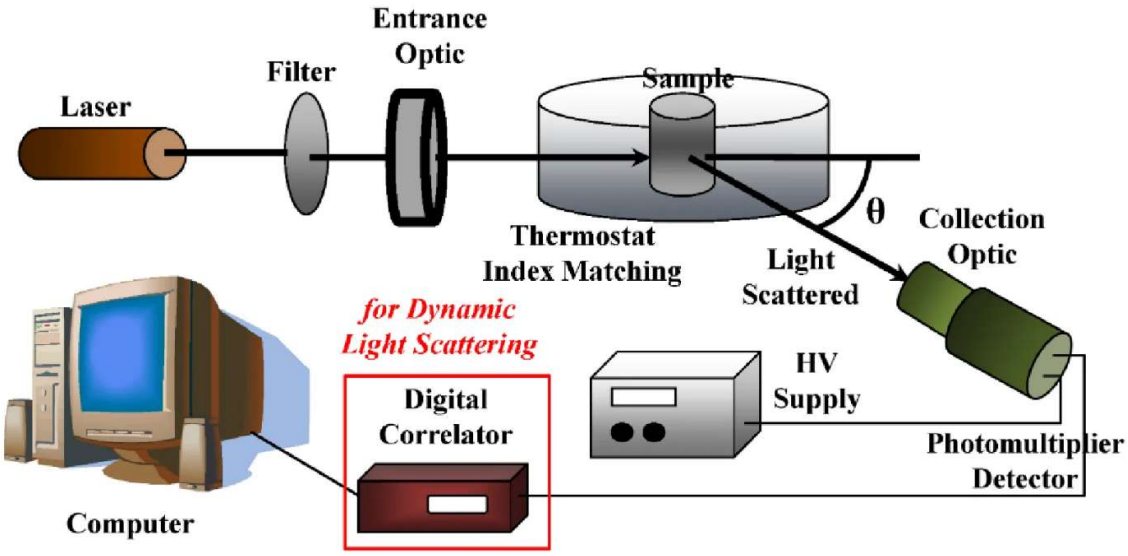
In general case this ration represented by 'Rθ'

$$R_\theta = \frac{i_\theta r^2}{I_0 \overline{V}} = \frac{K_e}{R_{90}} = \frac{HC}{\tau} = \frac{1}{\overline{M}_w P(\theta)} + 2\,BC$$

Where i_θ = Intensity of scattered light.

I_0 = Intensity of incident light.

P_θ = Polymer scattered constant.



SUMMARY:

- To learn about the hoe to determine Molecular weight of polymers.
- To study about End – Group Analysis and Osmometry methods for determination of Molecular Weight.
- To know about the Light Scattering Method Ultra Centrifugation Method and Viscometry methods for Molecular Weight determination.

SELF ASSESSMENT QUESTIONS

1. Discuss the for Molecular Weight determination of polymers by Osmometry.
2. Illustrate the Molecular Weight determination of polymers by End group Analysis.
3. Write a detailed discussion on the determination of Molecular Weight polymers by Ultra Centrifugation Method.

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Prof. R. Ramesh Raju

LESSON-10

FUNDAMENTALS OF ELECTRODE PROCESSES AND INTERFACIAL PHENOMENA

Objectives

After completing this lesson, students should be able to:

1. **Explain the concept and origin of electrode potential**, distinguish between oxidation and reduction potentials, and relate them to electrochemical equilibrium at metal–electrolyte interfaces.
2. **Describe the structure and behavior of the electrical double layer (EDL),** including the concept of **zeta potential**, and interpret their roles in interfacial charge distribution and colloidal stability.
3. **Discuss the kinetics of charge transfer at electrodes**, including the principles of the **Butler–Volmer equation, decomposition potential**, and their experimental determination.
4. **Define and analyze overpotential**, describe its types (activation, concentration, and ohmic), and **correlate interfacial phenomena with electrochemical performance** in cells and energy systems.

10.1. ELECTRODE POTENTIAL:

A metal (M) consists of (M^{n+}) ions, with the valence electrons that bind them together. Now, if a metal is in contact with a solution of its own salt, the positive ions in the metal come into equilibrium with those in the solution, leaving behind an equivalent number of electrons on the metal. Thus, the metal acquires a negative charge, since it is now left with excess number of electrons and a number of positive metallic ions are formed in solution, e.g., in case of Zn in $ZnSO_4$ solution. Conversely, if the positive metallic ions, from the solution, enter the metallic

lattices, then the metal acquires a positive charge, e.g., in case of Cu in $CuSO_4$ solution. Thus, following two chemical reactions takes place, when a metal is in contact with its salt solution:

(1). Positive metallic ions passing into solution.

$$M \rightarrow M^{n+} + n\,e^- \qquad \text{(Oxidation i.e., loss of electrons)}$$

When n electrons are left behind on the metal; and it acquires a negative charge. The rate of this reaction depends on : (i) the nature of the metal; (ii) the temperature, and (iii) the concentration of metal ions in the solution .

(2). Positive ions depositing on the metal electrode.

$$M^{n+} + n\,e^- \rightarrow M \qquad \text{(Reduction, i.e., gain of electrons)}$$

when metal acquires a positive charge, the rate of this reaction depends on the above three factors.

When a metal is placed in the solution of its own salt, the chemical reaction (1) or (2), takes place and ultimately a dynamic equilibrium is established, because negative or positive charge developed on the metal attracts the positively or negatively charged free ions in the solution. Due to this attraction, the positive or negative ions remain quite close to the metal. Thus, a short layer of positive ions or negative ions is formed all around the metal. This layer is called Helmholtz electrical double layer. A difference of potential is, consequently setup between the metal and the solution. The equilibrium potential so-established is called the "electrode potential" of the metal.

"The tendency of metallic electrode to lose or gain electrons, when it is in contact with its own salt solution of unit molar concentration at 25 ^{0}C is called electrode potential".

The tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized; and this tendency, is called oxidation potential. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced; and this tendency, is known as reduction potential. If the oxidation of potential of an electrode is +X volt, then its reduction potential will have a value of –X volt.

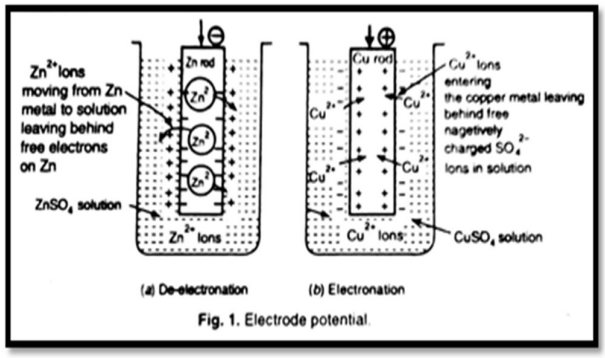


Fig. 1. Electrode potential

10.2. DOUBLE LAYER AT THE ELECTRODE–ELECTROLYTE INTERFACE

When a metallic electrode is brought into contact with an electrolyte solution, a separation of electrical charges occurs at the interface, leading to the formation of an electrical double layer (EDL). This interfacial region governs the electrochemical behavior of electrodes and plays a vital role in determining potential, charge transfer, adsorption, and the kinetics of electrode reactions. The origin of the double layer lies in the tendency of the electrode surface to acquire charge either through oxidation or reduction processes. To maintain overall electroneutrality, ions of opposite charge from the solution migrate toward the electrode surface, resulting in two

parallel regions of charge—one on the electrode and one within the solution. This arrangement acts analogously to a microscopic capacitor capable of storing electrical energy.

Structurally, the electrical double layer consists of two distinct regions: the compact layer (or Helmholtz layer) and the diffuse layer (or Gouy–Chapman layer). The compact layer lies adjacent to the electrode surface and contains specifically adsorbed ions and oriented solvent molecules. Within this region, two planes are defined—the Inner Helmholtz Plane (IHP), which passes through the centers of specifically adsorbed ions, and the Outer Helmholtz Plane (OHP), which passes through the centers of solvated ions closest to the electrode surface. Beyond the compact layer lies the diffuse layer, where ions are distributed in accordance with a balance between electrostatic attraction toward the charged electrode and random thermal motion. The ionic concentration gradually approaches that of the bulk solution as the distance from the electrode increases, and the potential correspondingly decreases in an exponential fashion.
Several models have been proposed to describe the structure and behavior of the double layer.

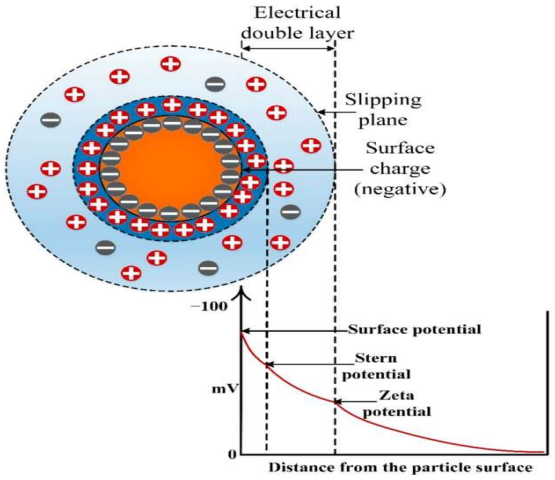
The **Helmholtz model** treats it as a simple parallel-plate capacitor with a fixed layer of ions but does not account for ion mobility or diffusion. The **Gouy–Chapman model** incorporates the effect of thermal motion, describing a diffuse ionic atmosphere near the electrode. The **Stern model** combines both concepts by dividing the double layer into a compact region and a diffuse region, providing a more realistic picture of interfacial structure. Later, the **Grahame model** refined this further by including specific adsorption of ions and introducing the concept of the **potential of zero charge (PZC)**—the potential at which the electrode surface carries no net charge.

The potential across the double layer decreases sharply within the compact region and more gradually through the diffuse region. The thickness of the diffuse layer, also known as the **Debye length**, depends on the ionic strength of the solution and is given by

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 RT}{2F^2 I}}$$

where I is the ionic strength. A higher electrolyte concentration leads to a thinner double layer. The entire interface behaves as a capacitor, with its capacitance expressed as C=dQ/dE. The total interfacial capacitance is influenced by ion concentration, electrode material, temperature, and solvent dielectric constant.

A simplified representation of the double layer can be described as follows:



In summary, the electrical double layer is the interfacial region that balances the electrode's charge with oppositely charged ions from the electrolyte. Its structure—comprising the compact and diffuse layers—controls the potential distribution, capacitance, and charge transfer behavior at the electrode–electrolyte boundary. A proper understanding of the EDL is fundamental to explaining and optimizing various electrochemical phenomena such as corrosion, electroplating, electrocatalysis, energy storage, and sensor applications.

10.3. ZETA POTENTIAL

When solid particles or colloidal systems are dispersed in a liquid medium, the surfaces of these particles usually acquire an electrical charge due to ionization of surface groups or adsorption of ions from the surrounding solution. This charge influences the arrangement of ions near the particle surface, resulting in the formation of an electrical double layer (EDL) at the solid–liquid interface. The EDL typically consists of two parts: a tightly bound layer of counter-ions (the Stern layer) directly attached to the particle surface, and a diffuse layer of ions that extends outward into the bulk liquid. Within this structure, there exists a notional boundary known as the slipping plane (shear plane)—the interface between the immobile layer of liquid that moves with the particle and the mobile liquid beyond it. The zeta potential (ζ) is defined as the electrical potential at this slipping plane. It is not the surface potential itself but rather the measurable potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. Zeta potential therefore provides practical insight into the degree of electrostatic repulsion or attraction between adjacent, similarly charged particles in a colloidal system.Mathematically, zeta potential can be related to electrophoretic mobility (u_e) through the **Smoluchowski equation**:

$$\zeta = \frac{4\pi\eta u_e}{\varepsilon}$$

where η is the viscosity of the medium, and ε is the dielectric constant of the liquid. In systems with small particles or low ionic strength, the Hückel equation may be applied instead. These relationships form the basis for determining zeta potential experimentally via techniques such as electrophoresis or electroacoustic methods.

The magnitude and sign of the zeta potential are key indicators of colloidal stability. When the zeta potential is large (typically greater than ±30 mV), strong electrostatic repulsion prevents particles from aggregating, and the dispersion remains stable. Conversely, when the zeta potential is close to zero, attractive van der Waals forces dominate, leading to coagulation or flocculation of the particles. Thus, the zeta potential serves as a crucial parameter in controlling and predicting the stability of colloids, emulsions, suspensions, and nanoparticles.

Zeta potential is influenced by several factors, including the pH of the medium, ionic strength, type of ions present, and specific adsorption of surface-active species. At a particular pH known as the isoelectric point (IEP), the zeta potential becomes zero, and the dispersion is most prone to aggregation. Adjustment of the solution pH or the addition of stabilizing agents (such as surfactants or polymers) is commonly used to manipulate the zeta potential and improve colloidal stability.

In summary, zeta potential is a measurable reflection of the electrokinetic behavior of charged interfaces. It bridges the concepts of the electrical double layer and colloidal stability, providing

valuable information for applications in electrochemistry, materials science, nanotechnology, environmental chemistry, and biopharmaceutical formulations.

10.4. RATE OF CHARGE TRANSFER

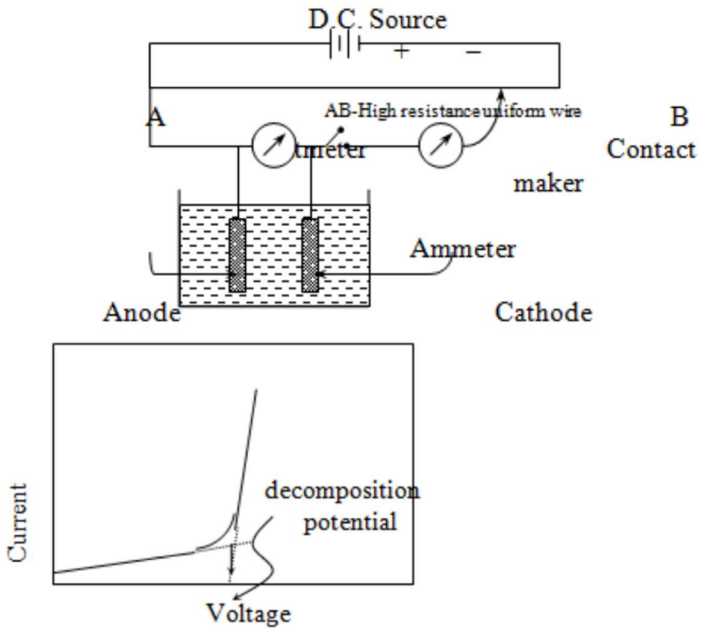
At the electrode–solution interface, the rate at which electrons are exchanged between the electrode and ions in the electrolyte determines the rate of charge transfer. When a potential is applied across an electrochemical cell, oxidation occurs at one electrode and reduction at the other. The rate of these electrode reactions depends on the activation energy for charge transfer and the magnitude of the applied potential. At equilibrium, the rate of oxidation equals the rate of reduction, and no net current flows. When the potential is altered, equilibrium is disturbed, and a net current is observed, proportional to the rate of charge transfer. This rate can be expressed by the Butler–Volmer equation, which relates current density (i) to overpotential (η):

$$i = i_0 \left[e^{\frac{\alpha n F \eta}{RT}} - e^{-\frac{(1-\alpha) n F \eta}{RT}} \right]$$

where i_0 is the exchange current density, α the transfer coefficient, n the number of electrons involved, F the Faraday constant, R the gas constant, and T the temperature. The exchange current density indicates the inherent rate of the redox process; a large i_0 value corresponds to a rapid charge-transfer process.

10.5. DECOMPOSITION POTENTIAL

Decomposition potential is the experimentally determined minimum external potential that needs to be applied in order to have continuous decomposition of the electrolyte. For example, in the decomposition of water, a dilute solution of either an acid or alkali is electrolyzed using smooth platinum electrodes. For the applied potential less than 1.68 V, there is initial surge of current which will drop to zero in a while. When the applied potential is 1.68 V or more, there is continuous decomposition of water with the liberation of hydrogen at cathode and oxygen at the anode. Thus, 1.68 V is the decomposition potential of water. A knowledge of discharge potentials of different electrodes helps in (i) Knowing the potential to be externally applied for electrolysis of any electrolyte. (ii) Predicting the order in which the different substances discharge or deposit at respective electrodes. For example, by the electrolysis of a solution containing Cu^{2+} ions, Zn^{2+} ions and Cd^{2+} ions, Ag ions, Hg ions the discharge or deposition of metals happens to be in the order: Ag, Hg, Cu, then Cd and later, Zn. Decomposition potential can be determined by the measurements of current for varying potentials (or voltages) applied across the electrodes immersed in electrolyte under investigation. The set up used for measurement is shown in the figure. A plot of current against potential (or voltage) helps in knowing the decomposition potential. For lower voltages, there is no significant rise in current till the reach of decomposition potential. Beyond this potential, it starts rising abruptly. Laws of electrolysis are applicable only in this region. Decomposition potential is obtained by the intersection of the two tangents drawn as shown in the figure.



10.6. OVERPOTENTIAL (η)

The overpotential or overvoltage is defined as the excess potential that must be applied beyond the equilibrium (or reversible) potential to make an electrode reaction proceed at a measurable rate. It is given by:

$$\eta = E_{applied} - E_{reversible}$$

Overpotential arises because of several physical and kinetic factors and can be divided into the following types:

1. Activation Overpotential (η_a): Caused by the energy barrier that must be overcome for charge transfer at the electrode surface.
2. Concentration Overpotential (ηc): Occurs when the concentration of reacting species at the electrode surface differs from that in the bulk solution due to mass-transport limitations.
3. Resistance (Ohmic) Overpotential (ηΩ): Due to the resistance of the electrolyte, electrodes, and electrical connections.

Overpotential reduces the efficiency of electrochemical processes since part of the energy input is lost in overcoming these barriers. Reducing overpotential is therefore essential in improving the performance of electrochemical cells, batteries, and fuel cells.

SUMMARY

- **Electrode potential** arises due to the equilibrium between metal and its ions.
- The **electrical double layer** governs interfacial charge and potential distribution.
- **Zeta potential** quantifies electrokinetic stability in colloidal systems.
- **Charge-transfer kinetics** follow the Butler–Volmer relationship.

- **Decomposition potential** defines the threshold for continuous electrolysis.
- **Overpotential** represents energy losses and is key to electrochemical efficiency.

Technical Terms

Term	Definition
Electrode Potential	Potential difference between metal and its ion solution at equilibrium
Electrical Double Layer	Region of charge separation at electrode–electrolyte interface
Zeta Potential	Potential at the slipping plane in colloidal systems
Exchange Current Density (i_0)	Rate of forward and backward reactions at equilibrium
Decomposition Potential	Minimum potential required for continuous electrolysis
Overpotential (η)	Extra potential beyond equilibrium potential for observable reaction
Helmholtz Layer	Compact layer of adsorbed ions near the electrode
Debye Length	Thickness of diffuse ionic atmosphere in EDL
Isoelectric Point (IEP)	pH where zeta potential is zero
Tafel Slope	Logarithmic relationship between overpotential and current density

Self-Assessment Questions

1. Define electrode potential. How is it related to oxidation and reduction potentials?
2. Describe the structure and components of the electrical double layer.
3. Differentiate between the Helmholtz, Gouy–Chapman, and Stern models.
4. What is zeta potential? How does it affect colloidal stability?
5. Derive the Butler–Volmer equation for charge transfer.
6. Define decomposition potential and explain how it can be experimentally determined.
7. What is overpotential? Discuss its types and significance in electrochemical reactions.
8. Explain how ionic strength affects the thickness of the double layer.
9. Write short notes on: (a) Potential of zero charge (PZC) (b) Exchange current density.

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Dr.CH. SUBRAMANYAM

LESSON-11
ELECTRODE KINETICS AND ELECTROCATALYSIS

OBJECTIVES

After completing this lesson, students should be able to:

1. **Explain the Tafel relationship** between current density and overpotential and interpret electrode kinetics using Tafel plots.
2. **Derive and apply the Butler–Volmer equation** for one-electron transfer and understand its relation to Tafel behavior.
3. **Define electrochemical potential** and describe its significance in ionic transport and equilibrium across electrochemical interfaces.
4. **Discuss the principles and importance of electrocatalysis and fuel cells**, including mechanisms, efficiency, advantages, and technological applications.

11.1. TAFEL EQUATION AND TAFEL PLOTS

At high overpotentials (generally greater than ±50 mV), one of the exponential terms in the Butler–Volmer equation becomes negligible, and the relationship between current density and overpotential simplifies to the Tafel equation:

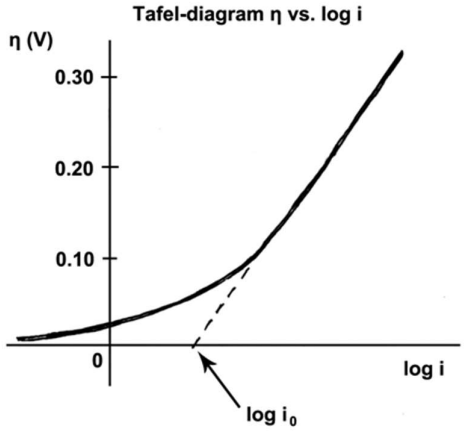
$$\eta = a + b \log i$$

Here, a is a constant (the intercept), and b is the **Tafel slope**, given by:

$$b = \frac{2.303RT}{\alpha nF}$$

The Tafel equation shows that a plot of overpotential (η) versus the logarithm of current density ($log\ i$) gives a straight line known as the Tafel plot. The slope (b) and intercept of this line provide valuable information about the reaction kinetics and mechanism. The exchange current

density (i_0) can be determined by extrapolating the linear portion of the plot to $\eta = 0$. A smaller Tafel slope indicates that the electrode process is more facile and proceeds with lower activation energy, whereas a higher slope implies sluggish kinetics. Tafel analysis is thus a fundamental method for characterizing electrode kinetics, reaction mechanisms, and catalytic efficiency in electrochemical systems.



SUMMARY

- The rate of charge transfer determines the kinetics of electrode reactions and is described by the Butler–Volmer equation.
- The decomposition potential represents the minimum voltage needed to start electrolysis.
- The overpotential accounts for the additional potential required in real systems to overcome kinetic and resistive effects.
- The Tafel equation provides a practical way to analyze electrode kinetics by relating current and overpotential through a logarithmic relationship.

Together, these concepts explain how electrical energy drives chemical transformations and how reaction rates and efficiencies can be optimized in electrochemical devices.

11.2. BUTLER–VOLMER EQUATION FOR ONE-ELECTRON TRANSFER

Consider a simple electrode reaction involving a single electron transfer:

$$\mathrm{O} + e^- \rightleftharpoons \mathrm{R}$$

where **O** is the oxidized species and **R** is the reduced species. At equilibrium, the rates of the forward (reduction) and reverse (oxidation) reactions are equal, and no net current flows. When an external potential is applied, this equilibrium is disturbed, resulting in a net current due to the difference in the rates of the two reactions. The total current density (i) at the electrode surface can be expressed as the difference between the cathodic and anodic current densities:

$$i = i_c - i_a$$

According to the Arrhenius equation, each partial current is proportional to the exponential of the activation energy for the respective reaction. When the electrode potential is changed by an amount $\eta = E - E_{eq}$ (known as the **over potential**), the activation energies for the forward (reduction) and reverse (oxidation) reactions are altered as follows:

$$\Delta G_c^{\ddagger} = \Delta G_c^{\ddagger,eq} - \alpha F \eta$$

$$\Delta G_a^{\ddagger} = \Delta G_a^{\ddagger,eq} + (1-\alpha) F \eta$$

where α is the **transfer coefficient**, indicating the fraction of applied potential that affects the activation energy of the cathodic reaction. Using the Arrhenius-type rate expression, the partial current densities may be written as:

$$i_c = nFk_cC_Oe^{-\frac{\Delta G_c^{\ddagger}}{RT}} = i_0e^{\frac{\alpha F\eta}{RT}}$$

$$i_a = nFk_aC_Re^{-\frac{\Delta G_a^{\ddagger}}{RT}} = i_0e^{-\frac{(1-\alpha)F\eta}{RT}}$$

Here, i_0 is the **exchange current density**, which represents the rate of the forward or backward reaction when the system is at equilibrium (η=0). Substituting these expressions into the total current equation gives:

$$i = i_0\left[e^{\frac{\alpha F\eta}{RT}} - e^{-\frac{(1-\alpha)F\eta}{RT}}\right]$$

This expression is known as the Butler–Volmer equation. It relates the current density (i) to the overpotential (η) for an electrode reaction involving one-electron transfer. At equilibrium (η=0), the two exponential terms are equal, and i=0, indicating no net current. For small overpotentials, both terms contribute significantly, but at large overpotentials, one term predominates. In that case, the Butler–Volmer equation reduces to the Tafel equation:

$$\eta = a + b\log i$$

where b=2.303RT/αF is the **Tafel slope**.

