M.Sc. Previous Year
Chemistry, MC-03

PHYSICAL CHEMISTRY

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल
MADHYA PRADESH BHOJ (OPEN) UNIVERSITY - BHOPAL

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SYLLABI-BOOK MAPPING TABLE

Physical Chemistry

Syllabi	Mapping in Book
UNIT - 1 QUANTUM CHEMISTRY A. Introduction to Exact Quantum Mechanical Results: The Schrödinger equation and the postulates of quantum mechanics, discussion of solutions of the Schrödinger equation to some model systems, viz. particle in a box, the harmonic oscillator, the rigid rotor, the Hydrogen atom. B. Approximate Methods: The variation theorem, linear variation principle, perturbation theory (first order and non-degenerate), applications of variation method and perturbation theory to the Helium atom. C. Angular Momentum: Ordinary angular momentum, generalized angular momentum, eigen functions for angular momentum, eigenvalues of angular momentum, operator using Ladder operators, addition of angular momenta, spin, antisymmetry and Pauli exclusion principle. D. Electronic Structure of Atoms: Electronic configuration, Russell-Saunders terms and coupling schemes, Slater-Condon parameters, term separation energies of the p-n configuration, term separation energies for the d-n configurations, magnetic effects: spin-orbit coupling and Zeeman splitting, introduction to the methods of self-consistent field and Virial theorem. E. Molecular Orbital Theory: Hückel theory of conjugated systems, bond order and charge density calculations, applications to ethylene, butadiene, cyclopropenyl radical, cyclobutadiene, etc. Introduction to extended Hückel theory.	**Unit-1:** Quantum Chemistry **(Pages 3-67)**
UNIT - 2 THERMODYNAMICS A. Classical Thermodynamics: Brief resume of concepts of laws of thermodynamics, free energy, chemical potential and entropies, partial molar properties; partial molar free energy, partial molar volume and partial molar heat content and their significance, determinations of these quantities, concept of fugacity and determination of fugacity. Non-Ideal Systems: Excess function for non-ideal solution, activity coefficient Debye- Hückel theory for activity coefficient of electrolytic solutions; determination of activity and activity coefficients; ionic strength. Application of phase rule to three component systems; second order phase transitions. B. Statistical Thermodynamics: Concept of distribution, thermodynamic probability and most probable distribution, ensemble averaging postulates of ensemble averaging, canonical, grand canonical and microcanonical ensembles, corresponding distribution laws (using Lagrange' method of undetermined multipliers). Partition Functions - Translational, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in terms of partition functions, application of partition functions. Heat Capacity Behaviour of Solids - Chemical equilibria and equilibrium constant in terms of partition functions, Fermi-Dirac statistics, distribution law and applications to metal, Bose-Einstein statistics distribution law and application to Helium. C. Non Equilibrium Thermodynamics: Thermodynamic criteria for non-equilibrium states, entropy production and entropy flow, entropy balance equations for different irreversible process (e.g., heat flow, chemical reaction, etc.) transformation of the generalized fluxes and forces, non-equilibrium stationary states, phenomenological equations, microscopic reversibility and Onsager's reciprocity relations, electrokinetic phenomena, diffusion, electric conduction, irreversible thermodynamics for biological systems, coupled reactions.	**Unit-2:** Thermodynamics **(Pages 69-175)**

UNIT - 3 CHEMICAL DYNAMICS

Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius equation and the activated complex theory; ionic reactions, kinetic salt effects, steady state kinetics, kinetic and thermodynamic control of reactions, treatment of unimolecular reactions.

Dynamic chain (Hydrogen-Bromine reaction, pyrolysis of acetaldehyde, decomposition of ethane) photochemical (Hydrogen-Bromine and Hydrogen-Chlorine reactions) and oscillatory reactions (Belousov - Zhabotinsky reactions), homogeneous catalysis, kinetics of enzyme reactions, general features of fast reactions, steady of fast reactions by flow method, relaxation method, flash photolysis and the nuclear magnetic resonance method.

Dynamics of molecular motions, probing the transition state, dynamics of barrierless chemical reactions in solution, dynamics of unimolecular reactions (Lindemann - Hinshelwood and Rice-Ramsperger - Kassel - Marcus (RRKM) theories of unimolecular reactions).

Unit-3: Chemical Dynamics
(Pages 177-222)

UNIT - 4 SURFACE CHEMISTRY

A. Adsorption: Surface tension, capillary action, pressure differences across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibb's adsorption isotherm, estimation of surface area (BET equation), surface films on liquids (Electro-Kinetic Phenomenon), catalytic activity at surfaces.

B. Micelles: Surface active agents, classification of surface, active agents, micellization, hydrophobic interaction, Critical Micellar Concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization - phase separation and mass action models, solubilization, micro emulsion, reverse micelles.

C. Macromolecules: Polymer - definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization, mechanism of polymerization.

Molecular mass, number and mass average molecular mass, molecular mass determination (osmometry, viscometry, diffusion and light scattering methods), sedimentation, chain configuration of macromolecules, calculation of average dimensions of various chain structures.

Unit-4: Surface Chemistry
(Pages 223-326)

UNIT - 5 ELECTROCHEMISTRY

Electrochemistry of solutions, Debye-Hückel- Onsager treatment and its extension, ion solvent interactions. Debye- Hückel -Jerum mode. Thermodynamics of electrified interface equations, derivation of electro-capillarity, Lippmann equations (surface excess), methods of determination.

Structure of electrified interfaces, Gouy - Chapman, Stern, Graham - Devanathan - Mottwatts, Tobin, Bockris, Devanathan models.

Over potentials, exchange current density, derivation of Butler - Volmer equation, Tafel plot.

Quantum aspects of charge transfer at electrodes-solution interfaces, quantization of charge transfer, tunneling.

Semiconductor Interfaces - Theory of double layer at semiconductor, electrolyte solution interfaces, structure of double layer interfaces, and effect of light at semiconductor solution interface.

Electrocatalysis - Influence of various parameters. Hydrogen electrode.

Bioelectrochemistry, threshold membrane phenomena, Nernst-Planck equation, Hodgkin-Huxley equations, core conductor models, electrocardiography.

Polarography theory, Ilkovi? equation; half wave potential and its significance.

Introduction to corrosion, homogeneous theory, forms of, corrosion, corrosion monitoring and prevention methods.

Unit-5: Electrochemistry
(Pages 327-384)

CONTENTS

INTRODUCTION

NOTES

Physical chemistry is the study of macroscopic, atomic, subatomic, and particulate phenomena in chemical systems in terms of the principles, practices, and concepts of physics, such as motion, energy, force, time, thermodynamics, quantum chemistry, statistical mechanics, analytical dynamics and chemical equilibrium. Physical chemistry, in contrast to chemical physics, is predominantly a macroscopic or supramolecular science, as majority of the principles on which it was founded relate to the mass and quantity rather than the molecular/atomic structure alone. It is also an essential component of the interpretation of the techniques