Thus, the Butler-Volmer equation provides a fundamental quantitative relationship between **current density** and **over potential**, describing the kinetics of charge transfer at an electrode surface. It forms the theoretical basis for understanding electrode reactions, exchange current density, and Tafel behavior in electrochemical systems.

11.3. ELECTROCHEMICAL POTENTIAL

In an electrochemical system, ions or charged species experience both **chemical** and **electrical** influences. The total potential governing their behavior is called the **electrochemical potential**. It represents the **effective potential energy per mole** of a species in a system where both chemical concentration gradients and electrical fields are present. If a species i carries an electrical charge z_i and has a chemical potential μ_i, then its **electrochemical potential** $\bar{\mu}_i$ is given by:

$$\bar{\mu}_i = \mu_i + z_iF\phi$$

where
μ_i = chemical potential of species i,
z_i = charge number of the ion,
F = Faraday constant, and
ϕ = electrical potential of the phase.

The first term μ_i accounts for the tendency of the species to move due to **concentration differences**, while the second term $z_iF\phi$ represents the **electrical work** required to move the

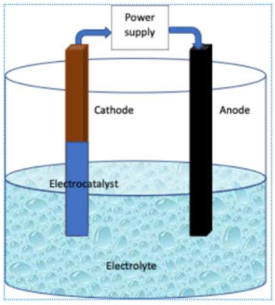
charged species in an electric field. Thus, the electrochemical potential combines the effects of both **chemical composition** and **electrical potential**.

The concept of electrochemical potential is essential in describing the **movement of ions across membranes, electrode–electrolyte interfaces**, and **phase boundaries** in cells. At equilibrium, the electrochemical potential of each ionic species is the same in all phases; hence, no net transfer occurs. This principle underlies the derivation of **Nernst's equation** and explains the distribution of ions in **electrochemical cells**, **semiconductors**, and **biological membranes**.

11.4. ELECTROCATALYSIS

Electrocatalysis refers to the acceleration of electrochemical reactions by modifying the electrode surface to lower the activation energy for charge transfer. An electrocatalyst is a material that facilitates an electrode reaction without being consumed in the process. It enhances the reaction rate by providing an energetically favorable pathway for electron transfer between the electrode and the reactant species.

In electrochemical reactions, the overall rate often depends on the activation energy barrier for charge transfer. The introduction of an electrocatalyst alters the adsorption characteristics of reactant molecules and modifies the electronic structure of the electrode surface, thereby reducing this barrier. The effect of an electrocatalyst can be represented schematically by the current–potential (i–E) curve, where the catalytic electrode shows a higher current at the same potential or achieves the same current at a lower overpotential compared to an unmodified electrode.



Electrochemical cell showing cathode, anode and electrocatalyst

Electrocatalysis may be of two types:

1. Homogeneous Electrocatalysis, where the catalyst is dissolved in the electrolyte and interacts directly with the reacting species in solution.
2. Heterogeneous Electrocatalysis, where the catalyst is present on the solid electrode surface and provides specific active sites for reaction.

Typical examples include the use of platinum, palladium, nickel, and ruthenium oxide as catalysts in reactions such as the hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and methanol oxidation. The activity of an electrocatalyst depends on several factors, including its surface area, electronic structure, adsorption energy, and surface cleanliness.

Electrocatalysis plays a crucial role in modern technologies such as fuel cells, batteries, electrolysis of water, corrosion protection, and sensors. By minimizing the overpotential and increasing reaction kinetics, electrocatalysts significantly improve the efficiency and energy output of electrochemical systems.

11.5. FUEL CELLS

A fuel cell is an electrochemical device that converts the chemical energy of a fuel directly into electrical energy through oxidation and reduction reactions. Unlike a battery, it is a continuous-flow galvanic cell that operates as long as the fuel and oxidant are supplied. The process is clean, efficient, and forms the basis for modern sustainable energy systems.

11.5.1. Principle

The working principle of a fuel cell is based on the electrochemical oxidation of a fuel (e.g., hydrogen) at the anode and the reduction of an oxidant (e.g., oxygen) at the cathode. For a hydrogen-oxygen fuel cell, the reactions are:

Anode (oxidation):

$$H_2 \rightarrow 2H^+ + 2e^-$$

Cathode (reduction):

$$\tfrac{1}{2}\, O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Overall cell reaction:

$$H_2 + \tfrac{1}{2}\, O_2 \rightarrow H_2O$$

Electrons released at the anode travel through the external circuit to the cathode, generating **direct current (DC)**, while protons move through the electrolyte to combine with oxygen and electrons to form water.

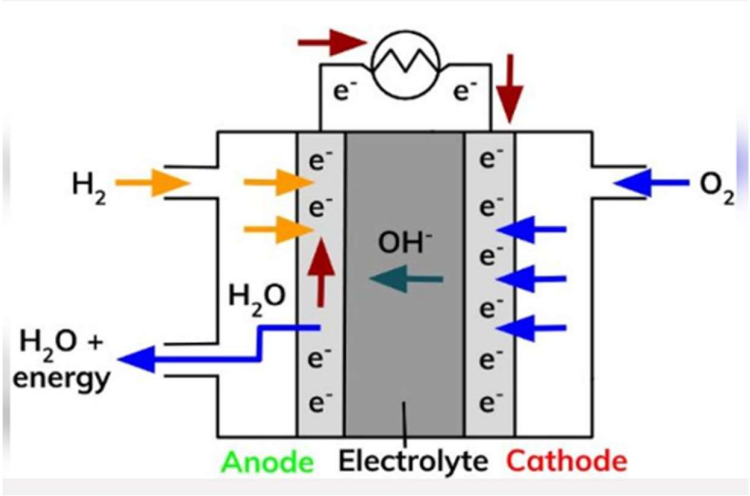


Figure: Schematic representation of a hydrogen-oxygen fuel cell showing electron flow through the external circuit and ion transport through the electrolyte.

11.5.2. Main Components

1. **Anode:** Where fuel (H_2) is oxidized.
2. **Cathode:** Where the oxidant (O_2) is reduced.
3. **Electrolyte:** Conducts ions (e.g., H^+, OH^-) between electrodes but blocks electrons.
4. **Catalyst:** Usually platinum or nickel, accelerates both electrode reactions.
5. **External Circuit:** Provides a path for electron flow to generate electric power.

11.5.3. Advantages

- High energy conversion efficiency
- Continuous power generation as long as fuel is supplied
- Environmentally clean (water is the only product for H_2 fuel cells)
- Silent operation, reliable, and modular in design

11.5.4. Limitations

- High cost of catalysts (Pt and other noble metals)
- Sensitivity to fuel impurities (e.g., CO poisoning)
- Problems in hydrogen production, storage, and distribution
- Limited durability of membranes and electrolytes

11.5.5. Applications

Fuel cells are used in **space missions (NASA), electric and hybrid vehicles, portable power devices**, and **stationary power generation systems**. They are also being integrated into **renewable energy storage systems** and **hydrogen-based infrastructure** for sustainable energy applications.

SUMMARY

- **Tafel equation** simplifies the Butler–Volmer relationship and helps analyze electrode kinetics.
- **Butler–Volmer equation** links current density with overpotential and describes charge-transfer kinetics.
- **Electrochemical potential** combines chemical and electrical effects governing ionic motion.
- **Electrocatalysis** enhances reaction rates by lowering activation energy at electrodes.
- **Fuel cells** directly convert chemical energy to electricity efficiently and cleanly.

Together, these topics explain how electrode reactions proceed, how catalysts influence them, and how electrochemical systems can be optimized for energy applications.

Technical Terms (Glossary)

Term	Definition
Tafel Equation	Logarithmic relation between overpotential and current density
Tafel Slope (b)	Measure of electrode reaction kinetics, derived from Tafel plot
Exchange Current Density (i_0)	Current density when forward and reverse reactions are balanced
Transfer Coefficient (α)	Fraction of applied potential affecting reaction activation energy
Electrochemical Potential	Sum of chemical and electrical potentials influencing ion movement
Electrocatalyst	Material that accelerates electrode reactions by reducing activation energy

Fuel Cell	Electrochemical device converting fuel's chemical energy to electrical energy
Overpotential	Additional potential beyond equilibrium required for reaction to proceed

SELF-ASSESSMENT QUESTIONS

1. Derive the Tafel equation from the Butler–Volmer expression and explain its significance.
2. What is exchange current density and how is it determined from a Tafel plot?
3. Write a note on the physical meaning of the transfer coefficient (α).
4. Define electrochemical potential and explain its importance in ionic equilibrium.
5. Differentiate between homogeneous and heterogeneous electrocatalysis with examples.
6. Describe the principle and operation of a hydrogen–oxygen fuel cell.
7. List the advantages and limitations of fuel cells as energy conversion devices.
8. Explain how electrocatalysts improve the efficiency of fuel cells and electrolysis reactions.

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Dr. CH.S UBRAMANYAM

LESSON-12
ELECTROANALYTICAL TECHNIQUES AND CORROSION

OBJECTIVES

After completing this lesson, students should be able to:

1. **Explain the principles and theory of polarography**, including the working of the dropping mercury electrode, Ilkovic equation, and factors affecting current–voltage behavior.
2. **Discuss the concept and application of amperometric titrations** and interpret titration curves for various electroactive systems.
3. **Describe the types, mechanisms, and theories of corrosion** (chemical and electrochemical) and the environmental factors influencing corrosion.
4. **Evaluate different corrosion prevention methods**, including cathodic protection, inhibitors, and engineering approaches for material durability.

12.1. POLAROGRAPHY

Polarography is an electroanalytical technique based on the measurement of current as a function of applied potential at a dropping mercury electrode (DME). The method was introduced by Jaroslav Heyrovský (who received the Nobel Prize in Chemistry, 1959) and is widely used for the quantitative and qualitative analysis of reducible or oxidizable ions in solution.

12.1.1. Theory of Polarography

In polarography, a potential that varies linearly with time is applied to a polarizable electrode (such as DME) immersed in an electrolyte containing a reducible or oxidizable species. The resulting current is recorded as a function of potential.

At low potentials, the current is small because the reduction or oxidation does not occur. As the potential becomes more negative (for reduction) or more positive (for oxidation), the electroactive species start to discharge at the electrode surface, and the current rises. Eventually, a limiting current is reached beyond which the current becomes nearly constant. This limiting value is known as the diffusion current and is controlled by the rate at which the electroactive species diffuse from the bulk of the solution to the electrode surface.

A typical polarogram (current–potential curve) shows an S-shaped wave, characterized by a steady rise in current up to the diffusion-limited value. The potential corresponding to the midpoint of this wave is called the half-wave potential ($E_{1/2}$), which is characteristic of the particular ion being reduced or oxidized.

12.1.2. Principle of polarography

The basic idea behind polarography is to apply a progressively increasing negative potential (voltage) between polarizable and non-polarizable electrodes and then record the resultant current. So, the basic principle of polarography is the analysis of solutions or electrode processes through electrolysis using two electrodes, one polarizable and one non-polarizable.

a. **Polarizable electrode or Working Electrode**:- Dropping mercury Electrode
b. **Non-polarizable Electrode or Reference Electrode**:- Calomel Electrode

Polarography is a voltammetric technique that involves the oxidation (loss of electrons) or reduction (gain of electrons) of chemical species (ions or molecules) at the surface of a dropping mercury electrode (DME) at an applied potential. Qualitative and quantitative analysis can be performed using the current-voltage curve.

12.1.3. Types of polarography

I) Direct current (DC) polarography

In DC polarography, a dropping mercury electrode (DME) is subjected to a constantly increasing DC potential, and the resulting current is continuously recorded. The concentration of the component to be examined in the solution can be calculated by measuring the current-potential curve obtained during the electrolysis process. This approach has the advantage of allowing the electrode potential to shift very slowly.

II) Alternating current polarography

The DC voltage of DC polarography is superimposed with a low-frequency sinusoidal voltage of tiny amplitude (several to tens of millivolts). The AC polarography wave is produced by measuring the branch current of an electrolytic cell. In this approach, a constantly increasing DC potential (E) is superimposed on a constant amplitude AC potential. If such a combination is applied to DME, it generates two types of current. The total current is the sum of DC and AC. This process is not influenced by irreversible processes such as oxygen reduction.

III) Pulse polarography

The procedures in pulse techniques are based on the application of pulse variations of potential, and the current response is measured at a suitable time relative to the time of the pulse. Since diffusion and capacitive current intensities vary with time, pulse methods increase detection limits. There are three different polarography methods that work under the content of pulse polarography. They are:

A. Normal pulse polarography
B. Differential pulse polarography
C. Square wave polarography

A. Normal pulse polarography (NPP)

It is also known as large-amplitude pulse polarography. Normal pulse polarography (NPP) alters the potential by using square wave potential pulses with increasing height (pulse amplitude Ep) placed over a constant initial potential, rather than a continually increasing potential ramp. NPP maintains the DME at a constant potential before the start of the Faradaic current. Subsequently, near the end of the drop's life, a voltage pulse is delivered, the amplitude of which steadily increases from drop to drop.

B. Differential pulse polarography (DPP)

In this approach, a constantly increasing DC potential is superimposed on a pulse of constant amplitude. The pulse is only applied at the end of drop times of 50mS. The current is measured twice during each drop. The current is measured just before and after the pulse is applied. The difference between these two currents is represented as a function of baseline potential (E). DPP varies from NPP in that the potential is not constant before the pulse application but is replaced by a ramp voltage with DC polarographic properties. In this process, the pulse amplitude is constant. The measured current is displayed as the difference between the current recorded immediately before the pulse and the current sampled after the pulse.

C. Square wave polarography

In Square Wave Polarography, the current at a working electrode is monitored while the potential between the working electrode and a reference electrode is swept linearly across time. The potential waveform is a superposition of a conventional square wave and an underlying staircase. It has a higher sensitivity than a differential pulse that does not involve reversed current. Due to the faster scan rates, it reduces analysis time.

Types of mercury electrodes

Mercury is often used as a working electrode in polarography because it is a liquid metal that can be renewed after each droplet. A drop suspended from the end of a capillary tube is frequently employed as the working electrode. There are three different types of mercury electrodes, they are as follows:

a. Dropping Mercury Electrode (DME)

Gravity causes mercury drops from the capillary tube's end of the dropping mercury electrode or DME. It increases continually as the mercury drips from the reservoir and has a finite lifetime of several seconds. The mercury drop is dislodged at the end of its lifetime, either manually or automatically, and replaced with a new drop.

b. Static Mercury Drop Electrode (SMDE)

To control the flow of mercury, the static mercury drop electrode, or SMDE, employs a solenoid-driven plunger. When the solenoid is activated, it temporarily lifts the plunger, allowing mercury to flow through the capillary and form a single, hanging Hg drop.

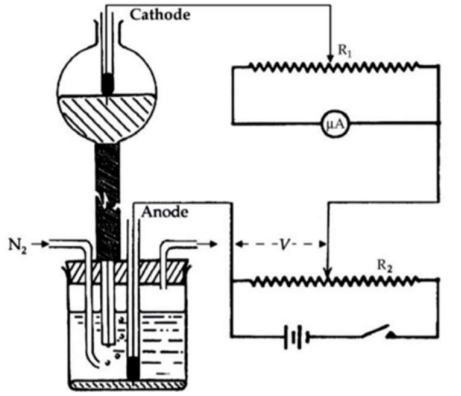
c. Hanging Mercury Drop Electrode (HMDE)

In this electrode, the mercury drop is released by revolving a micrometer screw, which forces mercury from a reservoir through a small capillary.

12.1.4. Instrumentation of polarography

The polarographic analysis apparatus consists of a cathode of dropping mercury electrode (DME), also known as a working or microelectrode, and an anode of a pool of mercury. Since the anode has a wide surface area, it is not polarized, which means its potential remains nearly constant in a solution containing anions capable of forming insoluble salts with Hg (Cl^-, SO_4^{2-}). It serves as an unstandardized reference electrode, the precise potential of which is

determined by the nature and concentration of the supporting electrolyte. The cell's polarization is thus determined by the reactions that occur at DME. The cell has inlet and outlet tubes for expelling dissolved oxygen from the solution by passing inert gases (He or N2) before but not during an experiment, otherwise, the polarogram of dissolved oxygen will appear in the current-voltage curve. Under those conditions, the current-voltage curve is the current cathode potential curve, but it has been displaced by a constant voltage corresponding to the anode's potential. An external anode of known potential, such as a saturated calomel electrode, is sometimes employed.



Polarography: Basic Apparatus

It is a polarographic analysis graph of current versus potential.

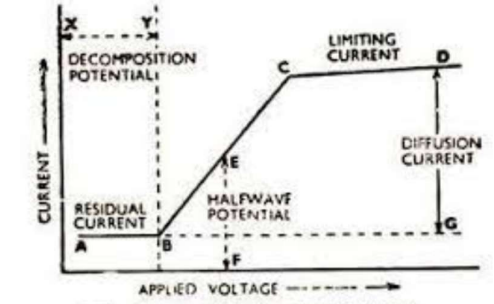


Fig. 1. Current-applied voltage curve (Polarogram)

12.1.5. Factors affecting the current-voltage curve

1. Residual current I_c

In polarography, the residual current is the small charging current detected in the absence of a reactive species. This current flows in the absence of the depolarizer (due to the supporting electrolyte). This must be taken into account when analyzing polarograms. When a current-voltage curve for a thoroughly degassed solution containing only a supporting electrolyte that does not reduce at the electrode surface is plotted, a tiny current is still recorded in the system at potentials greater than about -0.4V. This is due to the Hg drop and the solution acting as a tiny condenser; the Hg drop accumulates a -ve charge on its surface in comparison to the potential of the thin layer of the solution surrounding it. As the Hg drop descends, it takes this charge with it, resulting in a modest +ve current. This condensing or charging current is a non-faradaic current. It does not result from electrochemical processes at the electrode.

There are two sources of residual current.

a. The first is the reduction of trace contaminants (D.O., heavy metals, etc.) that are almost always present in the blank solution throughout time.

b. The second is the ensuing charging current electrons, which charge the droplets in relation to the solution.

2. Migration current (I_m)

It is caused by cation migration from the bulk of the solution to the cathode due to diffusive force, regardless of a concentration gradient. An electro-reducible or oxidizable ion in the solution can get to the DME by diffusion or migration in the absence of convection. The electrostatic interaction between the electrode and the oppositely charged ions causes migration. The migration current is also affected by the transport no.of ions.

The migration current complicates the investigation of the electrode reaction. It can be removed by introducing an excess of supporting electrolytes to the solution. The supporting electrolyte is chosen in such a way that it conducts current while not reacting with electroactive species. Since the supporting electrolyte is added in significant quantities, a state is generated in which the contribution of transport no. of the electroactive species is decreased to negligible levels and their migration is almost zero.

It is found that, I_l (cationic red") = $I_d + I_m$

I_l(anionic red") = $I_d + I_m$

Where, I_l, I_d, and Im, are limiting, diffusion, and migration currents, respectively.

3. Diffusion current

Diffusion Current (id) is the difference between Residual and Limiting current. Diffusion current is caused by electro-reducible ion diffusion from the bulk of the sample to the surface of the mercury droplet as a result of the concentration gradient. The rate of diffusion of an ion to an electrode surface is given by Fick's second law:

$$dc/dt = D\, d^2C/\, dx^2$$

Where, D = diffusion coefficient

C = Concentration at the time 't'

x = distance from the electrode surface

4. Conventional current (I_c)

Conventional current occurs when ions are brought to the electrode surface by mechanical processes, such as swirling in a solution affecting the limiting current.

5. Limiting current (I_l)

The current reaches a steady state value when it exceeds a particular potential, known as the limiting current. The limiting current is due to the contribution of three different types of current. Thus

$$I_l = I_c + I_m + I_d$$

where, Ic = convectional current

I_d = Diffusion current

I_m = Migration current

6. Kinetic current

The kinetic current, which is the rate of non-electrode reaction, might influence the limited current. The kinetic current is proportional to the rate constant and the interface volume. As a result, it is a direct function of size but is unaffected by the velocity of mercury flow. This

current occurs when an electroactive species' oxidized or reduced state is in chemical equilibrium with another material.

12.1.6. Ilkovic equation

In 1934 Ilkovic investigated the different factors that affect the ld and developed the polarography equation that relates the diffusion current (id) and the concentration of the non-polarisable electrode.

$$i_d = 607\ nD^{1/2}\ m^{2/3}\ t^{1/6}\ C$$

where. l_d = the average. diffusion current
n = no. of Faraday

D = a constant (Cm^2S^{-1})
C = analyte conc (m mol L-l)

M = mass of Hg dropping per sec

t = drop time (s)

12.1.7. Factors affecting diffusion current

1. Temperature

Diffusion current varies with temperature. As the ionic mobility changes with temperature, the Id changes.

2. Pressure

Pressure controls the Id by altering the mass flow of mercury and thus its speed. This can be regulated by adjusting the reservoir's height and speed.

3. Concentration

Diffusion current is directly proportional to the concentration of electro-reducible ions.

4. Interfacial surface tension

The diffusion current is affected by interfacial tension at the mercury surface, i.e. there is a gap between the surface of DME and the solution phase containing active ions. As a result, the current may be reduced by reducing the size of droplets as their interfacial tension can be reduced.

12.1.8. Half-Wave Potential ($E_{1/2}$)

The half-wave potential is the potential at which the current is exactly half of the diffusion current. It is a characteristic constant for each electroactive ion under given conditions (electrolyte, temperature, and electrode type). The general electrode reaction at the dropping mercury electrode can be written as:

$$\mathrm{Ox} + ne^- \leftrightharpoons \mathrm{Red}$$

According to the **Nernst equation**,

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

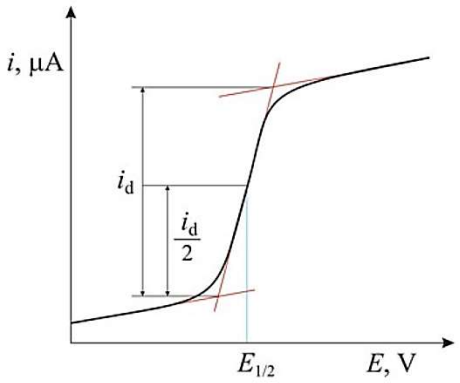
At any potential, the current is proportional to the rate of reduction and, therefore, to the concentration of the oxidized species at the electrode surface. By mathematical treatment (combining diffusion and Nernst relations), we obtain the **polarographic equation**:

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i}$$

or at 25°C,

$$E = E_{1/2} + \frac{0.0591}{n} \log \frac{i_d - i}{i}$$

Thus, the **half-wave potential ($E_{1/2}$)** depends on the standard electrode potential and on the nature of the metal ion and complex formation in solution. It is used for **qualitative identification** of species, while the **diffusion current (i_d)** is used for **quantitative estimation**.



12.1.9. **Applications of Polarography**

1. **Quantitative Analysis:**
   Since $i_d \propto C$, the method is used for determining the concentration of metal ions and reducible species (e.g., Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, etc.).
2. **Qualitative Identification:**
   The half-wave potential is characteristic of each ion; hence, it helps in identifying unknown species in a mixture.
3. **Determination of Stability Constants:**
   Polarography is used to determine stability constants of metal–ligand complexes from the shifts in half-wave potentials.
4. **Kinetic Studies:**
   Provides information on electrode reaction mechanisms and adsorption phenomena at the electrode surface.
5. **Determination of Trace Impurities:**
   Polarography can detect ions at very low concentrations (as low as 10^{-6} M), making it suitable for trace metal analysis.
6. **Study of Organic Compounds:**
   Certain organic molecules containing reducible groups (–NO_2, –C=O, –C≡N) can also be analyzed.
7. **Pharmaceutical and Environmental Applications:**
   Used in drug analysis, water testing, and pollution monitoring.

12.1.10. Limitations of polarography

1. It is said that the solution should not be disturbed throughout the polarographic experiment, although Hg itself disturbs the solution.
2. Capillaries are quite small and thus readily clogged.
3. Mercury is extremely poisonous.
4. Polarography cannot measure solutions with concentrations fewer than 10-5 M. Electrical noise and residual current are found at low concentrations, hence no good signal can be observed.
5. The surface area of a drop of mercury is never consistent.
6. It cannot be used at greater positive potentials due to mercury oxidation.

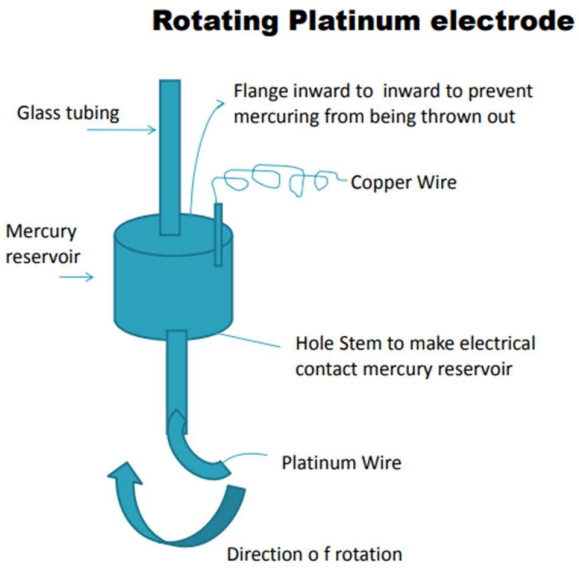
12.2. AMPEROMETRIC TITRATIONS

12.2.1. Introduction: In Amperometric titration current passes through the titration cell between a polarisable electrode and non-polarisable electrode is measured as function of volume of titrant added.

12.2.2. Principle: According to Ilkovic equation (I_d= 607 n $D^{1/2}$ $m^{2/3}$ $t^{1/6}$ C) , the diffusion current (= limiting current - residual current) is directly proportional to the concentration of the electro-active material in the solution. If some of the electro-active material is removed by interaction with reagent, the diffusion current will decrease. This is the fundamental principle of amperometric titrations. The observed diffusion current at a suitable applied voltage is measured as a function of the volume of the titrating solution: the end point is the point of intersection of two lines giving the change of current before and after the equivalence point.

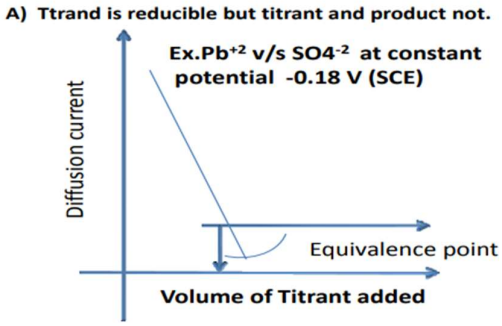
12.2.3. Instrumentation: Amperometric titration can be carried out with a rotating platinum electrode (See Fig.) .It consist of a glass tube of length 15 – 20 cm in length and 6 mm in diameter. The platinum wire extends 5-10 mm from the wall of glass tubing. The electrode is mounted on shaft of the motor and rotated at constant speed of 600 RPM . Electrical connection is made to the electrode by copper wire passing through the tubing to the mercury covering the platinum wire seal.

12.2.4. Advantages: 1) Diffusion current is 20 times larger than DME which allows measuring the small concentration of ion. 2) The rotating platinum electrode can be used at positive potential up to + 0.9 Volt whereas DME can be used only +0.4 volt to -2.0 Volt. 3) The electrode is simple to construct.

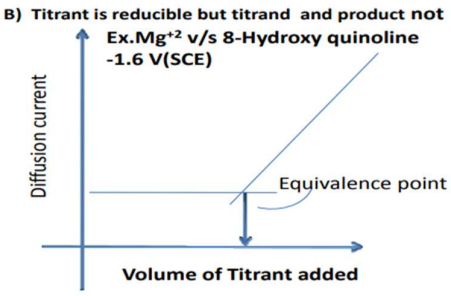


12.2.5. Nature of Titration Curves: Titrand + Titrant ----------⟶ Product.

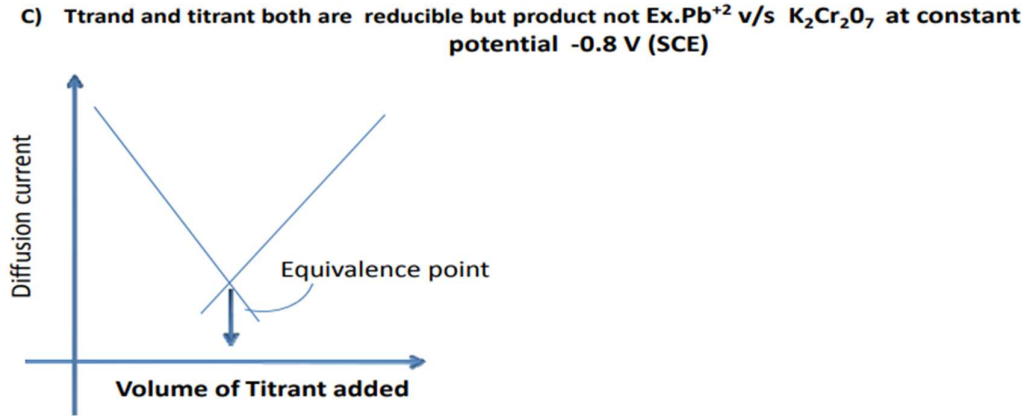
A) Titrand is reducible but titrant and product not: When solution containing Pb^{+2} ion is titrated against SO_4^{-2} ion. A precipitate of $PbSO_4$ is formed. The titration can be performed at fixed potential -0.8 Volt v/s saturated calomel electrode. As titration is proceeds concentration of Pb^{+2} ion decreases and diffusion current also decreases till it becomes minimum at equivalence point. The diffusion current remains constant beyond end point. The values of diffusion current is plotted against the volume of titrant added .The resulting titration curves is straight line leveling off at end point . The intersection of two extra plotted portions of the curves gives the end point.



B) Titrant is reducible but titrand and product not: When solution containing Mg^{+2} ion is titrated against with the reducible species such as 8-hydroxy-quinoline. At constant potential of -1.6 volt. In this titration the current is steady till the end point because Mg^{+2} ion does not undergoes reduction. Beyond the end point the 8-hydroxy-quinoline undergoes reduction. As its concentration increases diffusion current also increases.



C) Titrand and titrant both are reducible but product not: When solution containing Pb^{+2} ion is titrated against $K_2Cr_2O_7$. The titration is performed at potential of -0.8 Volt v/s SCE . Diffusion current is decreases due to removal of Pb^{+2} ion. The current is minimum at the end point. On further addition of the titrant the current once again increases. V shaped curve is obtained.



12.2.6. Advantages of amperometric titrations:

1. The titration can usually be carried out rapidly, since the end point is found graphically; a few current measurements at constant applied voltage before and after the end point suffice.
2. Titrations can be carried out in cases in which the solubility relations are such that potentiometric or visual indicator methods are unsatisfactory; for example, when the reaction product is markedly soluble (precipitation titration) or appreciably hydrolysed (acid-base titration). This is because the readings near the equivalence point have no special significance in amperometric titrations. Readings are recorded in regions where there is excess of titrant, or of reagent, at which points the solubility or hydrolysis is suppressed by the Mass Action effect; the point of intersection of these lines gives the equivalence point.
3. A number of amperometric titrations can be carried out at dilutions (ca 10-4M) at which many visual or potentiometric titrations no longer yield accurate results.
4. 'Foreign' salts may frequently be present without interference and are, indeed, usually added as the supporting electrolyte in order to eliminate the migration current. If the current-voltage curves of the reagent and of the substance being titrated are not known, the polarograms must first be determined in the supporting.

Applications: 1) Using amperometric titrations precipitation titration can be performed.
2) amperometric titrations method is used for redox titrations and to study complex formation.

12.3. CORROSION

Corrosion is an undesirable process. Due to corrosion there is limitation of progress in many areas. The cost of replacement of materials and equipments lost through corrosion is unlimited. Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interactions with the environment. Thus, it is exactly the reverse of extraction of metals from ores.

Example:

- A layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface of iron.
- A green film of basic carbonate [$CuCO_3 + Cu(OH)_2$] is formed on the surface of copper, when it is exposed to moist-air containing carbon dioxide.

12.4. THEORIES OF CORROSION

Based on the environment, corrosion is classified into (i) Dry *or* Chemical Corrosion, (ii) Wet *or* Electrochemical Corrosion

12.4.1. Dry or Chemical Corrosion:

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid, etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment.

Example: (i) Silver materials undergo chemical corrosion by Atmospheric H_2S gas. (ii) Iron metal undergo chemical corrosion by HCl gas.

Types of Dry or Chemical Corrosion:

1. Corrosion by Oxygen or Oxidation corrosion
2. Corrosion by Other gases
3. Liquid Metal Corrosion

1). Oxidation Corrosion:

Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

Mechanism:

1) Oxidation takes place at the surface of the metal forming metal ions M^{2+}

$$2M \rightarrow 2M^{n+} + 2ne^-$$

2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.

$$n/_2\ O_2 + 2n\ e^- \rightarrow nO^{2-}$$

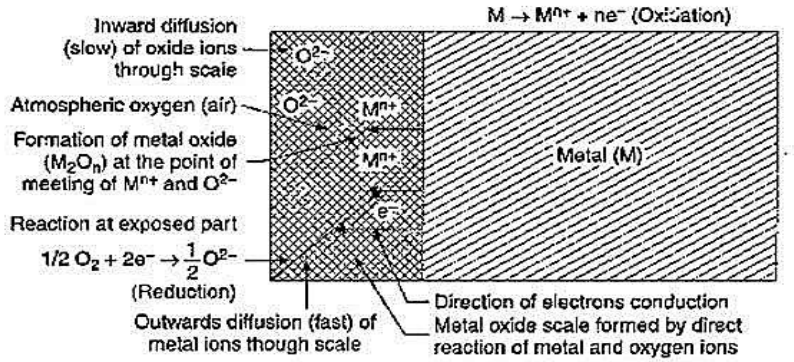
3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

$$2\ M + n/2\ O_2 \rightarrow 2\ M^{n+} + nO^{2-}$$

The Nature of the Oxide formed plays an important part in oxidation corrosion process.

Metal + Oxygen → Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is



i) Stable layer:

A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (ie., which cuts-off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable, tightly adhering and impervious in nature.

(ii) Unstable oxide layer:

This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) Volatile oxide layer:

The oxide layer film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO_3 is volatile in nature.

(iv) Porous layer:

If the layer having pores or cracks, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

Pilling-Bed worth rule:

According to it "an oxide is protective or non-porous, if the volume of the oxide is atleast as great as the volume of the metal from which it is formed". On the other hand, "if the volume of the oxide is less than the volume of metal, the oxide layer is porous (or non-continuous) and hence, non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below".

Thus, alkali and alkaline earth metals (like Li, K, Na, Mg) form oxides of volume less than the volume of metals. Consequently, the oxide layer faces stress and strains, thereby developing cracks and pores in its structure. Porous oxide scale permits free access of oxygen to the underlying metal surface (through cracks and pores) for fresh action and thus, corrosion continues non-stop. Metals like Aluminium forms oxide, whose volume is greater than the volume of metal. Consequently, an extremely tightly-adhering non-porous layer is formed. Due to the absence of any pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

2). Corrosion by other gases:

The Gases like SO_2, CO_2, Cl_2, H_2S, $F_{2,...}$etc. The extent of corrosive effect mainly depends on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non-protective films on the metal surface.

A) If the film formed is protective or non porous, the extent of attack decreases.
   Eg: AgCl film , resulting from the attack of Cl_2 on Ag.

B) If the film formed is non- protective or porous, the surface of the whole metal is gradually destroyed.
   Eg ; Dry Cl_2 gas attack on tin (Sn) forming a volitle $SnCl_4$, there by leaving fresh metal surface for further attack.

3). Liquid metal corrosion:

This is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either: (i) dissolution of a solid metal by a liquid metal or (ii) internal penetration of the liquid metal into the solid metal. Both these modes of corrosion cause weakening of the solid metal.

12.4.2. WET OR ELECTROCHEMICAL CORROSION:

Electrochemical corrosion involves:

i) The formation of anodic and cathodic areas or parts in contact with each other
ii) Presence of a conducting medium
iii) Corrosion of anodic areas only and
iv) Formation of corrosion product somewhere between anodic and cathodic areas.

This involves flow of electron-current between the anodic and cathodic areas.

At anodic area oxidation reaction takes place (liberation of free electron), so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc.). Hence corrosion always occurs at anodic areas.

M (metal)	→	$M^{n+} + n\ e^-$
M^{n+} (metal ion)	→	Dissolves in solution
	→	forms compounds such as oxide

At cathodic area, reduction reaction takes place (gain of electrons), usually cathode reactions do not affect the cathode, since most metals cannot be further reduced. So at cathodic part, dissolved constituents in the conducting medium accept the electrons to form some ions like OH-and O^{2-}.

Cathodic reaction consumes electrons with either by

(a) evolution of hydrogen or
(b) absorption of oxygen, depending on the nature of the corrosive environment

a). <u>Hydrogen Evolution Type</u>:

All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

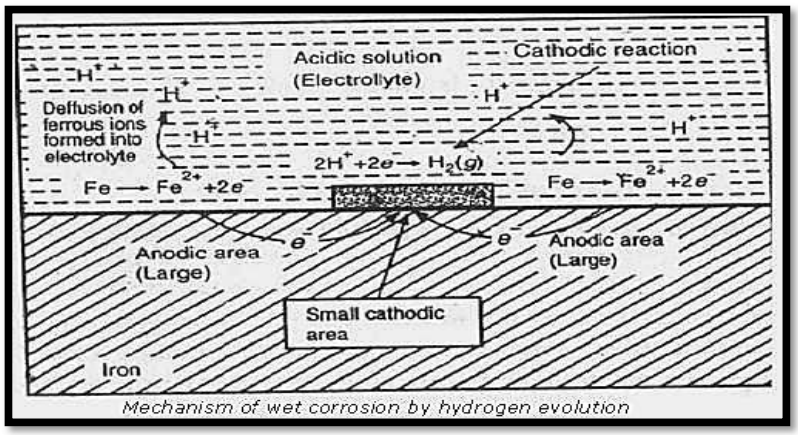
It occurs in acidic environment. Consider the example of iron

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$

These electrons flow through the metal, from anode to cathode, where H+ ions of acidic solution are eliminated as hydrogen gas.

At cathode: $2\ H^+ + 2\ e^- \rightarrow H_2\uparrow$

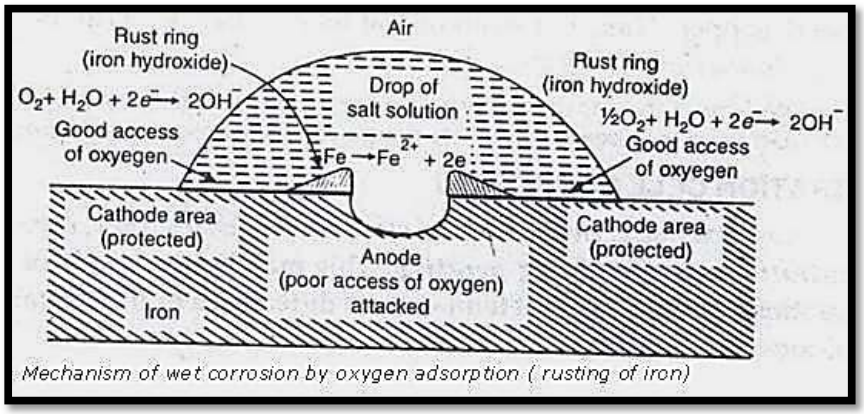
The overall reaction is: $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$



Mechanism of wet corrosion by hydrogen evolution

b). Absorption of Oxygen Type:

Rusting of iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts acts as cathodes.



Mechanism of wet corrosion by oxygen adsorption (rusting of iron)

At Anode: Metal dissolves as ferrous ions with liberation of electrons.

$Fe \rightarrow Fe^{2+} + 2e^-$

At Cathode: The liberated electrons are intercepted by the dissolved oxygen.

$\frac{1}{2} O_2 + H_2O + 2 e^- \rightarrow 2OH^-$

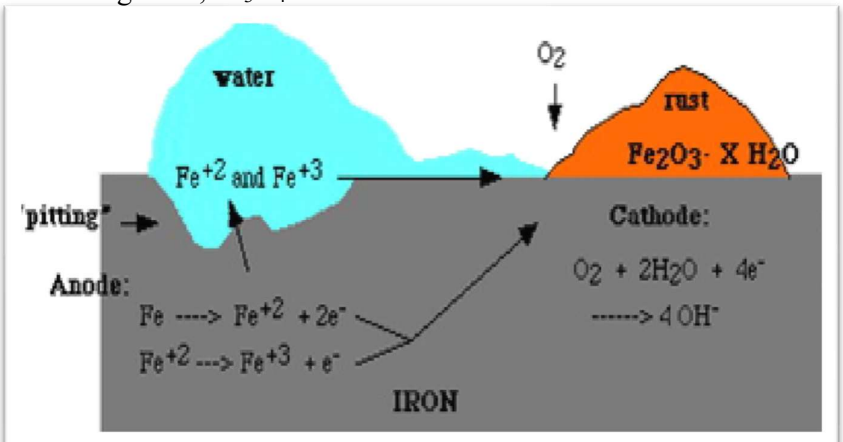
The Fe^{2+} ions and OH- ions diffuse and when they meet, ferrous hydroxide is precipitated.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

(i) If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ (Yellow rust $Fe_2O_3.H_2O$)

(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4.



12.5. TYPES OF ELECTROCHEMICAL CORROSION:

The electrochemical corrosion is classified into the following two types:

(i) Galvanic (or Bimetallic) Corrosion
(ii) Differential aeration or concentration cell corrosion.
(iii) Pitting Corrosion

i). Galvanic Corrosion:

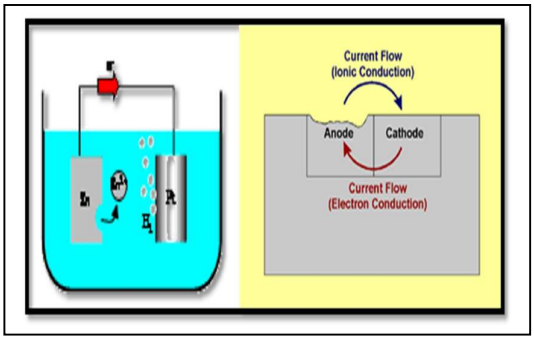
When two dissimilar metals (eg., zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. In this process, the more active metal (with more negative electrode potential) acts as a anode while the less active metal (with less negative electrode potential) acts as cathode.

In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series or more noble)acts as cathode. Mechanism: In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anode metal zinc to the cathode metal, copper.

$$Zn \longrightarrow Zn^{2+} + 2e^{-} \text{ (Oxidation)}$$

Thus it is evident that the corrosion occurs at the anode metal; while the cathodic part is protected from the attack.

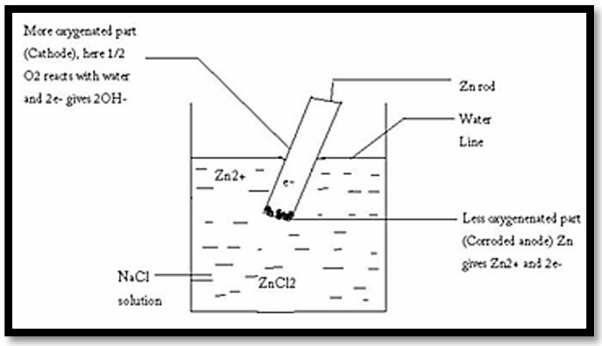
Example: (i) Steel screws in a brass marine hardware (ii)Lead-antimony solder around copper wire; (iii) a steel propeller shaft in bronze bearing (iv Steel pipe connected to copper plumbing.



ii). Concentration Cell Corrosion: Differential aeration Corrosion

It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration. It occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that poor-oxygenated parts are anodic.

Examples: i) The metal part immersed in water or in a conducting liquid is called water line corrosion. ii) The metal part partially buried in soil.



Explanation: If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion

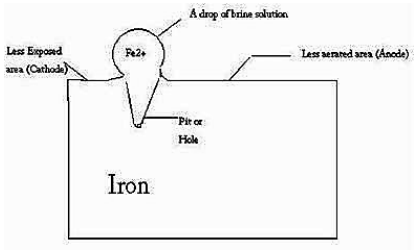
At anode: Corrosion occurs (less aerated): $M \longrightarrow M^{2+} + 2e^-$

At cathode: OH- ions are produced (more aerated): $\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

iii). Pitting Corrosion:

Pitting is a localized attack, which results in the formation of a hole around which the metal is relatively un-attacked. The mechanism of this corrosion involves setting up of differential aeration or concentration cell. Metal area covered by a drop of water, dust, sand, scale etc. is the aeration or concentration cell. Pitting corrosion is explained by considering a drop of water or brine solution (aqueous solution of NaCl) on a metal surface, (especially iron).

The area covered by the drop of salt solution as less oxygen and acts as anode. This area suffers corrosion, the uncovered area acts as cathode due to high oxygen content. It has been found that the rate of corrosion will be more when the area of cathode is larger and the area of the anode is smaller. Hence there is more material around the small anodic area results in the formation hole or pit.



At anode: Fe is oxidized to Fe^{2+} and releases electrons.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

$$Fe^{2+} + 2OH^- + \frac{1}{2} O_2 \longrightarrow Fe(OH)_2 \downarrow$$

The above mechanisms can be confirmed by using ferroxyl indicator (a mixture containing phenolphthalein and potassium ferricyanide). Since OH^- ions are formed at the cathode, this area imparts pink colour with phenolphthalein indicator. At the anode, iron is oxidized to Fe2+ which combines with ferricyanide and shows blue colour.

12.6. CORROSION CONTROL (PROTECTION AGAINST CORROSION):

As the corrosion process is very harmful and losses incurred are tremendous, it becomes necessary to minimize or control corrosion of metals. Corrosion can be stopped completely

only under ideal conditions. But the attainment of ideal conditions is not possible. However, it is possible only to minimize corrosion considerably. Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different, diverse methods are used to control corrosion. As the corrosion is a reaction between the metal or alloy and the environment, any method of corrosion control must be aimed at either modifying the metal or the environment.

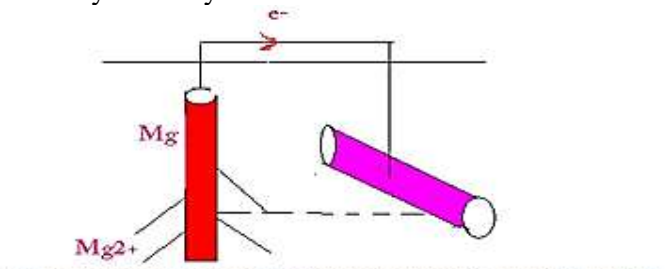
12.6.1. Cathodic Protection:

The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell is called cathodic protection. Since there will not be any anodic area on the metal, corrosion does not occur. There are two methods of applying cathodic protection to metallic structures.

i. Sacrificial anodic protection (galvanic protection)
ii. Impressed current cathodic protection

i. **Sacrificial Anodic Protection Method:**

In this method, the metallic structure to be protected is made cathode by connection it with more active metal (anodic metal). Hence, all the corrosion will concentrate only on the active metal. The parent structure is thus protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Magnesium has the most negative potential and can provide highest current output and hence is widely used in high resistivity electrolytes like soil.



In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (e.g., a pipeline, bridge, ship hull or boat).

Applications:

1. Protection as buried pipelines, underground cables from soil corrosion.
2. Protection from marine corrosion of cables, ship hulls, piers etc.
3. Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.
4. Calcium metal is employed to minimize engine corrosion.

Advantages:

i. Low installation and operating cost.
ii. Capacity to protect complex structures.
iii. Applied to wide range of severe corrodents.

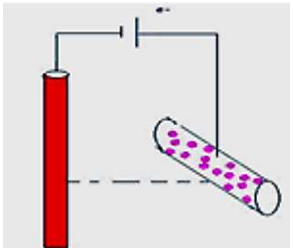
Limitations:

1. High starting current is required.
2. Uncoated parts cannot be protected.
3. Limited driving potential, hence, not applicable for large objects

ii. **Impressed Current Cathodic Protection Method**

In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

Usually the impressed current is derived from a direct current sources (like battery or rectifier on AC line) with an insoluble, inert anode (like graphite, scrap iron, stainless steel, platinum or high silica iron).



A sufficient DC current is applied to an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is, usually, a back fill, composed of coke breeze or gypsum, so as to increase the electrical contact with the surrounding soil. Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid up ships etc. This kind of protection technique is particularly useful for large structures for long term operations.

12.6.2. By using inhibitors:

Inhibitors are organic or inorganic substances which decrease the rate of corrosion. Usually the inhibitors are added in small quantities to the corrosive medium. Inhibitors are classified into

1. Anodic inhibitors (chemical passivators)
2. Cathodic inhibitors (adsorption inhibitors)

12.8 SUMMARY

- **Polarography** analyzes redox-active species using mercury electrodes; diffusion current and half-wave potential are key analytical parameters.
- **Ilkovic equation** quantitatively relates diffusion current to concentration.
- **Amperometric titration** measures current versus titrant volume for endpoint detection.
- **Corrosion** is the deterioration of metals via chemical or electrochemical means.
- **Prevention methods** include cathodic protection, inhibitors, and design improvements.

12.9 TECHNICAL TERMS

Term	Definition
Polarography	Electroanalytical method measuring current vs. potential at DME
Diffusion Current (id)	Limiting current governed by ion diffusion rate
Half-Wave Potential (E½)	Potential where current equals half of diffusion current
Ilkovic Equation	Relates diffusion current to concentration and mercury parameters

Amperometric Titration	Current–volume method for titration endpoint determination
Corrosion	Deterioration of metals by chemical or electrochemical action
Pilling–Bedworth Rule	Predicts protectiveness of oxide films
Galvanic Corrosion	Corrosion of active metal in contact with a noble metal
Cathodic Protection	Technique preventing corrosion by making structure cathodic
Inhibitors	Chemicals reducing corrosion rate

12.10 SELF-ASSESSMENT QUESTIONS

1. Define **polarography** and explain the theory of diffusion current.
2. Derive the **Ilkovic equation** and discuss factors affecting diffusion current.
3. What is the **half-wave potential** and how is it used for qualitative analysis?
4. Explain the **principle and instrumentation** of amperometric titration.
5. Discuss the **types of corrosion** with suitable examples.
6. What is the **difference between dry and wet corrosion**?
7. Describe the **mechanism of galvanic and pitting corrosion**.
8. Explain **cathodic protection methods** with applications.
9. Write short notes on: (a) Pilling–Bedworth rule (b) Corrosion inhibitors.

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Dr. CH. SUBRAMANYAM

LESSON-13

CHEMICAL KINETICS- BRANCHING CHAIN REACTIONS; CONDITIONS FOR DIFFERENT TYPES OF EXPLOSION LIMITS; REACTION PROFILE OF H_2-O_2 EXPLOSION

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the Branching Chain Reactions.
- To study about Conditions for Different Types of Explosion limits.
- To study about Lower and Upper explosion limits.
- To learn about reactions involving Explosion of H_2-O_2.

13.1 BRANCHING CHAIN REACTIONS

Based on the chain carriers produced in each propagation step, the chain reactions can primarily be classified into two categories; non-branched or the stationary reactions and branched or the non-stationary reactions. A typical chain reaction can be written as given below.

$$\textit{Initiation}: \quad A \xrightarrow{k_1} R^* \tag{1}$$

$$\textit{Propagation}: \quad R^* + A \xrightarrow{k_2} P + nR^* \tag{2}$$

$$\textit{Termination}: \quad R^* \xrightarrow{k_3} \textit{destruction} \tag{3}$$

Where P, R^* and A represent the product, radical (or chain carrier) and reactant molecules, respectively. The symbol represents a number that equals unity for stationary chain reactions and greater than one for non- stationary or the branched-chain reactions. Furthermore, the destruction of the radical in the termination step can occur either via its collision with another radical (in gas phase) or by striking the walls of the container.

The steady-state approximation can be employed to determine the concentration of intermediate or the radical involved in the propagation step. The general procedure for which is to put the overall rate of formation equals to zero. In other words, the rate of formation of R^* must be equal to the rate of decomposition of the same i.e.

$$\textit{Rate of formation of } R^* = \textit{Rate of disappearance of } R^* \tag{4}$$

$$k_1[A] = k_3[R^*] - k_2(n-1)[R^*][A] \tag{5}$$

$$k_1[A] - k_3[R^*] + k_2(n-1)[R^*][A] = 0 = \frac{d[R^*]}{dt} \tag{6}$$

or

$$-k_3[R^*] + k_2(n-1)[R^*][A] = -k_1[A] \quad (7)$$

$$[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_3} \quad (8)$$

Now because the destruction of the radical in the termination step can occur either via its collision with another radical (in gas phase) or via striking the walls of the container, the rate constant $k3$ can be replaced by the sum of the rate constants of two i.e. $k_3 = k_W + k_g$. After using the value of k_3 in equation (8), we have

$$[R^*] = \frac{k_1[A]}{k_2(1-n)[A] + k_W + k_g} \quad (9)$$

$$[R^*] = \frac{k_1[A]}{-k_2(n-1)[A] + k_W + k_g} \quad (10)$$

For non-stationary or branched chain reactions, more and more radicals are generated in each successive step ($n > 1$). In other words, for every radical consumed in a chain propagation step, more than one chain carriers or radicals are generated. Therefore, the possibility of explosion arises when

$$k_2(n-1)[A] = k_W + k_g \quad (11)$$

The situation can be explained in terms of equation (10) because the abovementioned condition will make the denominator zero, and therefore, making radical concentration to approach infinite. Now because the rate is usually proportional to radical's concentration, a very high rate may lead to an explosion.

13.2 Conditions for Different Types of Explosion limits

However, it is also worthy to mention that the occurrence of explosion depends upon the experimental temperature and pressure. Typically, three explosion limits are observed as the pressure of the reacting system is raised. To understand the different explosion limits, the behavior of the denominator in equation (10) must be analysed with pressure (**Figure 13.1**).

1. The first explosion limit:

When the pressure is very low, the movement of chain carriers towards the wall of the container is very fast resulting in a very large rate of radicals' destruction at walls i.e. high k_W. Conversely, the probability of radicals colliding with each other at very low pressure resulting in a very low value of k_g. Therefore, we can conclude that the denominator in equation (10) has a sufficiently large positive value at low pressure giving smooth progression of the reaction without any explosion. However, with the rise in pressure, k_W declines very rapidly than the

increase in k_g. When a certain pressure value is achieved, the explosion condition is satisfied i.e.

$$k_2(n-1)[A] = k_W + k_g \qquad (12)$$

Which is the first explosion limit.

2. The second explosion limit:

The first explosion limit exists over a wide range of pressure. However, if the pressure is raised continuously, the movement of chain carriers towards the wall of the container is more and more hindered resulting in a very small rate of radicals' destruction at walls i.e. low k_W. Conversely, the probability of radicals colliding with each other further increases with pressure resulting in the very large value of k_g. Eventually, we can conclude that the denominator in equation (10) again becomes sufficiently positive giving a steady progression of the reaction. Which is the second explosion limit.

3. The third explosion limit: After the second explosion limit, the steady reaction-rate continues over a range of pressure. However, if the pressure is raised continuously, the heat produced in various propagating steps would not be able to leave the system at a rate equal to the rate at which it is produced. Therefore, this thermal effect will keep supporting the rate, eventually leading to a thermally-induced explosion. Which is the third explosion limit.

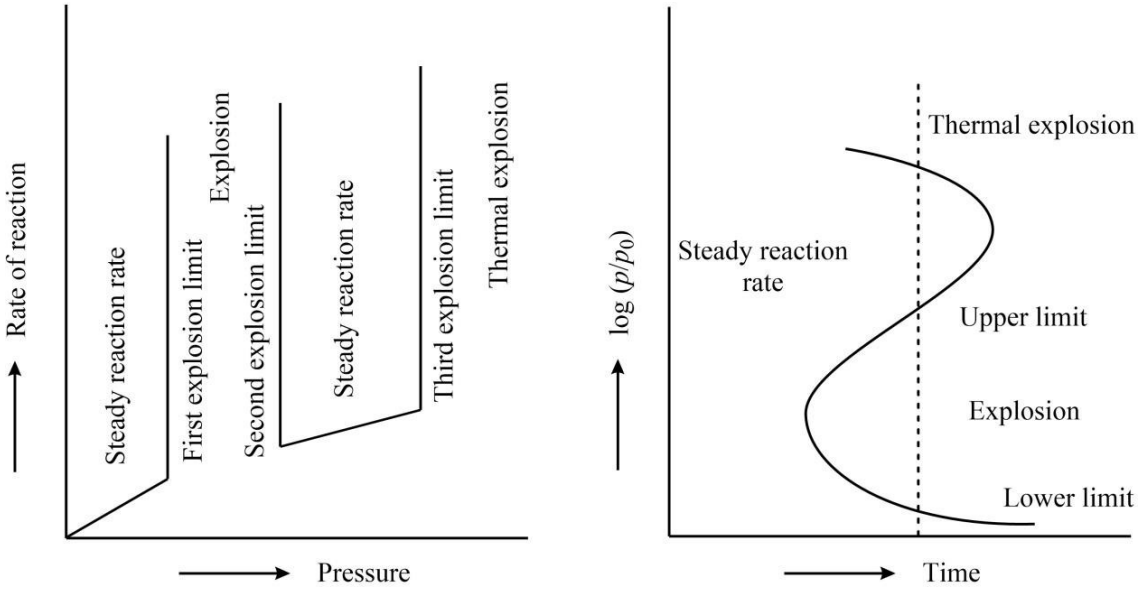


Figure 13.1: The variation of reaction with pressure in branching chain reactions (left) and variation of relative pressure with time on a logarithmic scale (right)

13.3 Reaction Profile of H_2-O_2 Explosion

The reaction between H_2 and O_2 is a typical example in which all three explosion limits are observed.

The net reaction is

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad (1)$$

Furthermore, the elementary steps for the same can be proposed as

$$\textit{Initiation}: \quad H_2 + O_2 \xrightarrow{k_1} HO'_2 + H' \qquad (2)$$

$$\textit{Propagation}: \quad H_2 + HO'_2 \xrightarrow{k_2} HO' + H_2O \qquad (3)$$

$$H_2 + HO' \xrightarrow{k_3} H' + H_2O \qquad (4)$$

$$H' + O_2 \xrightarrow{k_4} HO' + O' \qquad (5)$$

$$O' + H_2 \xrightarrow{k_5} HO' + H' \qquad (6)$$

The step 3rd and 4th produce more radicals than they consume, producing an explosion.

SUMMARY:

- To learn about the Branching Chain Reactions.
- To study about Conditions for Different Types of Explosion limits.
- To study about Lower and Upper explosion limits.
- To learn about reactions involving Explosion of H_2-O_2

SELF ASSESSMENT QUESTIONS

1. Explain Lower and Upper explosion limits with their graphs.
2. Explain the branching chain reactions.
3. Write the reactions involving H_2-O_2 Explosion.

Prof. R. Ramesh Raju

LESSON-14
FAST REACTIONS AND FLOW METHODS

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the Fast Reactions.
- To study about different methods for e Fast Reactions.
- To study about Continuous flow technique, Stopped flow technique and Quenched Flow Approach.
- To learn about chemical relaxation method and Flash photolysis method.

14.1 FAST REACTIONS

Fast reactions are those types of chemical reactions that occur quickly, i.e., within a few seconds.

Chemical kinetics, as we all know, is a field of physical chemistry that deals with reaction speed or the rate at which reactant concentration changes over time. There are many different kinds of reactions, including chain reactions, polymerization reactions, rapid reactions, and simple chemical reactions. Some reactions are slow and take longer time to complete. On the other hand, some reactions are so quick that it completes in a short period. Fast reactions are those types of chemical reactions that occur in a very short period i.e. within a few seconds. They finish in mere 10^{-13} sec. As a result, these reactions cannot be studied using conventional techniques.

14.2 Characteristics of fast reactions

- These reactions are so fast that they complete in a split second as soon as the reactants are brought together. These reactions can be completed in 10^{-14} to 10^{-16} sec. It is due to this fact that it is almost impossible to determine the rates of these reactions.
- Various special analytical methods and techniques are being used and developed to study such reactions.
- The half-life of such reactions is within a few milliseconds or less.
- They take place instantaneously.
- In comparison to the reaction's half-life, the time required to combine the reactants or raise their temperature may be important.
- NMR techniques are utilized to collect kinetic data in solutions. The technique is based on the observation that two substances with dissimilar NMR chemical shifts combine into one peak when they undergo fast changes in one direction to the other.

Examples:

- Ionic reactions, for instance, can occur very quickly. Silver chloride can precipitate quickly when sodium chloride and silver nitrate are combined in aqueous solutions.
- Neutralization reaction between acids and bases.
- Combustion of natural gas.

14.3 Different methods for the study of fast reactions

1. Flow Methods

- This technique is the extension of the classical mix and shake method where reactants are mixed within a fraction of a second.
- Developed by Roughton and Hastridge in 1923.
- Allows to measure reactions having half-life in the range of 10 sec to 10^{-3} sec.
- Involves a continuous flow technique and a stopped-flow technique.

A) Continuous flow technique:

- The two reactants are allowed to pass to the mixing chamber from their respective reservoirs as shown in the figure.
- The mixed solution then moves through the observation tube.
- The reaction occurs in the mixing chamber. As the name suggests the flow in this technique is continuous at a constant rate.
- Since the flow rate is constant, the concentration at a particular point along the observation tube does not change. This will provide an opportunity to make observations in a few milliseconds after missing.
- Light is allowed to fall on the observation tube.
- If the distance between the points at which the reaction is initiated and the product is known, then the time interval can be found from the flow rate as the flow rate is constant. By varying this distance, the time required to obtain the maximum yield can then be determined.
- This technique can be coupled with spectrophotometric equipment at the point of mixing.
- Measurement of light absorption may be used to determine the extent of reaction if the absorption spectrum of reactant and product differs **(Figure 14.1)**.

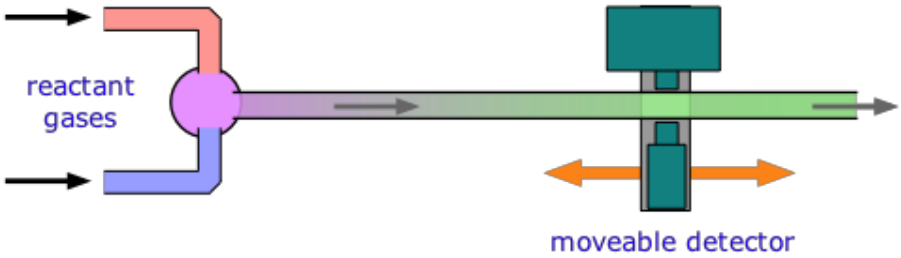


Figure 14.1: A continuous flow fast kinetic system

B) Stopped flow technique:

This method is used to overcome the disadvantages of continuous flow techniques. The main problem of the continuous flow method is that it requires a large volume of reactants and is mostly suited for gas-phase reactions. The stopped-flow technique is the most common means of studying fast solid-phase reactions that complete within a millisecond.

The basic working principle of the stopped-flow technique is also similar to the continuous-flow technique. The difference is that in this technique, the flow is stopped suddenly so there is rapid change in the concentration of reactants. This change can be observed by coupling the

instrument with the instrument that measures absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. The change in the concentration of reactant before and after mixing will give kinetics of reactions (**Figure 14.2**).

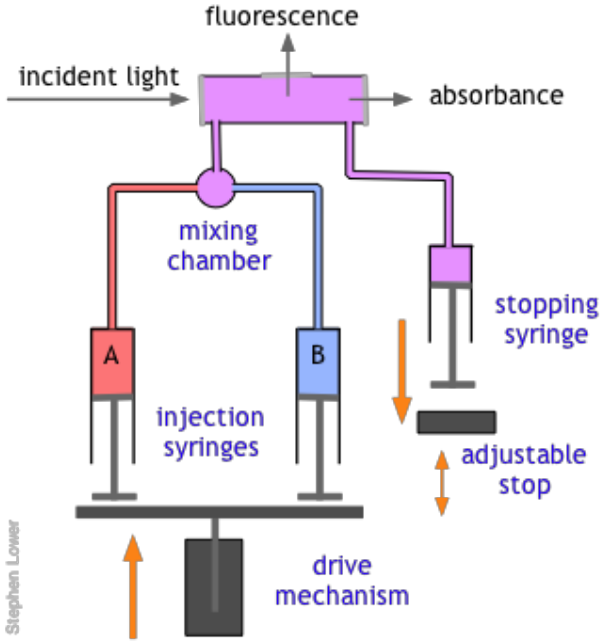


Figure 14.2: A stop flow fast kinetic system.

C) Quenched Flow Approach

In a quenched-flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).

Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored. In such cases, it is often practical to *quench* (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner **(Figure 14.3**).

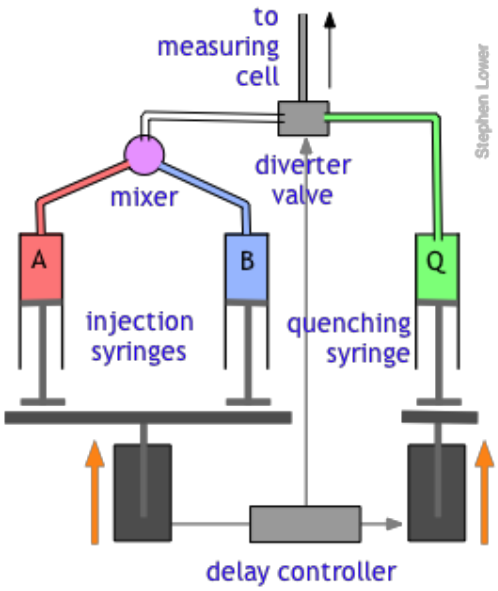


Figure 14.3: A quench flow fast kinetic system.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

2. Chemical relaxation method

In the relaxation technique, a system is perturbed i.e. its equilibrium is disturbed by a rapid change in external parameters such as temperature, pressure, or electrified intensity. The time required to attain a new equilibrium known as relaxation time, is measured. The relaxation time can be measured by various methods.

A) Temperature Jumps

- In this method, a system is perturbed by changing the temperature to several degrees (10 ^{o}C) in 10^{-5} sec. Then the relaxation time is measured.
- The sudden change in temperature results in a change in the equilibrium concentration and this change can be observed by spectrophotometer.
- It has been discovered that a 1 ^{o}C temperature change affects the equilibrium concentration by roughly 3%.

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured (**Figure 14.4**).

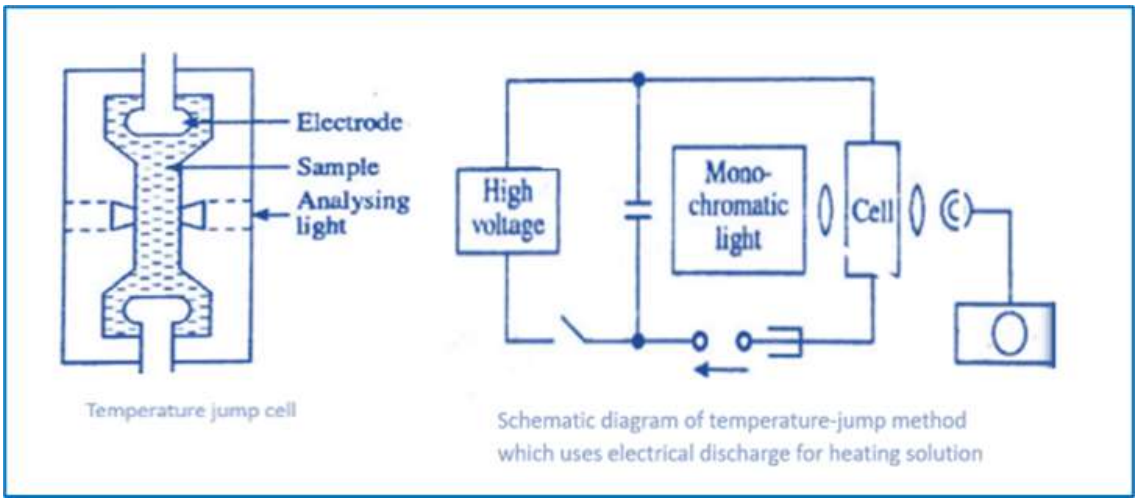


Figure 14.4: Schematic diagram of temperature-jump method which uses electrical discharge for heating solution

B) Pressure jump:

In this method sudden change is pressure is applied that disturbs the equilibrium.

- A flexible cell is used to hold the sample.
- After that, it is attached to a pressure vessel that has an inert liquid inside of it.
- Next, the vessel is pressured to roughly 65 atmospheres.
- Then, the pressure is reduced in roughly 10^{-4} seconds to an atmospheric pressure by piercing a thin metal drill bit into the vessel's wall (**Figure 14.5**).

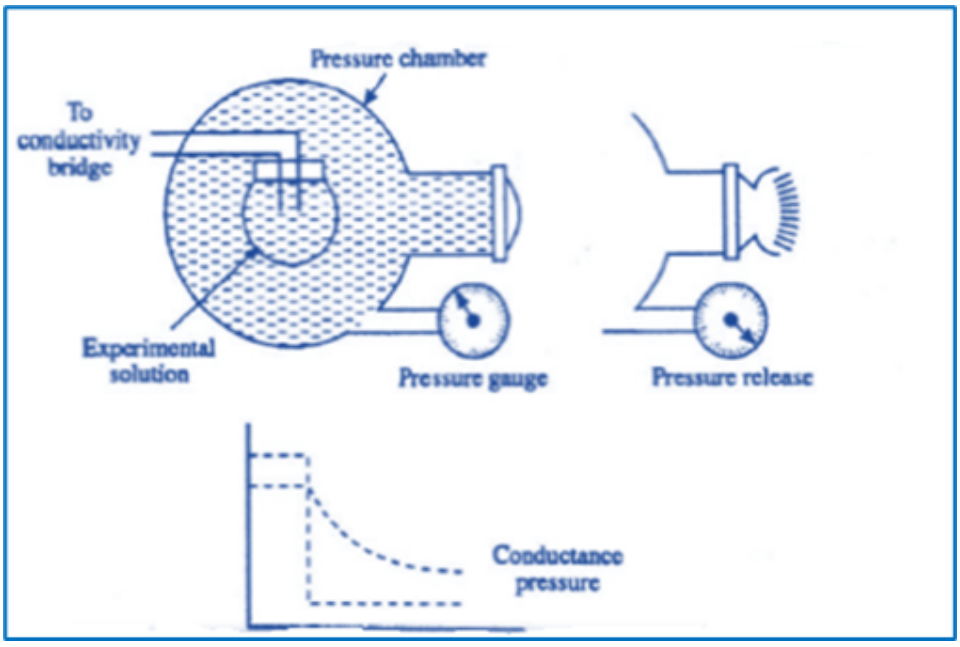


Figure 14.5: Schematic diagram of pressure-jump method

C) Flash photolysis method

This method was given by George Porter and Ronald Norrish in 1949. This method is extensively used to study reaction kinetics in solution as well as in gaseous phases. The working principle of flash photolysis includes using a short pulse of light that is used to initiate a reaction. The progress of the reaction can be observed by optical and other means. A good example is the formation of hydrochloric acid by the combination of hydrogen and chloride, which proceeds explosively when the system is illuminated with visible light.

- The reactants are kept in a cylindrical quartz vessel which is present next to the photolytic flash tube. They are coated with a MgO reflector.
- A quartz tube filled with rare gas (xenon) is placed next to it.
- The photoflash lamp is parallel to the reaction cell.
- The reaction is initiated by the intense flash of visible or UV light that is generated by a photoflash lamp. The duration of flash is very short about 5 to 10 microseconds.
- Monochromatic light from the lamp is passed through the sample and the wavelength is selected by the monochromator.
- The intensity is measured by a photomultiplier and then displayed on an oscilloscope.
- When a flash is applied to a system, the system gets perturbed and rapidly from equilibrium, and a change in concentrations is seen. This will help to ascertain the kinetics of fast reactions **(Figure 14.6)**.

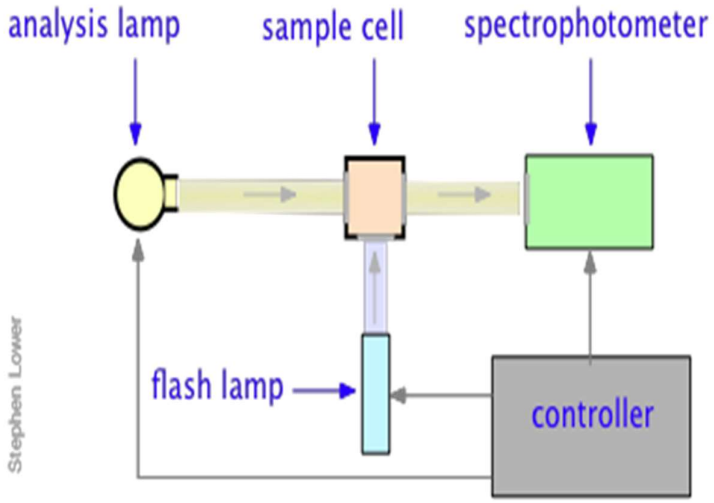


Figure 14.6: A flash- photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

$$2H_2O \rightarrow H_3O^+ + OH^-$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^-$$

Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

SUMMARY

- To learn about the Fast Reactions.
- To study about different methods for e Fast Reactions.
- To study about Continuous flow technique, Stopped flow technique and Quenched Flow Approach.
- To learn about chemical relaxation method and Flash photolysis method.

SELF ASSESSMENT QUESTIONS

1. Discuss briefly about fast reactions.
2. What is flash photolysis? explain it with an example.
3. Describe study of kinetics by flow methods.

Prof. R. Ramesh Raju

LESSON-15

ACID-BASE CATALYSIS & ENZYME CATALYSIS; MICHAELIS-MENTEN ENZYME CATALYSIS

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about Acid-Base Catalysis.
- To study about Protolytic mechanism and Prototrotopic mechanism.
- To study about enzyme catalysis and kinetics of enzyme catalysis
- method.
- To learn about Michaelis-Menten Enzyme Kinetics.

15.1 Acid-Base Catalysis

The acid catalysed reaction, in general, involves a transfer of proton to the reactant (substrate) from the acid (BH^+). The protonated substrate undergoes the reaction which is the rate determining stage ultimately producing the products and the hydrogen ion is released. The hydrogen ion may be taken up by water present in the medium or by the conjugate base (B) of the acid catalyst. If the hydrogen ion is taken up by water forming H_3O^+ the mechanism is called protolytic mechanism.

15.2 ACID - BASE CATALYSIS - PROTOLYTIC MECHANISM:

Scheme I:

$$S + BH^+ \xrightarrow{k_1} SH^+ + B$$

$$k_{-1} \qquad \ldots[1]$$

$$SH^+ + H_2O \xrightarrow{k_2} \text{products} + H_3O^+$$

$\ldots[2]$

Protolytic mechanism:

The derivation of the rate-equation for this mechanism is carried out by applying steady state approximation with respect to the intermediate, SH^+ (i.e.)

$$\frac{d}{dt}[SH^+] = k_1[S][BH^+] - k_{-1}[SH^+][B] - k_2[SH^+] = 0$$

$\ldots[3]$

OR

$$[SH^+] = \frac{k_1 [S][BH^+]}{k_{-1}[B] + k_2} \quad ...[4]$$

The rate of the reaction, defined as rate of formation of products is given by the eq [4].

$$\text{rate} = k_2[SH^+] = \frac{k_1 k_2 [S][BH^+]}{k_{-1}[B] + k_2} \quad ..[5]$$

Now two situations have been envisaged. depending upon the relative magnitudes of k_2, and $k_{-1}[B]$. If k_2 is negligibly small conferred to $k_{-1}[B]$, the intermediate. SH^+, is called Arrhenius complex and the rate law assumes the form.

$$\text{rate} = \frac{k_1 k_2 [S][BH]}{k_{-1}[B]} \quad \ldots[6]$$

of the ionization of equilibrium of the acid catalyst, BH+, is considered,

$$BH^+ \underset{}{\overset{Ka}{\rightleftharpoons}} B + H^+$$

$$K_a = \frac{[B][H^+]}{[BH^+]} \quad \text{or} \quad \frac{[BH^+]}{[B]} = \frac{[H^+]}{K_a}$$

$$\text{rate} = \frac{k_1 k_2 [S][H^+]}{k_{-1} K_a} \quad \ldots[7]$$

The rate is directly proportional $[H^+]$ i.e. the reaction involves only H^+ as the catalyst but not BH^+, the undissociated acid. If $k_{-1}[B]$ is far less than k_2 the rate law becomes.

$$\text{rate} = k_1 [S][BH^+] \quad \ldots[8]$$

The rate is directly proportional t the concentration of the undissociated acid catalyst, BH^+.

15.3 ACID - BASE CATALYSIS - PROTOTROTOPIC MECHANISM:

If the hydrogen ion released, after the products are formed, is taken up by the conjugate base of the acid catalyst, B, the mechanism is called prototropic mechanism.

Scheme-II

$$S + BH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + B \qquad \ldots[A]$$

$$SH^+ + B \xrightarrow{k_2} \text{products} + BH^+ \qquad \ldots[B]$$

Applying the steady state hypothesis with respect to the intermediate, SH^+, one gets

$$\frac{d}{dt}[SH^+] = k_1[S][BH^+] - k_{-1}[SH^+][B] - k_2[SH^+] = 0$$

$$[SH^+] = \frac{k_1[S][BH^+]}{k_{-1}[B] + k_2[B]}$$

rate = rate of formation of products (step B)

$$= k_2[SH^+][B] = \frac{k_2 k_1[S][BH^+]}{k_{-1}[B] + k_2[B]}$$

$$= \frac{k_2 k_1}{k_{-1} + k_2}[S][BH^+] \qquad \ldots[8]$$

The reaction involves the undissociated acid, BH^+ as catalysing species.

15.4 ENZYME CATALYSIS

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products.

Michaelis-Menten Enzyme Kinetics

Enzymes are highly specific catalysts for biochemical reactions, with each enzyme showing a selectivity for a single reactant, or substrate. For example, the enzyme acetylcholinesterase catalyzes the decomposition of the neurotransmitter acetylcholine to choline and acetic acid. Many enzyme–substrate reactions follow a simple mechanism that consists of the initial formation of an enzyme–substrate complex, ES, which subsequently decomposes to form product, releasing the enzyme to react again **(Figure 15.1)**.

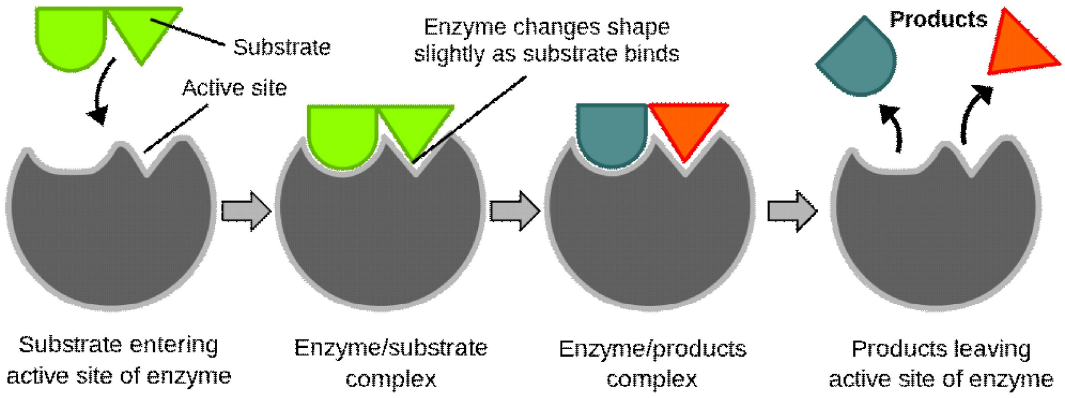


Figure 15.1: An enzyme catalyzes the reaction of two substrates and to form one product.

This is described within the following multi-step mechanism

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

….[1]

where K_1, K_{-1}, K_2, and K_{-2} are rate constants. The reaction's rate law for generating the product [P] is

$$rate = \frac{d[P]}{dt} = k_2[ES] - k_{-2}[E][P]$$

….[2]

However, if we make measurement early in the reaction, the concentration of products is negligible, i.e.,

$$[P] \approx 0$$

….[3]

and we can ignore the back reaction (second term in right side of Equation 2). Then under these conditions, the reaction's rate is

$$rate = \frac{d[P]}{dt} = k_2[ES] \quad \text{....[4]}$$

To be analytically useful we need to write Equation 4 in terms of the reactants (e.g., the concentrations of enzyme and substrate). To do this we use the *steady-state approximation*, in which we assume that the concentration ES of remains essentially constant. Following an initial period, during which the enzyme–substrate complex first forms, the rate at which ES forms

$$\frac{d[ES]}{dt} = k_1[E][S] = k_1([E]_0 - [ES])[S] \quad \text{....[5]}$$

is equal to the rate at which it disappears

$$-\frac{d[ES]}{dt} = k_{-1}[ES] + k_2[ES] \quad \text{....[6]}$$

Where $[E]_o$ is the enzyme's original concentration.

Combining Equations [5] and [6] gives

$$k_1([E]_0 - [ES])[S] = k_{-1}[ES] + k_2[ES] \quad \text{....[7]}$$

which we solve for the concentration of the enzyme–substrate complex

$$[ES] = \frac{[E]_0[S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{[E]_0[S]}{K_m + [S]} \quad \text{....[8]}$$

Where K_m is the **Michaelis constant**. Substituting Equation [8] into Equation [4] leaves us with our final rate equation.

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]} \quad \text{....[9]}$$

Equation [9] is known as Michaelis-Menten Enzyme equation for the formation of products.

When all the enzyme has reacted with the substrate [S] at high concentrations, the reaction will be going on at maximu rate. No free enzyme will remain also that $[E]_o = [ES]$, then from equation [4]

$$r_{maximum} = V_{maximum} = K_2[E]_o \quad \text{....[10]}$$

$V_{maximum}$ is the maximum rate for the catalyzed reaction

Equation [9] can be written as

$$r = \frac{V_{max}[S]}{Km + [S]} \quad \ldots. [11]$$

A plot of Equation [9], as shown in **Figure 15.2**, is instructive for defining conditions where we can use the rate of an enzymatic reaction for the quantitative analysis of an enzyme or substrate.

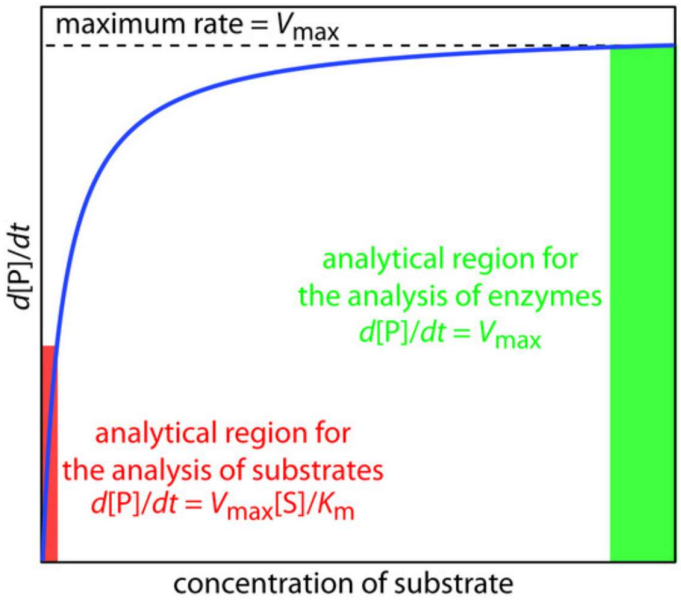


Figure 15.2: Plot of Equation showing limits for the analysis of substrates and enzymes in an enzyme-catalyzed chemical kinetic method of analysis.

Case i),

For high substrate concentrations, where [S] >> K_m, Equation [9] simplifies to

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]} \approx \frac{k_2[E]_0[S]}{[S]} = k_2[E]_0 = V_{max} \quad \ldots[12]$$

where is the V_{max} is the maximum rate for the catalyzed reaction. Under these conditions the reaction is zero-order in substrate and we can use V_{max} to calculate the enzyme's concentration, typically using a variable-time method.

Case ii),

At lower substrate concentrations, where [S] << K_m, Equation [9] becomes

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]} \approx \frac{k_2[E]_0[S]}{K_m} = \frac{V_{max}[S]}{K_m} \quad \ldots.[13]$$

The reaction is now first-order in substrate, and we can use the rate of the reaction to determine the substrate's concentration by a fixed-time method.

The Michaelis K_m constant is the substrate concentration at which the reaction rate is at half-maximum, and is an inverse measure of the substrate's affinity for the enzyme- as a small K_m indicates high affinity, meaning that the rate will approach V_{max} more quickly. The value K_m of is dependent on both the enzyme and the substrate, as well as conditions such as temperature and pH.

From the last two terms in Equation [13], we can express V_{max} in terms of a turnover number (K_{cat}):

$$V_{max} = k_{cat}[E]_o \quad \text{……[14]}$$

Where $[E]_o$ is the enzyme concentration and K_{cat} is the turnover number, defined as the maximum number of substrate molecules converted to product per enzyme molecule per second. Hence, the turnover number is defined as the maximum number of chemical conversions of substrate molecules per second that a single catalytic site will execute for a given enzyme concentration $[E]_o$.

SUMMARY

- To learn about Acid-Base Catalysis.
- To study about Protolytic mechanism and Prototrotopic mechanism.
- To study about enzyme catalysis and kinetics of enzyme catalysis
- method.
- To learn about Michaelis-Menten Enzyme Kinetics.

SELF ASSESSMENT QUESTIONS

1. Explain the kinetic study of acid-base catalysis.
2. Discuss prototropic and protolytic mechanisms.
3. Write the kinetics of enzyme catalysis by Michaelis-Menton equation.

Prof. R. Ramesh Raju

LESSON-16

PHOTO CHEMISTRY - INTRODUCTION TO PHOTO CHEMISTRY; LAWS OF PHOTOCHEMISTRY; QUANTUM YIELD; ACTINOMETRY; PHOTOSENSITIZATION; EXCIPLEX AND EXCIMERS

OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about photochemistry and their laws.
- To study about Quantum yield and Low and High Quantum yields with their determination.
- To study about Actinometry.
- To learn about Photosensitization.
- To know the importance of Exciplex and Excimers in photochemistry.

16.1 INTRODUCTION

Photochemistry is the study of effect of light on the chemical reactions. The light energy used will be in the ultraviolet or visible regions. The effect of higher energy radiations on chemical reactions like the effect of y-rays is a separate discipline called radiation chemistry.

The most important requirement for the light energy to have effect on chemical reactions is that the light energy that is incident on the reactant must be absorbed by the reactant. If the energy of the light radiation is equal to or greater than the bond dissociation energy then the bonds are, in general, homolytically broken resulting in a chemical reaction. In many photochemical reactions, the free radicals forming on homolytic rupture are detectable by spectroscopic (ESR) or other means. If the energy of the light radiation is such that the bonds cannot be broken, the absorbed energy is reemitted in the form of fluorescence or phosphorescence involving no permanent chemical change and hence these phenomena are called photophysical processes.

16.2 LAWS OF PHOTOCHEMISTRY

Photochemistry is concerned with the effect of light energy on chemical reactions the light energy being in the ultra-violet and visible regions (200- 800 nm). The effect of light is felt only if the light is felt only if he light energy is absorbed by the reacting substances and this is governed by certain laws. The first law is the lambert's law, which states that when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of the medium is proportional to the intensity of the radiation.

$$-\frac{dI}{dt} = kI$$

where 't' is the thickness and 'I' is the intensity of radiation after passing through medium.

$$-\int \frac{dI}{I} = \int k\,dt, \quad -\ln I = kt + \text{constant}$$

Assuming that at t=0
$I = I_0$ (the intensity of light before entering the medium)

$$\therefore \ln \frac{I}{I_0} = -kt \quad \text{or } I = I_0 e^{-kt}$$

The intensity of radiation absorbed $= I_0 - I$
$= I_0 - I_0 e^{-kt}$
$= I_0 (1 - e^{-kt})$

Beer's law

According.to this law, when a beam of monochromatic radiation is passed. through a solution of an absorbing substance the rate of decrease in intensity of radiation with thickness is proportional to concentration of the solution and intensity of radiation.

$$-\frac{dI}{dt} = k'IC$$

$$-\int \frac{dI}{I} = \int k'C\,dt$$

or $-\ln I = k' C_t$ + constant of integration if t=0, $I = I_0$ (intensity of radiation before entering the solution). Hence the integration constant is equal to I_0

$$\therefore \ln \frac{I}{I_0} = k'Ct$$

$$\log \left(\frac{I}{I_0}\right) = -\frac{k'}{2.303} C t = -\varepsilon C t$$

$$\text{or } \log \left(\frac{I_0}{I}\right) = \varepsilon Ct = \text{Optical density or absorbance}$$

'ε' represents the molar extinction coefficient which has the units, litr/mol^{-1}/ cm^{-1}. The ratio, I/I_o is called the transmittance (T) and represents the fraction of total light transmitted and it is easy to see that absorbance or optical density is equal to log (l/T).

16.3 QUANTUM YIELD

Quantum yield, also known as quantum efficiency is an important parameter that measures the efficiency of a photochemical reaction.

Quantum yield is defined as the number of molecules reacting per quantum of light absorbed. It is denoted by Φ.

In another word, Quantum efficiency is defined as the number of moles of the light-absorbing substance that react chemically for each einstein of absorbed radiation.
Mathematically, Quantum yield can be expressed as:

$$\Phi = \frac{\text{No.of moles reacting in a given time}}{\text{No.of quanta of light absorbed in the same time}}$$

If the law of photochemical equivalence is true, Φ should have a value of 1. Since the value of Φ may vary from zero to 10^6, It was realized that the law of photochemical equivalence is applicable to the only primary process.

There are two types of photochemical reactions on the basis of quantum yield. One is a high quantum yield reaction and another is a low quantum yield reaction.

High quantum yield
A reaction is said to have a high quantum efficiency if the value of Φ is greater than 1 for that reaction. Let's see some examples of such reactions.

High Quantum Yield Reaction

$$H_2 + Cl_2 \xrightarrow{>4500\ \text{Å}} 2HCl \qquad \text{Quantum yield} = 10^4 \text{ to } 10^6$$

$$CO + Cl_2 \xrightarrow{4000 \text{ to } 4300\ \text{Å}} COCl_2 \qquad \text{Quantum yield} = 10^3$$

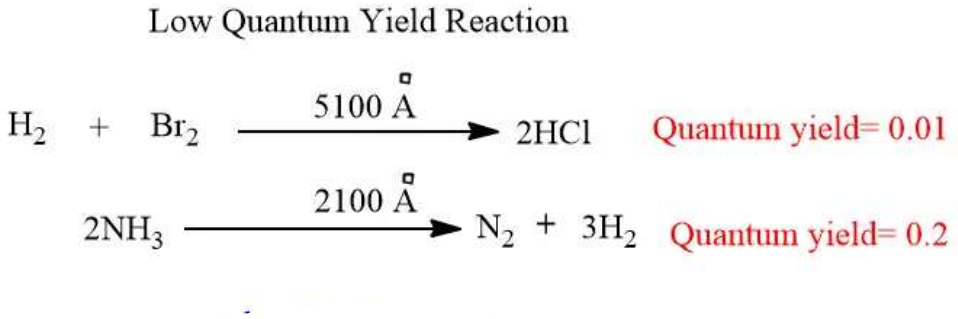
Reasons of high quantum yield

There are some reasons which may be responsible for the high quantum efficiency.

1. The primary process of absorption of radiation produce excited atoms, molecules or free radicals which initiates a series of chain reaction called secondary processes. Thus, by absorbing only one quantum of radiation, several reactant molecules undergo chemical reaction. Hence Φ will be greater than unity.
2. Formation of an intermediate product acts as a catalyst and readily propagate the reaction.
3. The secondary reaction may be exothermic which activates other secondary process as a result more reactant molecules undergo chemical change without absorption of radiation

Low quantum yield

A reaction is said to have a low quantum efficiency if the value of Φ is less than 1 for that reaction. Let's see some examples of such reactions.



Reasons for low quantum yield

Some photochemical reactions are reported to have very low quantum efficiency and the reason for such phenomenon are given below:

1. If excited molecules formed in primary process are such that they can't react due to their deactivation by collisions or by internal arrangement, the quantum yield will be extremely low.
2. Collision of excited molecules with non-excited molecules may cause to loss their energy. This is another cause of low quantum yield.
3. The excited molecules produced in the primary process may recombine to form the reactant to give low quantum yield.
4. If a reacting molecule Is initially present at such a low energy level, so that it does not acquire an optimum energy level to take part in photochemical process by photoexcitation.
5. Some of the photochemically excited molecules in primary process do not undergo secondary reaction. Thus, there is some time interval between primary and secondary process. And they lose some energy. This will give low quantum yield.

16.4 ACTINOMETRY

A device that measures the total amount of incident radiation on sample is called an actinometer, and the measurement method is known as actinometry.

Two types of actinometer are commonly used.

One is Thermopile: It consists of a number of thermocouples connected in series, with their hot junction imbedded at a blackened surface which absorbs almost all the incident light and converts it into heat. Calibrated lamps of known energy are available from National Bureau of Standards. The e.m.f. developed by the Thermofile is measured with the standard lamp and then with the source of radiation of unknown intensity. The reaction vessel is mounted between Thermofile and the light, and the radiation absorbed by the reacting system is measured by the difference between filled and empty. Instead of Thermofile, it is possible to employ relative methods of actinometry, which is based on chemical change produced. One of the most reproducible reaction is the decomposition of oxalic acid photosensitized by Uranyl salts. Uranyl ion UO^{++} absorbs radiation from 250 nm to 450 nm, becoming an excited ion $(UO^{++})^*$, which decomposes oxalic acid. This reaction has quantum yield ($\boldsymbol{\phi}$) 0.50

$$UO_2^{++} + h\nu \longrightarrow (U_2O^{++})$$

$$(UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO_2 + H_2O + CO$$

The oxalic acid concentration is easily followed by titration with permanganate. A quartz vessel filled with the uranyl oxalate mixture can be used exactly like the thermopile, the light absorbed being calculated from the oxalic acid decomposed and the known quantum yield.

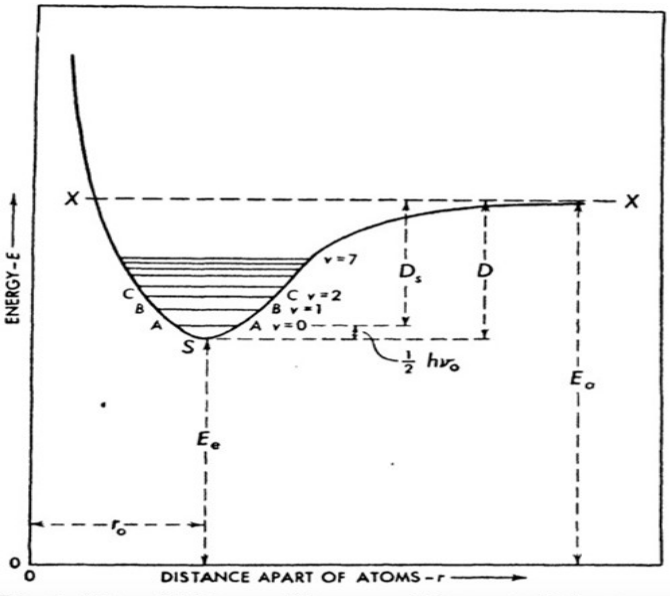


Fig. 4. Potential Energy Diagram of Diatomic Molecule

Potential energy diagram of diatomic molecule

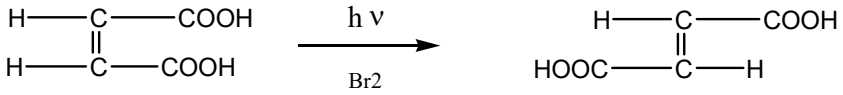
16.5 PHOTOSENSITIZATION

Certain reactions are known which are not sensitive to light. These reactions can be made sensitive by adding a small amount of foreign material which can absorb light and stimulate the reaction without itself taking part in the reaction such as added material is known as Photosensitizer and the phenomena as Photosensitization.

Role played by a Photosensitizer

The formation of a photosensitizer is to absorb light, become excited and then pass on this energy to oner of the reactants and there by activate them for rection, without itself taking part in the reaction. Thus, a Photosensitizer acta as a carrier of energy.

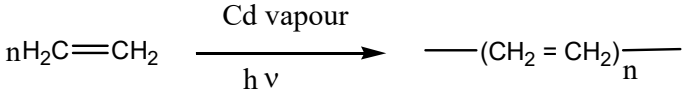
Example: 1) Bromine acts as a Photosensitizer, in the conversion of maleic acid to fumaric acid.



Malic acid
(Cis form)

Fumaric Acid
(Trans form)

2) cadmium vapour acts as a photosensitizer for the polymerization of ethylene for the decomposition of ethane.



16.6 EXCIPLEX AND EXCIMERS

Exciplex and excimer are excited states of some chemical reactions in organic chemistry.

An exciplex (or excited complex) is a complex formed between two different conjugated molecules (monomers) when one of which is in an excited state. This short-lived complex will occur when the monomers are near one another, and it results in a lower energy than if the two existed separately. What makes exciplexes unique is that the two monomers would not form a complex if both were in the ground state. They can therefore only form if the monomers interact before the excited one has time to relax.

If the two monomers are of the same species, the complex is instead called an excimer (excited dimer). An excimer can be described as a short-lived dimeric or heterodimeric molecule that forms from two species where at least one species has a valence shell with a completed electron configuration. The term excimer stands for “excited dimer.” Often, excimers are diatomic, and these consist of two atoms or molecules that do not bind if both species are in the ground state.

Typically, the lifetime of an excimer is very short, and it is measured on the nanoseconds scale. Moreover, if many excited atoms are bonded, it forms Rydberg matter clusters, and its lifetime can increase by many seconds.

When considering the formation of this state, a typical ground-state molecule has electrons in the lowest possible energy level; at most, only two electrons occupy a given orbital where two electrons are of opposite spin states. HOMO is the highest occupied molecular orbital,

while LUMO is the lowest unoccupied molecular orbital. These two orbitals have an energy gap, and the absorption of light with the same energy as of the energy gap can cause the formation of a molecule's excited state. An excimer is formed when the dimer components are in the excited state.

Exciplex:

Exciplex is a short-lived molecule in the excited state that is formed from more than two species. Therefore, it is an excited state complex that forms between a molecule that donates electrons and one that accepts electrons.

Generally, these complexes are of interest for the favourable light-emission properties they have. We can understand exciplex emission from potential energy diagrams of exciplex-forming species. An excimer is also a type of exciplex and contains only two species forming the complex molecule.

Since there are more than two monomers in an exciplex, it is highly unstable and has a very short-lived nature compared to other types of excited states such as excimers.

Theory

When one molecule is in an excited state, it is possible for two conjugated molecules (monomers) in close proximity to form an excited dimer complex. When the two monomers are the same species, the complex is called an excimer (excited dimer); when they are different, the complex is known as an exciplex (excited complex).

This process can be described by:

$$A + B^* \rightarrow (AB)^*$$

Here, A and B are monomers and * denotes an excited state. In the case of an excimer, A=B, whereas for an exciplex, A≠B.

When both monomers are in the ground state, electronic interactions between them are not possible as all orbitals are completely full. Therefore, the monomers are repulsive due to Coulomb interactions. However, when one of them is in the excited state, interactions with the orbitals of the ground state monomer stabilise the excited state monomer, leading to a lower energy state as well as an attraction between the molecules. This is usually facilitated by π-π stacking, the mutual attraction between aromatic rings.

As the excimer/exciplex is of a lower energy than the monomer, when it relaxes back to the ground state, the photon emitted is of lower energy then the emission of the monomer. Hence, it is redshifted. In addition to this redshift, the excimer/exciplex emission is also broad and featureless (no transitions to vibrational states). This is because the exciplex ground state is very unstable and the two ground state monomers are repulsive, giving a continuum of emission energies. The diagram below illustrates how the energy of the system varies with the separation of the monomers A and B.

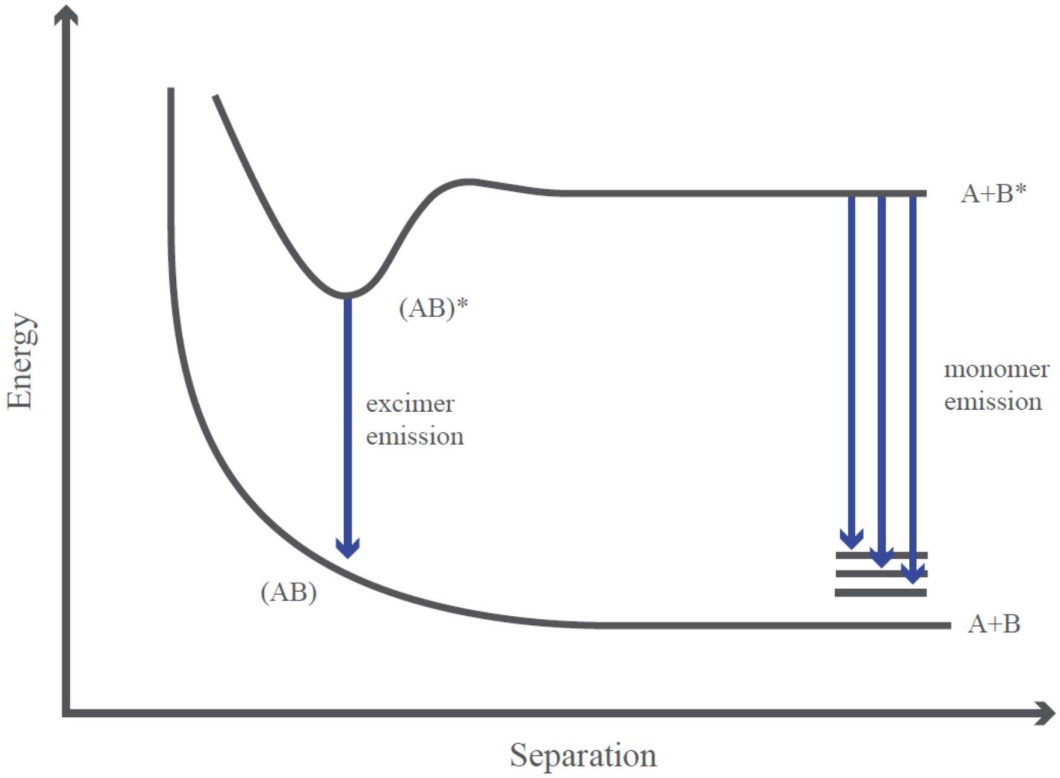


Diagram illustrating the energy of an excimer/exciplex system.

In the above diagram, you can see that when the separation between A and B* is sufficiently small, the total energy of the system is lower. Any emission from this state will therefore be redshifted compared to the monomer emission. In addition to this, the emission is broader due to the unstable nature (no energy well) of the ground-state excimer, and featureless due to the lack of excimer vibrational states.

Excimer/exciplex formation depends heavily on the density of the molecules. If the density is too low, the excited state will relax back down to its ground state before encountering another monomer. Therefore, exciplex emission will increase as the density is increased and emission from the monomer will be reduced. Excimers/exciplexes are generally formed in solutions due to the high likelihood of collisions between monomers. Although collisions are not possible in the solid state, in the crystalline form stacking can occur. This leads to excimers when one molecule is excited. Similarly, in amorphous solids, molecules that are near one another can result in excimers.

SUMMARY:

- To learn about photochemistry and their laws.
- To study about Quantum yield and Low and High Quantum yields with their determination.
- To study about Actinometry.
- To learn about Photosensitization.
- To know the importance of Exciplex and Excimers in photochemistry.

SELF ASSESSMENT QUESTIONS

1. Discuss the actinometry.
2. Discuss in detail about Exciplex and Excimers in photochemistry.
3. Explain the terms of photosensitization.
4. Define Quantum yield? Explain low and high quantum yield with their determination.

Prof. R. Ramesh Raju

CHAPTER - 17
PHOTOCHEMICAL EQUILIBRIUM; CHEMILUMINESCENCE; QUENCHING; KINETICS OF COLLISIONAL QUENCHING - STERN - VOLMER EQUATION; PHOTO GALVANIC CELLS

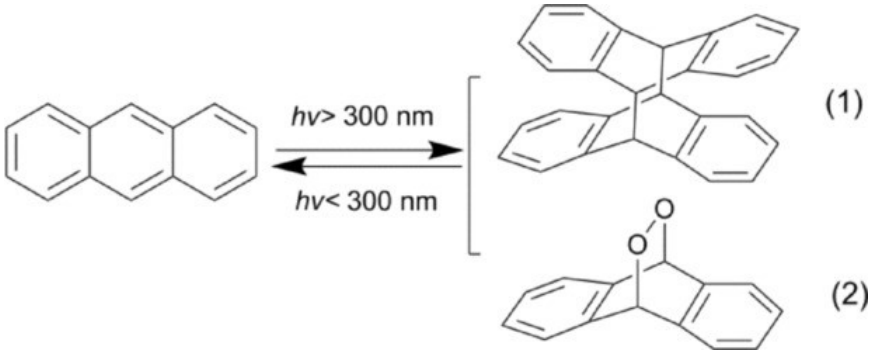
OBJECTIVES:

After studying this lesson, you should be able to:

- To learn about the Photochemical Equilibrium.
- To know about the Chemiluminescence.
- To study about Quenching and their types.
- To study about Kinetics of collisional quenching using Stern - Volmer Equation.
- To learn about photo galvanic cells with their mechanism.

17.1 PHOTOCHEMICAL EQUILIBRIUM (OR) PHOTOSTATIONARY STATE

Absorbed light has an interesting effect on a system in chemical equilibrium. The absorption of light by a reactant can increase the rate of the forward reaction without directly influencing the rate of the reverse reaction; this disturbs the equilibrium. The concentration of products increases somewhat, increasing the rate of the reverse reaction. In this way the rates of the forward and reverse reaction can be brought into balance with the system This new state in not an equilibrium state but a stationary state, called a Photostationary state. The dimerization of anthracene offers a convenient example, The reaction



occurs upon irradiation of a solution of anthracene by ultraviolet solution. The plausible mechanism of the dianthracence formation is

$$A + h\nu \longrightarrow A^* \qquad Rate = I_a$$

$$A^* + A \xrightarrow{k_2} A_2$$

$$A^* \xrightarrow{k_3} A + h\nu'$$

$$A_2 \xrightarrow{k_4} 2A$$

The net rate of formation of A_2 is

$$\frac{d[A_2]}{dt} = k_2[A][A^*] - k_4[A_2]$$

In the steady state,

$$\frac{d[A^*]}{dt} = I_a - k_2[A^*][A] - k_3[A^*] = 0$$

$$[A^*] = \frac{I_a}{k_2[A] + k_3}$$

In the Photostationary state we have additional requirement that,

$$\frac{d[A_2]}{dt} = 0$$

$$or \;\; k_2[A][A^*] - k_4[A_2] = 0$$

$$or \;\; [A_2] = \frac{k_2[A][A^*]}{k_4}$$

$$or \;\; [A_2] = \frac{k_2[A]}{k_4} \quad \frac{I_a}{k_2[A] + k_3}$$

$$or\,[A_2] = \frac{1}{k_4} \quad \frac{I_a}{\frac{k_2[A] + k_3}{k_2[A]}}$$

$$or \;\; [A_2] = \frac{1}{k_4} \quad \frac{I_a}{1 + \frac{k_3}{k_2[A]}}$$

If the concentration of monomer [A] is very high, then

$$1 + \frac{k_3}{k_2[A]} \approx 1 \qquad [A_2] = \frac{I_a}{k_4}$$

The concentration of diantharcene is independent of monomer concentration and for the usual equilibrium $[A_2] = K[A]^2$.

17.2 CHEMILUMINESCENCE

Chemiluminescence may be defined as emission of light radiation as a result of chemical reaction at temperatures when light rays are not normally expected. The chemiluminescence is due to formation of products in excited state and when they return to ground state _they emit light.

A classical example is that when atomic hydrogen comes into contact with mercury surface, blue luminescence appears with a resonance line at 2537 A characteristic of mercury along with band spectrum due to HgH. The process may be explained according to the following mechanism. Hg H is formed which acts as a third body for combination of H atoms and the excited Hg H is formed.

Chemiluminescence is also observed when alkali metal vapours react with halogens and with organic halides and low pressures. In order to account for the observation it is necessary to postulate/that Na_2 molecule combine with CI atoms which liberates sufficient energy to excite NaCl molecule which then excites sodium atom.

$$\mathbf{Hg\text{-}H + H\text{-}H \rightarrow Hg\text{-}H^* + H_2}$$

$$\mathbf{Hg\text{-}H + Hg\text{-}H^* \rightarrow Hg + H_2 + Hg\ (\beta P_1)}$$

The excited Na* atom emits its characteristic spectrum.

$$NaCl^* + Na \rightarrow NaCl + Na^*$$

Grignard reagents emit chemiluminescence when they are oxidized by air in ethereal solution. The luminescence is greenish blue and contains a single broad band. Only Grignard reagents in which magnesium atom is attached to unsaturated carbon atom are chemiluminescent in solution but in solid state both aliphatic and aromatic compounds exhibit this phenomenon.

Another classical reaction is the oxidation of 5-aminophthalic hydrazide with hydrogen peroxide in which chemiluminescence is observed.

Bioluminescence: This is due to biochemical reaction. The intensity of the emitted radiation is weak and the spectra observed are broad and
structureless. The intensity varies with time.

Example: The oxidation of protein luciferin in presence of enzyme luciferase in fireflies, produces excited complex. Once it falls back down to a ground state a photon is released.

$$Luciferin + O' + ATP \rightarrow Oxyluciferin + ADP + PPi + Light$$

Bioluminescence is due to chemiluminescence in biological reactions most well-known among which is the oxidation of luciferin by atmospheric oxygen in the presence of the enzyme luciferase.

Luminescence:
It is generally observed that when a metal is heated to a high temperature, it initially becomes red hot and then white. Here light is emitted by the application of heat.

But if the emission of radiation occurs from a body by the application of agencies other than heat that phenomenon is called luminescence.

E.g: Fluorescence, phosphorescence.

17.3 QUENCHING

Fluorescence quenching refers to any process which decreases the fluorescence intensity of any sample or may stopped the fluorescence from any sample. A variety of molecular interaction can result in quenching. These include excited-state reactions, molecular rearrangement, energy transfer, ground-state complex formation, and collisional quenching.

If the excited molecule undergo collision with another molecule the fluorescence will be quenched., i.e. the intensity of the emitted radiation for fluorescence may be reduced or stopped. The quenching of fluorescence is due to transfer of energy from the excited molecule to that one with which it collides. At low pressure, the number of molecule per unit area is small and the excited molecule take longer time to collide with other molecule. In that case excited molecule releases excess energy as fluorescence. But when the pressure increases, the number of molecule per unit area increases, therefore, the probability of collision is higher. In that case appreciable quenching of fluorescence is observed. In case of liquid collisions are very frequent due to presence of large number of molecule per unit area. The quenching of fluorescence is appreciable.

Types of quenching:

1) Dynamic or collisional quenching:

The collisional encounter between fluorophore and quencher decreases the intensity of radiation of the emitted photon for fluorescence, this type of quenching process is known as dynamic or collisional quenching.

2) Static quenching:

Quenching can occur as a result of the formation of a nonfluorescent complex between fluorophore and quencher without presence of any excitation light source. When this complex absorbs light, it immediately returns to the ground state with emission of a photon.

17.4 KINETICS OF COLLISIONAL QUENCHING - STERN - VOLMER EQUATION

The medium may also contain molecules or ions which colliding with the excited state will extract the energy and deactivate them. This may involve transient formation of complex between the excited state and the quencher. The mathematical relation showing the effect of quencher on the intensity of fluorescence has been derived by Stern and Volmer and is called the Stern-Volmer equation. The following scheme represents the various processes involved.

$S_0 \xrightarrow{h\upsilon} S_1$ Rate of excitation = I (intensity of light)

$S_1 \xrightarrow{k_{IC}} S_0 + \text{heat}$

$S_1 \xrightarrow{k_{ISC}} T_1$

$S_1 \xrightarrow{k_f} S_0 + h\upsilon'$

In the scheme, molecule in ground state, excited singlet state and triplet state is denoted as S_o, S_1 and T_1. k_{ISC} and k_f refer to rate constants of internal conversion, intersystem crossing and fluorescence emission.

The concentration of the molecules in the excited state $[S_1]$ is calculated by applying steady state approximation with respect to the excited state S_1.

According to this $\frac{d[S1]}{Dt} = 0$ = rate formation -rate of removal

Rate of formation is equated to the intensity of incident light, I and rate of removal = $(k_{IC}[S_1] + k_{ISC}[S_1] + K_f[S_1]$

i.e. $I - k_{IC}[S_1] + k_{ISC}[S_1] + K_f[S_1] = 0$

or

$$S_1 = \frac{1}{k_{IC} + k_{ISC} + K_f}$$

$$\text{Rate of fluorescence} = k_f [S_1] = \frac{K_f I}{k_{IC} + k_{ISC} + k_f}$$

The quantum yield of fluorescence

$$\phi_o = \frac{\text{rate of fluorescence}}{\text{Intensity}} = \frac{k_f}{k_{IC} + k_{IC} + k_f}$$

In the presence of quencher, the step $S_1 + Q \xrightarrow{hQ} S_0 + Q + \text{heat}$ is to be added to this scheme.

$$S_o + h_0 \longrightarrow S_1$$

$$S_1 \xrightarrow{h_{IC}} S_0 + \text{heat}$$

$$S_1 \xrightarrow{h_{ISC}} T_1$$

$$S_1 \xrightarrow{h_f} S_0 + h\upsilon'$$

$$S_1 + Q \xrightarrow{k_Q} S_0 + Q + \text{heat}$$

$$\frac{d[S_1]}{dt} = 0 = I - (k_{ISC} + k_{ISC} + k_f + k_\varphi[\varphi]$$

$$\text{or } [S_1] = \frac{I}{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}$$

Where [φ] is the concentration of quencher

$$\text{Rate of fluorescence} = k_f[S_1] = \frac{k_f f}{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}$$

$$\text{Quantum yield in the presence of quencher } \varphi = \frac{\text{rate of fluorescence}}{\text{Intensity}}$$

$$= \frac{k_f f}{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}$$

The quantum yield, Φ, is determined in the presence of different concentrations of quencher and Φ_0/Φ is calculated in each case and plotted against [Φ]

$$\frac{\phi_u}{\phi} = \frac{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}{k_{IC} + k_{IS} + _f}$$

$$= 1 + \frac{k_\varphi[\phi]}{k_{IC} + k_{ISC} + k_f}$$

The above equation is called Stern-Volmer equation. A straight line is obtained with slope equal to $K_\Phi / k_{IC} + k_{ISC} + K_f$ and intercept equal to unity.

$K_\Phi / (k_{IC} + k_{ISC} + K_f)$ is called Stern-Volmer constant

$\frac{1}{k_{IC} + k_{ISC} + K_f}$ is equal to life time of the excited state in the absence of quencher. The rate constant k_Φ is a function of ionic strength and when Bronsted equation is applied one gets

$$\log k_\varphi = \log k_Q^0 + 0.5\,\delta Z^2 \sqrt{\mu}$$

Where $\Delta Z^2 = Z^2_{A\varphi} - (Z^2_A + Z^2_\varphi]$

$Z_{A\varphi}$ is Z_A are Z_φ being the charges of Aφ, A and φ respectively.

17.5 PHOTO GALVANIC CELLS

Photo galvanic cells operate based on photoelectrochemical principles. They involve two inert electrodes and dye solution as electrolyte. The light is absorbed by the electrolyte, for instance a dye solution and an electron transfer occurs between the excited dye molecules and electron donor or acceptor molecules added to the electrolyte These pairs induce redox reactions at the interface with the electrolyte, resulting in a current flow.

Photo galvanic cells, also known as photoelectrochemical cells, operate on a different principle compared to photovoltaic cells. They utilize light-induced redox reactions in solution to generate electrical current. Here's how they work:

a. Inert Electrodes: Photo galvanic cells consist of two inert electrodes in contact with an electrolyte solution.
b. Dye solution: Photo galvanic cell contain dye solution as electrolyte. When light (photons) of sufficient energy strikes one of the inert electrode surface contacted with electrolyte, it excites electrons within the electrolyte (Dye), creating redox species.
c. Redox Reactions at the Interface: The excited electrons can migrate to the electrode-electrolyte interface, where they participate in redox (oxidation-reduction) reactions with species in the electrolyte solution.
d. Generation of Photocurrent: The redox reactions in the solution lead to movement of charge carriers constitutes a photocurrent that flows through an external circuit.

Materials for Photo galvanic Cells:
Often employ inert electrode (such as platinum electrode and saturated calomel electrode) along with specific electrolytes that facilitate redox reactions.

Electrode Materials:
Platinum electrode: Photo galvanic cells often use first metal electrode such as platinum electrode. This electrode has specific dimension (1cm2, 2cm2 etc.) and facilitate charge separation and transfer.

Saturated calomel electrode: Photo galvanic cells often use second electrode such as saturated calomel electrode (SCE) with different molar inner solution (KCl).

***Other electrode*:** Depending on the specific design and application, graphite electrode is also use.

Electrolyte:

***Dye Aqueous Solutions without surfactant*:** Photo galvanic cells require an electrolyte that can facilitate redox reactions. This can be an ionic liquid or an aqueous solution containing redox-active species. This is generally prepared with Dye (Toluidine Blue, Malachite Green etc.) and reductant (Carbohydrates, Acids, etc.) alkaline mixture.

Dye Aqueous Solutions with surfactant: Sometimes, surfactants such as NaLS, CTAB etc., are added to the electrolyte to avoid the dye coagulation and the electrolyte, enhancing overall cell performance.

Mechanism of Electricity Generation:

The photogalvanic cells are based on some chemical reaction, which give rise to high energy products on excitation by a photon. In photogalvanic cells the photochemical changes occur in the electrolyte. It is, therefore, more easily identifiable and the storage capacity of the cell can be large. On the other hand, in photovoltaic / photoelectrochemical cell photochemical changes take place in the surface layers of the electrode (illuminated).

Mechanism:

Light Absorption:

o Light is absorbed by a photosensitive dye or a light-sensitive redox couple in the electrolyte solution.

o This absorption causes the dye molecules to transition from a ground state to an excited state.

Excitation and Electron Transfer:

* The excited dye molecule transfers an electron to an acceptor species in the solution, creating a reduced form of the acceptor and an oxidized form of the dye.

* This results in the generation of a photo-induced voltage (photovoltage).

Electrochemical Reactions at Electrodes:

At the anode, the oxidized dye or the product of the oxidation process releases an electron to the external circuit, moving towards the cathode.

The electrons flow through the external circuit to do electrical work.

Regeneration:

o At the cathode, the reduced acceptor is oxidized, and the electron is transferred back to the dye, regenerating its ground state.

o This process closes the circuit and allows continuous generation of electrical energy as long as light is available.

Overall Reaction:

o The overall reaction involves the conversion of light energy into a separation of charges that can drive an external current.

o Photo galvanic cells are often limited by the kinetics of the redox reactions and the recombination of charges within the cell.

Advantages and Challenges:

Photo galvanic Cells: Potential advantages in flexibility, scalability, and lower manufacturing costs, but current efficiencies are typically lower than traditional photovoltaic technologies, and stability over extended periods remains a challenge.

SUMMARY:

- To learn about the Photochemical Equilibrium.
- To know about the Chemiluminescence.
- To study about Quenching and their types.
- To study about Kinetics of collisional quenching using Stern - Volmer Equation.
- To learn about photo galvanic cells with their mechanism.

SELF ASSESSMENT QUESTIONS

1. Write a note Chemiluminescence.
2. Discuss in detailed about the derivation of Stern - Volmer Equation.
3. Write a note on photogalvanic cells.
4. Write about Photochemical Equilibrium.

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Prof. R. Ramesh Raju

LESSON-18

ENERGETICS AND STRUCTURAL ASPECTS OF BIOPOLYMERS

OBJECTIVES:

After studying this lesson, you should be able to:

- Study the concept of standard free energy change (ΔG°) and its significance
- Discuss the structure of ATP and analyze how its hydrolysis provides energy for cellular processes
- Identify various chain configurations of biopolymers
- Calculate the average dimensions of biopolymer chains using statistical models.

STRUCTURE:

18.1 INTRODUCTION

Biopolymers such as proteins, nucleic acids, and polysaccharides are essential macromolecules that form the structural and functional framework of all living cells. Understanding their **energetics and structural aspects** is fundamental to biophysical chemistry.

The **energetics** of biopolymers deals with the flow and transformation of energy in biological systems. It explains how biochemical reactions occur spontaneously or require energy input, governed by parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). Processes like **ATP hydrolysis** and **energy coupling** are key examples that illustrate the role of energy in sustaining cellular functions.

The **structural aspects** of biopolymers involve the study of their molecular configuration, conformation, and stability. The unique three-dimensional arrangement of atoms in a biopolymer determines its biological role—such as enzyme activity, DNA replication, or membrane transport. Intermolecular forces like hydrogen bonding, hydrophobic interactions, and van der Waals forces play crucial roles in maintaining these structures. Thus, the combined study of energetics and structure provides insight into how biopolymers achieve their specific functions through a balance of energy and molecular organization.

18.2 Standard Free Energy Change

The energy required for anabolism and the energy liberated in catabolism are all on account of chemical changes in the organism. Every chemical substance has a certain amount of energy built into it which is the energy of the chemical bonds holding the atoms together. This is described as the free energy of that substance.

18.2.1 DEFINITION

The standard free energy change ($\Delta G^{\circ\prime}$) is the change in Gibbs free energy when a biochemical reaction occurs under standard biological conditions. It predicts whether a reaction is spontaneous, non-spontaneous, or at equilibrium under those conditions.

$\Delta G^{\circ\prime} = -RT \ln K'eq$

where:

- $\Delta G^{\circ\prime}$ = Standard free energy change (kJ mol^{-1})
- R = Gas constant = 8.314 J mol^{-1} K^{-1}
- T = Temperature (usually 298 K)
- K′eq = Apparent equilibrium constant at pH 7

18.2.2 STANDARD BIOCHEMICAL CONDITIONS ($\Delta G^{\circ\prime}$)

Parameter	Chemical Standard (ΔG°)	Biochemical Standard ($\Delta G^{\circ\prime}$)
Temperature	25°C (298 K)	25°C (298 K)
Pressure	1 atm	1 atm
Solute concentration	1 M	1 M
pH	0 ($[H^+] = 1$ M)	7 ($[H^+] = 10^{-7}$ M)

$\Delta G^{\circ\prime}$ is used in biochemistry instead of ΔG° because most biochemical reactions occur around pH 7.

18.2.3 RELATION BETWEEN ΔG AND $\Delta G^{\circ\prime}$

The actual free energy change (ΔG) depends on the actual concentrations of reactants and products in the cell:

$\Delta G = \Delta G^{\circ\prime} + RT \ln([\text{products}]/[\text{reactants}])$

- $\Delta G^{\circ\prime}$ indicates the tendency of the reaction under standard conditions.

• ΔG indicates the spontaneity of the reaction under actual cellular conditions.
At equilibrium, ΔG = 0, so: ΔG°′ = -RT ln K′eq.

18.2.4 INTERPRETATION OF ΔG°′

Interpretation table:

ΔG°′ Value	Reaction Type	Nature
ΔG°′ < 0	Exergonic	Spontaneous (energy released)
ΔG°′ > 0	Endergonic	Non-spontaneous (energy absorbed)
ΔG°′ = 0	—	Reaction at equilibrium

18.3 EXERGONIC AND ENDERGONIC REACTIONS

18.3.1 Definitions

Exergonic Reactions

Reactions that release free energy (ΔG°′ < 0).
Nature: Spontaneous; products have lower free energy than reactants.
Example: ATP + H_2O → ADP + Pi, ΔG°′ = –30.5 kJ mol^{-1}.

Endergonic Reactions

Definition: Reactions that require energy input (ΔG°′ > 0).
Nature: Non-spontaneous; products have higher free energy than reactants.
Example: Glucose + Pi → Glucose-6-phosphate, ΔG°′ = +13.8 kJ mol^{-1}.

18.3.2 Coupled Reactions in Biochemistry

Many endergonic reactions are driven by coupling them with exergonic reactions, especially ATP hydrolysis, to make the overall process spontaneous.
Overall $\Delta G^{\circ\prime} = \Delta G^{\circ\prime}_1 + \Delta G^{\circ\prime}_2$

18.3.3 Summary Table

Type	ΔG°′ Sign	Spontaneity	Energy Flow	Example
Exergonic	Negative	Spontaneous	Energy released	ATP → ADP + Pi
Endergonic	Positive	Non-spontaneous	Energy absorbed	Glucose → Glucose-6-phosphate

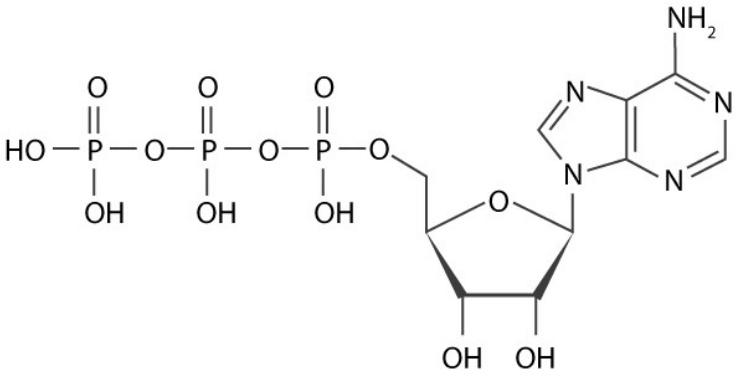
18.4 HYDROLYSIS OF ATP

Adenosine triphosphate or ATP is the energy currency of the cell. ATP hydrolysis releases the energy present in the high-energy terminal phosphate bonds, which is utilized to carry out various cellular reactions, such as muscle contraction, carbon fixation, etc. Various reactions are coupled with ATP hydrolysis.

ATP hydrolysis is an exergonic process. It produces ADP (Adenosine diphosphate), Pi (inorganic phosphate) and energy. ADP can undergo further hydrolysis in some cases to produce AMP (Adenosine monophosphate) and Pi.

18.4.1 ATP Structure

ATP is ribonucleic acid. It is made up of a nitrogenous base, pentose sugar and phosphate. In ATP, the nitrogenous base is adenosine and the sugar is ribose, which is linked to phosphate.



18.4.2 ATP Hydrolysis

The terminal phosphoanhydride bonds are known as high-energy bonds. They release a large amount of energy on hydrolysis to power the energy-requiring cellular processes.

The reaction of ATP hydrolysis is as follows:

$ATP + H_2O \leftrightharpoons ADP + Pi + Energy$

This reaction is reversible. The reversible reaction requires energy to produce ATP. ADP and Pi regenerate ATP. Thus, energy gets stored in the form of ATP and when energy is required, ATP is hydrolysed. The reverse reaction of ATP hydrolysis or the reaction for ATP synthesis is as follows:

$ADP + Pi + Energy \leftrightharpoons ATP + H_2O$

The enzyme ATP synthase catalyses the synthesis of ATP.

18.4.3 Energy Output in ATP Hydrolysis

The hydrolysis of 1M of ATP into ADP and inorganic phosphate, releases −7.3 kcal/mol of energy. The energy released in the living cell is almost double the value in standard conditions, it is equal to −14 kcal/mol.

$ATP + H_2O \rightarrow ADP + Pi\ \Delta G° = -7.3$ kcal/mol (−30.5 kJ/mol)

The hydrolysis of ATP into AMP and pyrophosphate (PPi) releases −10.9 kcal/mol of energy.

$ATP + H_2O \rightarrow AMP + PPi\ \Delta G° = -10.9$ kcal/mol (−45.6 kJ/mol)

18.4.4 Significance of ATP Hydrolysis

Energy is stored in the form of ATP in living organisms. Most ATP is produced during respiration. The energy released by the oxidation of carbohydrates and respiratory substrates is trapped and stored in the form of ATP, which can later be utilised as and when the requirement arises.

The energy released during ATP hydrolysis is utilised to power the cellular processes. There are many processes that require energy, such as muscle contraction, active transport, cell signalling, DNA RNA synthesis, etc.

There are many reactions that are coupled to ATP hydrolysis. These reactions are endergonic, i.e. they require energy. An example of reaction coupling is phosphorylation, e.g. glucose to glucose 6 phosphate catalysed by the enzyme hexokinase in the glycolysis process. The phosphate group released in ATP hydrolysis is used to phosphorylate glucose. Sodium-potassium pump is another example where ATP hydrolysis is coupled to the change of shape of transport proteins, leading to transport of ions across the membrane.

18.5 Thermodynamics of biopolymer solutions

The thermodynamics of biopolymer solutions is governed by the principles of entropy and enthalpy changes, which determine the spontaneity of the dissolution process through the Gibbs free energy equation. Factors such as the large size of biopolymers, intermolecular interactions (ionic, hydrophobic, or specific binding), and solution composition influence the equilibrium between dissolved and aggregated states, affecting properties like solubility and phase separation. Theories like the Flory-Huggins theory provide a framework for understanding these complex systems by considering polymer-solvent interactions and excluded volume effects.

The behavior of biopolymer solutions is characterized by several key thermodynamic functions:

Spontaneity: A process is spontaneous if the change in Gibbs free energy (ΔG) is negative. This is determined by the balance between the change in enthalpy (ΔH) and the change in entropy (Δs), according to the equation

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

Enthalpy and Entropy: The overall change in Gibbs free energy depends on the enthalpy of mixing and the entropy of mixing (randomness). For biopolymers, dissolution often involves a large positive entropy change due to increased disorder, which can overcome an unfavorable enthalpy change.

Gibbs Free Energy (ΔG): Determines the spontaneity of mixing or conformational change.
$\Delta G = \Delta H - T\Delta S$
A negative ΔG indicates a spontaneous process.

Enthalpy (ΔH): Represents heat exchange due to interactions between polymer and solvent molecules.
Exothermic ($\Delta H < 0$) — favorable interactions (e.g., hydrogen bonding)
Endothermic ($\Delta H > 0$) — unfavorable interactions (e.g., hydrophobic hydration)

Entropy (ΔS): Associated with disorder changes upon dissolution or folding.
- Polymer chain flexibility contributes positively to entropy.
- Water structuring around hydrophobic regions decreases entropy.

18.6 CHAIN CONFIGURATION OF BIOPOLYMERS

Biopolymer chains have configurations that can be linear, branched, or cross-linked, formed from repeating monomer units. These chains can organize into hierarchical structures, including primary (monomer sequence), secondary (local molecular shape), and tertiary (three-dimensional) structures, which are determined by the specific monomers and their bonding.

18.6.1 Types of chain configurations

- Linear: Monomers are linked together in a single, unbranched chain. Examples include cellulose and chitin.
- Branched: The main polymer chain has side chains branching off from it. Some biopolymers can be branched.
- Cross-linked: Multiple polymer chains are linked together to form a network. This can involve covalent bonds or other strong interactions.

18.6.2 Examples in Biopolymers

Proteins: Chains of L-amino acids form specific configurations that enable α-helix or β-sheet conformations.

Nucleic Acids (DNA/RNA): Sugar–phosphate backbone with β-D-configuration in ribose/deoxyribose; base-pairing leads to helical structures.

Polysaccharides: The α- or β-linkages in monosaccharides determine whether the polymer forms coils (starch) or straight fibers (cellulose).

18.6.3 Importance

Determines **secondary and tertiary structures** of biomolecules.

Affects **solubility, flexibility, and biological activity**.

Plays a vital role in **molecular recognition** (enzyme–substrate binding, DNA–protein interactions).

18.7 CALCULATION OF AVERAGE DIMENSIONS OF BIOPOLYMER CHAINS

Biopolymers such as proteins, nucleic acids, and polysaccharides are **macromolecular chains** made of repeating monomeric units connected by covalent bonds. Due to the random rotation of bonds and flexibility of chains, the polymer does not have a fixed length — instead, we describe it using **average dimensions** that represent the chain's overall size in solution.

18.7.1 Average dimensions

Most of natural polypeptide chains contain between 50 and 2000 amino acid residues and are commonly referred to as proteins. The molecular weight of most proteins lies between 5.5 KDa and 220 KDa. Though chemically DNA and RNA are similar, DNA and RNA differ in size. Molecules of DNA are enormous. They have molecular weight of upto 150 billion and length of 4 to 12 cm when stretched out, and they are found mostly in the nucleus of cells. In contrast,

molecules of RNA are much smaller as low as 35 KDa in molecular weight and are found mostly outside the cell nucleus.

18.7.2 Random Coil Model

In dilute solution, a flexible polymer chain behaves like a **random coil** due to free rotation around single bonds. If the polymer has *n* bonds of equal length *l*, the **end-to-end distance (r)** varies due to random orientations. The average dimensions of biopolymers can be calculated using the root-mean-square end-to-end distance formula for simplified models, like the freely jointed chain model, which is given by $R_{rms} = b\sqrt{N}$, where b is the bond length and N is the number of bonds. For a more realistic or complex biopolymer, advanced methods like dynamic light scattering (DLS) or computational simulations (e.g., molecular dynamics) are used to determine average dimensions such as radius of gyration and hydrodynamic radius.

18.8 SUMMARY

The energetics and structure of biopolymers are interrelated aspects that

- Study the concept of free energy change, exergonic and endegonic reactions with examples.
- Discuss the structure of ATP and analyze how its hydrolysis provides energy for cellular processes
- Define the dynamic behavior of biological macromolecules and understanding these principles provides insights into how life processes are maintained through molecular organization and energy regulation.

18.9 TECHNICAL TERMS

Free energy change, ATP, Thermodynamics, Bio-polymers, Chain configurations, Average dimensions.

18.10 SELF ASSESSMENT QUESTIONS

1. What is meant by standard free energy change (ΔG°), and how is it related to the spontaneity of a biochemical reaction?
2. Distinguish between exergonic and endergonic reactions with suitable biological examples.
3. Explain the role of ATP hydrolysis in driving endergonic reactions within the cell.
4. What is meant by chain configuration in biopolymers? Give examples of different conformations.
5. Write a short note on average dimensions of biopolymer chains.

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Dr. CH.N.S. SAI PAVAN KUMAR

LESSON-19
MEMBRANE EQUILIBRIUM AND TRANSPORT PHENOMENA

OBJECTIVES:

After studying this lesson, you should be able to:

- Study the concept of membrane equilibrium and the factors that influence in it.
- Describe the mechanism of ion transport across cell membranes.
- Explain the principle and process of dialysis and its biological applications.
- Differentiate between passive and active transport processes.

STRUCTURE:

19.1 INTRODUCTION

Cell membranes play a vital role in maintaining the internal environment of living organisms by regulating the movement of ions and molecules. The concept of **membrane equilibrium** describes the balance of forces governing diffusion and ion distribution across membranes. Understanding **ion transport mechanisms** helps explain how cells maintain electrical potential, osmotic balance, and nutrient exchange. **Dialysis**, an important physicochemical process, illustrates how selective permeability and diffusion can be used for purification and medical treatment.

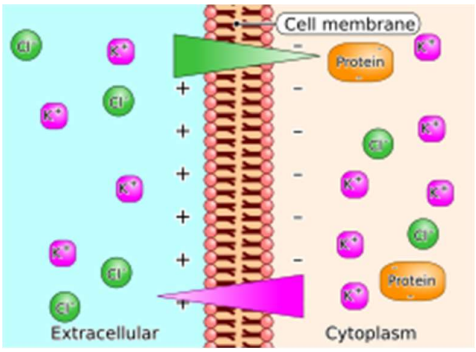
19.2 MEMBRANE EQUILIBRIUM

The **Gibbs–Donnan effect** (also known as the Donnan's effect, Donnan law, Donnan equilibrium, or Gibbs–Donnan equilibrium) is a name for the behaviour of charged

particles near a semi-permeable membrane that sometimes fail to distribute evenly across the two sides of the membrane. The usual cause is the presence of a different charged substance that is unable to pass through the membrane and thus creates an uneven electrical charge. For example, the large anionic proteins in blood plasma are not permeable to capillary walls. Because small cations are attracted, but are not bound to the proteins, small anions will cross capillary walls away from the anionic proteins more readily than small cations.

Thus, some ionic species can pass through the barrier while others cannot. The solutions may be gels or colloids as well as solutions of electrolytes, and as such the phase boundary between gels, or a gel and a liquid, can also act as a selective barrier. The electric potential arising between two such solutions is called the Donnan potential.

The effect is named after the American Josiah Willard Gibbs who proposed it in 1878 and the British chemist Frederick G. Donnan who studied it experimentally in 1911



For two ions (A^+ and B^-) diffusing across the membrane:
$[A^+]_1[B^-]_1 = [A^+]_2[B^-]_2$
This leads to unequal ion concentrations and an electric potential difference (membrane potential) across the membrane. It is vital in explaining the ionic balance in cells, nerve impulses, and muscle contraction.

Membrane equilibrium is crucial for many biological processes. The unequal distribution of ions across a cell membrane is essential for creating membrane potentials, which are fundamental for nerve cell function and other physiological activities. It Supports transport processes such as active and passive diffusion.

19.3 ION TRANSPORT THROUGH CELL MEMBRANE

The cell membrane, also known as the plasma membrane is a lipid bilayer that separates the cell interior from the extracellular space.

The cell membrane is a partition between intracellular and extracellular spaces, but some substances needed by the cell need to enter and some products or wastes need to exit the cell. The cell membrane allows a selective movement of substances in and out of the cell in several ways.

19.3.1 Simple Diffusion

Nonpolar molecules, such as O_2, CO_2, and N_2, can move across the membrane from a higher concentration region to a lower concentration region through the process of diffusion,

as illustrated in Figure . Diffusion does not require energy and hence this is called passive transport.

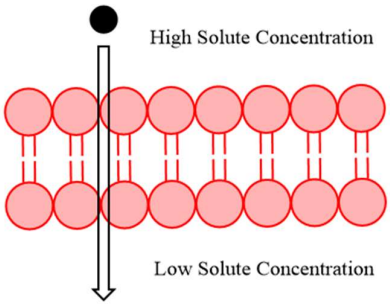


Fig. Illustration of diffusion across the cell membrane.

19.3.2 Facilitated Diffusion

Proteins that span the membrane form channels through which polar molecules and ions can diffuse more rapidly than by simple diffusion. The proteins have the channel size that match the size of the substance or they change the shape to adjust to the size of the substance that needs to be selectively transported through the facilitated transport, as illustrated in Figure right. Ions such as chloride ion (Cl^-), bicarbonate ion ($HCO3^-$), and Polar molecules like glucose molecules do not move fast enough through simple diffusion and are transported by the facilitated diffusion process to meet the need of the cells. Movement of water involves facilitated diffusion with the help of protein channels called aquaporins. Movement of water across cell membranes gives rise to osmosis. Facilitated diffusion does not require energy and hence this is also an example of passive transport.

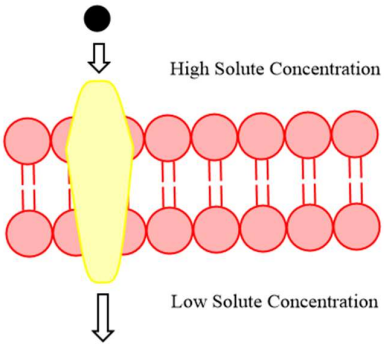


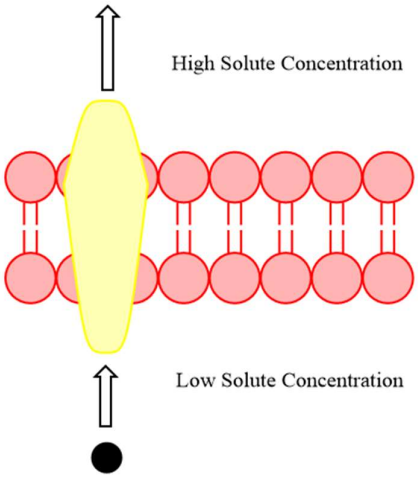
Fig. Illustration of facilitated diffusion transport across the cell membrane.

The rate of passive transport follows Fick's Law of Diffusion:
$J = -D\ (dC/dx)$
where J is flux, D is diffusion coefficient, and dC/dx is the concentration gradient.

19.3.3 Active transport

Sometimes substance need to be moved against the concentration gradient, from lower to higher concentration. This process requires the input of Energy Polar molecules and ions are transported across membranes through a protein channel in the direction of lower to higher

concentration. For example, concentration is greater inside the cell and is greater outside the cell. In the conduction of nerve impulses and contraction of muscles, moves into the cell, and moves out of the cell by active transport. The active transport process, is illustrated in the below figure.



The equilibrium potential for an ion across the membrane is given by the Nernst equation:
E = (RT / zF) ln([ion]_outside / [ion]_inside)
This predicts the voltage at which there is no net ion movement across the membrane.

19.3.4 The Electron Transport Chain

Facilitated diffusion and active transport of the hydrogen ion, (H^+) is encountered in a process called the electron transport chain which happens in the inner mitochondrial membrane. At the end of a turn of the citric acid cycle, energy-rich harvest molecules such as GTP, FADH2 and 3 NADH molecules are produced. The primary task of the last stage of cellular respiration, the electron **transport chain**, is to transfer the potential energy from NADH and FADH2 to ATP molecules. The ATP molecule is the "battery" which power work within the cell.The electron transport chain is a group of protein embedded in the inner mitochondrial membrane (see figure). These proteins are energy carrier molecules and are arranged in sequence within the membrane so that energy-carrying electrons pass from one to another, losing a little energy in each step. Complex I accepts electrons from NADH. As a result NADH is oxidized to NAD+. Complex II accepts electrons from FADH2. FADH2 is oxidized to FAD. Electrons supplied by NADH and FADH2 move from one protein complex to another in the inner mitochondrial membrane. The energy is harnessed to pump hydrogen ions, from the matrix (low H^+ concentration) into the inter-membrane space (high H^+ concentration) in a process called active transport. As a result the concentration of concentration of H^+ ions become higher in the inter-membrane space creating an electrochemical gradient.

Hydrogen ions then flow down the gradient - from high concentration region to low concentration. The ion channel/enzyme ATP synthase allows the H^+ to flow from inter-membrane space to the matrix in a facilitated diffusion process. The energy released during the facilitated diffusion of hydrogen ions converts a ADP and a phosphate ion to an ATP in a process known as oxidative phosphorylation.

19.4 DIALYSIS AND ITS FUNCTION

Dialysis removes harmful waste products and excess fluid from the blood when the kidneys are unable to. It acts as an artificial kidney, cleaning the blood and helping to maintain blood pressure and mineral balance, making it a life-sustaining treatment for kidney failure.

19.4.1 How dialysis works

Uses a semipermeable membrane: Blood is passed by a special fluid (dialysate) across a thin membrane that filters waste from the blood.

Uses diffusion: Waste products and excess electrolytes move from the blood, where they are in high concentration, into the dialysate, where they are not.

Removes excess fluid: Fluid is removed from the blood by creating a pressure gradient across the membrane.

Dialysis is a separation technique used to remove small solute molecules or ions from colloidal macromolecules such as proteins, nucleic acids, or polymers through a **semipermeable membrane**.

19.4.2 Principle of Dialysis

It is based on the **principle of diffusion**—the movement of solute molecules from a region of high concentration to a region of low concentration through a selectively permeable membrane. The semipermeable membrane (usually made of **cellophane or cellulose acetate**) allows **small molecules and ions** (like salts, urea, and buffer components) to pass through, but **retains large molecules** such as proteins or polysaccharides. Over time, the small solutes diffuse out of the membrane bag into the surrounding solvent until **equilibrium** is reached between the inside and outside solutions. The process continues until the **chemical potential** of diffusible solutes is equal on both sides of the membrane.

19.4.3 Experimental Setup

The sample containing macromolecules (e.g., proteins) is placed inside a **dialysis bag or tubing** made of semipermeable membrane. The bag is immersed in a large volume of **buffer or solvent**. The surrounding medium is **stirred gently** to maintain concentration gradient. Over several hours, small solutes diffuse out of the bag, while macromolecules remain inside. To achieve better purification, the external solution is replaced several times.

The rate of diffusion during dialysis can be approximated using **Fick's first law**:

J=−DdCdxJ = -D \frac{dC}{dx}J=−DdxdC

where:

J = diffusion flux (amount diffused per unit area per unit time),

D = diffusion coefficient,

dC/dx = concentration gradient.

The diffusion continues until the **concentration of diffusible solutes** is equal on both sides of the membrane.

19.5 SUMMARY

- Membrane equilibrium and transport processes are essential for maintaining life at the cellular level.
- The balance between chemical and electrical gradients determines ion distribution and membrane potential.
- Passive and active transport mechanisms enable selective movement of molecules necessary for cellular metabolism.
- Dialysis illustrates the principle of diffusion through semipermeable membranes, both in biological systems and medical treatments.

19.6 TECHNICAL TERMS

Membrane Equilibrium, Donnan Equilibrium, Diffusion, Membrane potential, Dialysis.

19.7 SELF ASSESSMENT QUESTIONS

1. Explain the Donnan equilibrium and its biological importance.
2. Differentiate between passive and active ion transport with suitable examples.
3. Define membrane equilibrium and how it is maintained in the cells.
4. Explain the principle of dialysis and its applications in medicine.
5. Write a short note on oxidative phosphorylation.

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Dr. CH.N.S. SAI PAVAN KUMAR

LESSON-20
MOLECULAR STRUCTURE & FUNCTIONS OF BIOPOLYMERS

OBJECTIVES:

After studying this lesson, you should be able to:

- Know the primary, secondary, tertiary, and quaternary structures of proteins.
- Explain the structural and catalytic roles of enzymes in biochemical reactions.
- Outline the structure and functions of DNA and RNA.
- Identify and explain the major forces involved in stabilizing biopolymer structures.
- Interpret how non-covalent interactions influence biomolecular recognition and activity.

STRUCTURE:

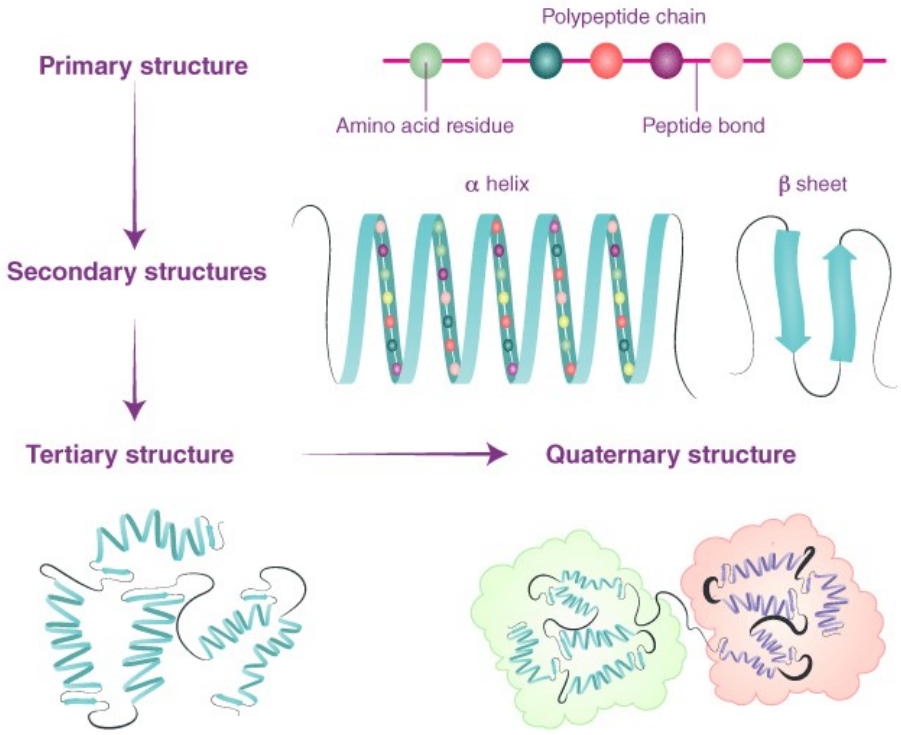
20.1 INTRODUCTION

Biopolymers such as **proteins, nucleic acids (DNA and RNA),** and **enzymes** are the fundamental macromolecules responsible for the structure and function of living cells. Proteins, enzymes, DNA, and RNA are the fundamental biological macromolecules essential for all known forms of life, working together in a complex system to store, express, and catalyze the instructions for life. DNA storing the genetic blueprint, RNA translating that information into proteins, and enzymes being a type of protein that catalyzes biochemical reactions. Proteins and enzymes perform vital cellular functions, while nucleic acids store and transfer genetic information. Their unique three-dimensional structures determine their specific biological roles.

Understanding the **forces involved in biopolymer interactions**—such as hydrogen bonding, hydrophobic interactions, electrostatic forces, and van der Waals forces—is essential for explaining the stability, folding, and function of these molecules.

20.2 Proteins Structure and Function

Proteins are known as the building blocks of life because they are the most abundant molecules present in the body and form about 60% of the dry weight of cells.

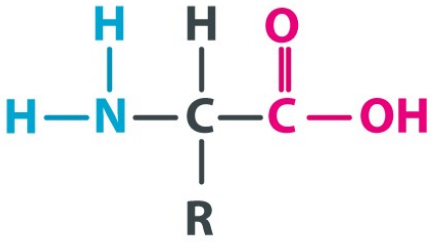


They make up the majority of the cells in all living things. Aside from cells, proteins make up the majority of the body's structural, regulatory, and enzyme components. They are therefore crucial for an individual's growth and development.

Food like eggs, pulses, milk and other milk products form the major high-protein foods for the body.

20.2.1 Proteins Structure

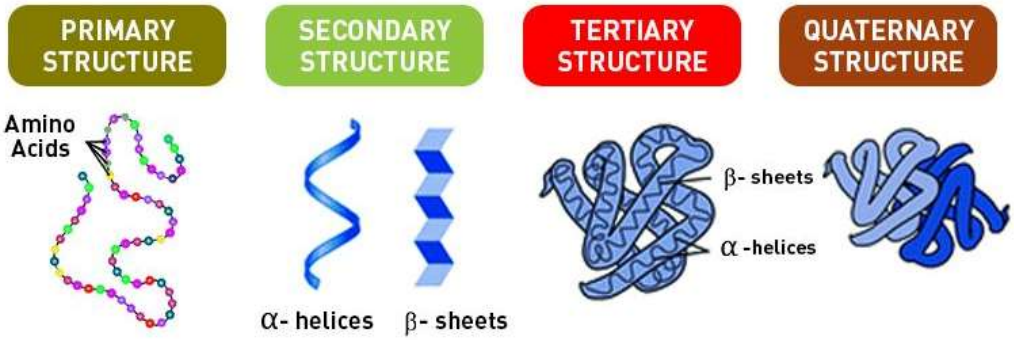
A polymeric chain of amino acid residues constitutes proteins. A protein's structure is primarily made up of long chains of amino acids. The arrangement and placement of amino acids give proteins certain characteristics. All amino acid molecules contain an amino ($-NH_2$) and a carboxyl (-COOH) functional group. Hence, the name "Amino-Acid".



Polypeptide chains are synthesized by linking together amino acids. A protein is created when one or more of these chains fold in a specific way. Methane is substituted by amino acids, with hydrogen, amino groups, carboxyl groups, and a variable R- group filling the first three valencies of the – alpha carbon.

There are many sorts of amino acids depending on the R-group, and a polypeptide chain contains 20 of them. The final structure and purpose of proteins are determined by all these characteristics of amino acids.

The structure of the protein is classified at 4 levels:-



- Primary – The primary structure of a protein is the linear polypeptide chain formed by the amino acids in a particular sequence. Changing the position of even a single amino acid will result in a different chain and hence a different protein.
- Secondary – The secondary structure of a protein is formed by hydrogen bonding in the polypeptide chain. These bonds cause the chain to fold and coil in two different conformations known as the α-helix or β-pleated sheets. The α-helix is like a single spiral and is formed by hydrogen bonding between every fourth amino acid. The β-pleated sheet is formed by hydrogen bonding between two or more adjacent polypeptide chains.

- Tertiary – The tertiary structure is the final 3-dimensional shape acquired by the polypeptide chains under the attractive and repulsive forces of the different R-groups of each amino acid. This is a coiled structure that is very necessary for protein functions.
- Quaternary – This structure is exhibited only by those proteins which have multiple polypeptide chains combined to form a large complex. The individual chains are then called subunits.

20.2.2 Functions of Proteins

The body uses proteins for a variety of purposes, and their structure determines how they work. Several notable functions include:

1. Digestion – The digestive enzymes, which are primarily proteinaceous in origin, carry out digestion.
2. Movement – Muscles include a protein called myosin, which helps muscles contract, allowing for movement.
3. Structure and Support – The structural protein known as keratin is what gives humans and other animals hair, nails, and horns.
4. Cellular communication – Through receptors on their surface, cells can communicate with other cells and the outside world. These receptors are made of proteins.
5. Act as a messenger – These proteins serve as chemical messengers that facilitate communication among cells, tissues, and organs.

20.3 ENZYMES STRUCTURE AND FUNCTION

Enzymes can be defined as biological polymers that catalyze biochemical reactions. Enzymes are a linear chain of amino acids, which give rise to a three-dimensional structure. The sequence of amino acids specifies the structure, which in turn identifies the catalytic activity of the enzyme. Upon heating, the enzyme's structure denatures, resulting in a loss of enzyme activity, which typically is associated with temperature.

Compared to its substrates, enzymes are typically large with varying sizes, ranging from 62 amino acid residues to an average of 2500 residues found in fatty acid synthase. Only a small section of the structure is involved in catalysis and is situated next to the binding sites. The catalytic site and binding site together constitute the enzyme's active site. A small number of ribozymes exist which serve as an RNA-based biological catalyst. It reacts in complex with proteins.

20.3.1 Enzyme structure

Globular proteins: Most enzymes are globular proteins with a complex 3D shape.

Amino acid sequence: The specific sequence of amino acids determines the enzyme's structure and, therefore, its function.

Active site: A small region on the enzyme where the substrate binds. The active site has a specific shape, and some models suggest it changes shape slightly to better fit the substrate (induced fit model).

Cofactors and coenzymes: Some enzymes require non-protein helper molecules to function, called cofactors or coenzymes.

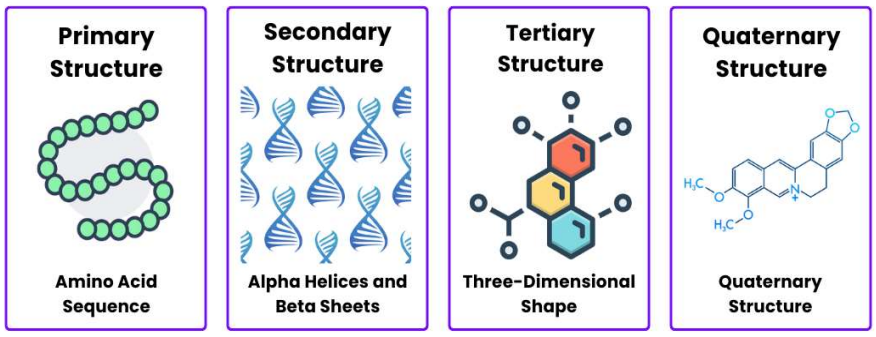
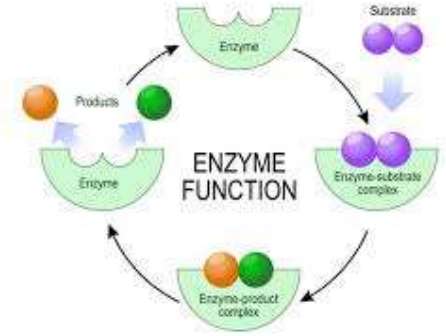


Fig. Structure of enzymes

20.3.2 Functions of Enzymes

The enzymes perform a number of functions in our bodies. These include:

1. Enzymes help in signal transduction. The most common enzyme used in the process includes protein kinase that catalyzes the phosphorylation of proteins.
2. They break down large molecules into smaller substances that can be easily absorbed by the body.
3. They help in generating energy in the body. ATP synthase is the enzyme involved in the synthesis of energy.
4. Enzymes are responsible for the movement of ions across the plasma membrane.
5. Enzymes perform a number of biochemical reactions, including oxidation, reduction, hydrolysis, etc. to eliminate the non-nutritive substances from the body.
6. They function to reorganize the internal structure of the cell to regulate cellular activities.



20.4 DNA Structure and Function

Friedrich Miescher discovered nucleic acids (both DNA and RNA) in 1868, which he called "nuclein". Later, other scientists made key discoveries about the individual molecules, such as Albrecht Kossel identifying the building blocks of DNA in 1881, and Watson and Crick determining the double helix structure of DNA in 1953.

DNA's structure is a **double helix**, resembling a twisted ladder, where two sugar-phosphate backbones are connected by paired nitrogenous bases (Adenine with Thymine, and Guanine

with Cytosine). Its function is to carry the genetic instructions for the development, functioning, growth, and reproduction of all known organisms by storing information in the sequence of these bases, which directs protein synthesis and is passed from one generation to the next.

20.4.1 Structure

Double Helix: DNA is a two-stranded molecule that coils around itself in a spiral shape known as a double helix.
Nucleotides**:** The building blocks of DNA are nucleotides, each composed of three parts: a deoxyribose sugar, a phosphate group, and one of four nitrogenous bases:

- Adenine (A)
- Guanine (G)
- Cytosine (C)
- Thymine (T)

Backbone: The sugar and phosphate groups of adjacent nucleotides form the alternating sugar-phosphate backbone on the outside of the helix.
Base Pairing: The two strands are linked together by hydrogen bonds between complementary bases: Adenine always pairs with Thymine (A-T), and Guanine always pairs with Cytosine (G-C).

Antiparallel Strands: The two strands run in opposite directions, described as being anti-parallel (one runs 5' to 3', and the other runs 3' to 5').

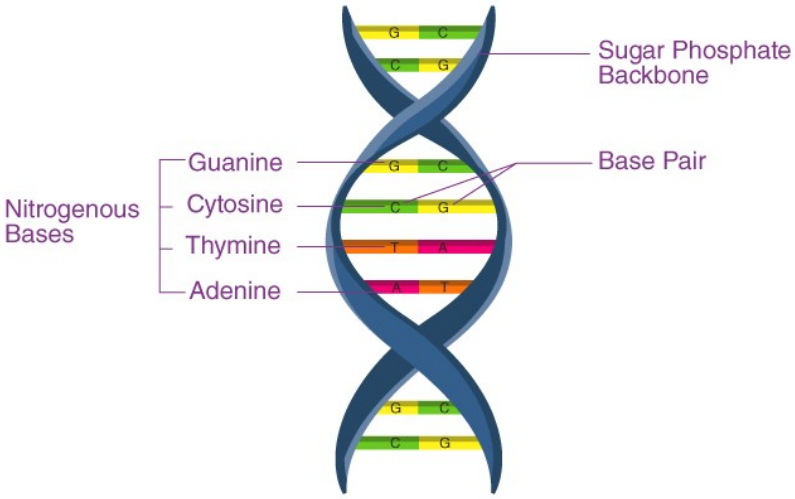


Fig. Structure of DNA

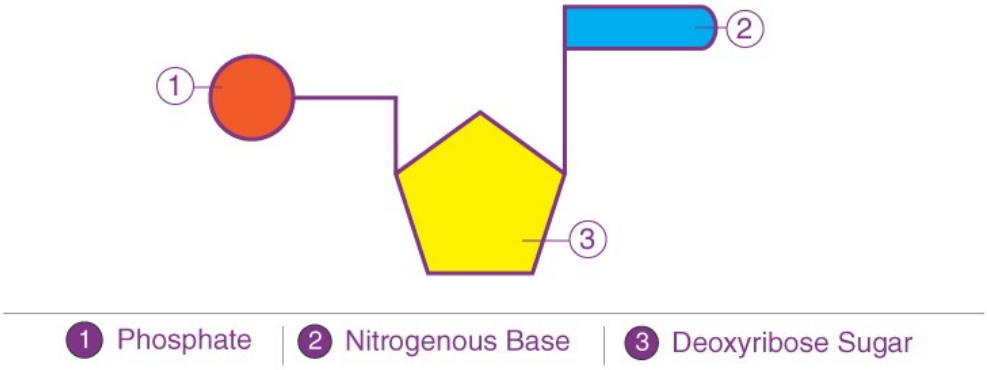


Fig. Components of DNA

20.4.2 DNA Function

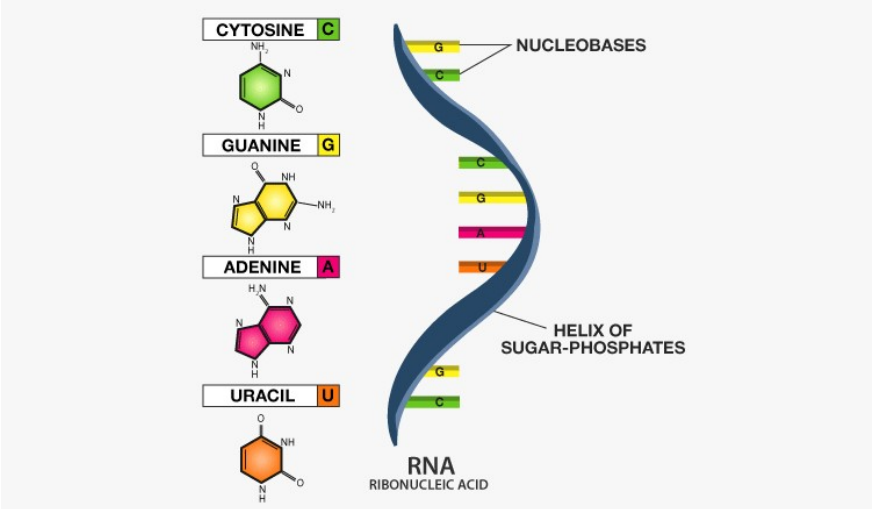
DNA is the genetic material which carries all the hereditary information. Genes are the small segments of DNA, consisting mostly of 250–2 million base pairs. A gene code for a poly-peptide molecule, where three nitrogenous bases sequence stands for one amino acid.

- Genetic Information Storage: DNA contains the code that holds the instructions for making proteins, which are essential for virtually all cellular activities. The specific order of the bases along the DNA strand forms this genetic code.
- **Protein Synthesis**: The information in DNA is used to build proteins. This process involves transcription (copying the DNA code into RNA) and translation (using the RNA to assemble amino acids into proteins).
- Replication: The structure of DNA is key to its ability to copy itself accurately during cell division. The double helix unwinds, and each single strand serves as a template to build a new complementary strand, ensuring that the genetic information is duplicated.
- Heredity: DNA carries the hereditary information that is passed from parents to their offspring, determining inherited traits.

20.5 RNA Structure and Function

RNA is a ribonucleic acid that helps in the synthesis of proteins in our body. This nucleic acid is responsible for the production of new cells in the human body. It is usually obtained from the DNA molecule. RNA resembles the same as that of DNA, the only difference being that it has a single strand unlike the DNA which has two strands and it consists of an only single ribose sugar molecule in it. Hence is the name Ribonucleic acid. RNA is also referred to as an enzyme as it helps in the process of chemical reactions in the body.

20.5.1 RNA Structure



The ribonucleic acid has all the components same to that of the DNA with only 2 main differences within it. RNA has the same nitrogen bases called the adenine, Guanine, Cytosine as that of the DNA except for the Thymine which is replaced by the uracil. Adenine and uracil are considered as the major building blocks of RNA and both of them form base-pair with the help of 2 hydrogen bonds. RNA is assembled as a chain of nucleotides.

RNA resembles a hairpin structure and like the nucleotides in DNA, nucleotides are formed in this ribonucleic material(RNA). Nucleosides are nothing but the phosphate groups which sometimes also helps in the production of nucleotides in the DNA.

20.5.2 Functions of RNA

The ribonucleic acid – RNA, which are mainly composed of nucleic acids, are involved in a variety of functions within the cell and are found in all living organisms including bacteria, viruses, plants, and animals. These nucleic acid functions as a structural molecule in cell organelles and are also involved in the catalysis of biochemical reactions. The different types of RNA are involved in various cellular process.

The primary functions of RNA:

Protein synthesis: This is the primary role of RNA, involving mRNA, tRNA, and rRNA.

- **Messenger RNA** (mRNA): Transcribes the genetic code from DNA in the nucleus and carries it to the ribosome in the cytoplasm.
- **Transfer RNA** (tRNA): Acts as an adapter molecule, reading the mRNA codons and delivering the corresponding amino acids to the ribosome to build a protein chain.
- **Ribosomal RNA** (rRNA): Forms the core structure of ribosomes and helps in catalyzing the formation of peptide bonds between amino acids.
    - Facilitate the translation of DNA into proteins
    - Functions as an adapter molecule in protein synthesis
    - Serves as a messenger between the DNA and the ribosomes.
    - They are the carrier of genetic information in all living cells
    - Promotes the ribosomes to choose the right amino acid which is required in building up of new proteins in the body.

20.6 Forces Involved in Biopolymer Interactions

Biopolymers such as proteins, nucleic acids, and polysaccharides interact with each other and with solvent molecules through several non-covalent forces. These weak interactions determine the structure, stability, folding, and biological function of macromolecules. The main types of forces involved are electrostatic forces, hydrophobic forces, molecular expansion (conformational forces), and dispersive (van der Waals) forces.

20.6.1 Electrostatic Forces

These are Coulombic interactions between charged groups on biopolymers. They occur between ionized side chains of amino acids (e.g., $–COO^-$, $–NH_3^+$) and between charged phosphate groups in nucleic acids.
Coulomb's Law:
$F = (1 / 4\pi\varepsilon_0\varepsilon_r) \times (q_1q_2 / r^2)$
where F = force of interaction, q_1 and q_2 = charges, ε_0 = permittivity of free space, ε_r = dielectric constant of the medium, and r = distance between charges.
Electrostatic forces can be attractive or repulsive, stronger in non polar environments, and are important in protein–DNA interactions, enzyme–substrate binding, and salt bridges.

20.6.2 Hydrophobic Forces

Hydrophobic interactions arise due to the tendency of non polar groups to avoid contact with water molecules. When hydrophobic side chains come together, water molecules around them become more ordered, reducing entropy. By clustering non polar groups, the system minimizes the disruption of hydrogen bonding in water, increasing overall entropy.
Examples include protein folding and formation of lipid bilayers in membranes. Hydrophobic interactions are entropy-driven and crucial for stabilizing tertiary and quaternary protein structures.

20.6.3 Molecular Expansion (Conformational Forces)

These internal forces influence the shape and flexibility of biopolymer chains. They are governed by bond stretching, bond angle bending, torsional strain, and steric hindrance. The total conformational energy can be expressed as:
$E_{total} = E_{bond} + E_{angle} + E_{torsion} + E_{non\text{-}bond}$
Examples include coiling/uncoiling of DNA, folding/unfolding of proteins, and elastic behavior of polymers. These forces determine molecular expansion or compactness of a biopolymer in solution.

20.6.4 Dispersive Forces (van der Waals Forces)

These are weak, short-range attractive forces arising from temporary dipoles due to electron cloud fluctuations. They include London dispersion, dipole–dipole, and dipole–induced dipole interactions.

Potential energy equation:

$V(r) = -A / r^6 + B / r^{12}$

The first term represents attractive forces and the second term repulsive forces. Though individually weak, van der Waals forces collectively have a significant stabilizing effect on macromolecular structures and play key roles in molecular recognition, ligand binding, and protein–protein interactions.

20.7 SUMMARY

- Proteins, enzymes, DNA, and RNA form the structural and functional foundation of life. Proteins and enzymes perform vital cellular functions, while nucleic acids store and transfer genetic information.
- The stability and activity of these macromolecules depend on various non-covalent interactions such as hydrogen bonding, hydrophobic forces, electrostatic interactions, and van der Waals forces.
- Understanding these structural and energetic aspects provides deep insight into molecular recognition, catalysis, and biological regulation.

20.8 TECHNICAL TERMS

Protein, Enzyme, DNA (Deoxyribo Nucleic Acid), RNA (Ribo Nucleic Acid), Electrostatic forces, Hydrophobic interaction.

20.9 SELF ASSESSMENT QUESTIONS

1. Define proteins and describe their four levels of structure.
2. What are the main functions of proteins in living organisms?
3. Explain how enzymes act as biological catalysts.
4. Describe the structural differences between DNA and RNA.
5. List and explain the non-covalent forces involved in biopolymer interactions.

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- Dr. CH.N.S. SAI PAVAN KUMAR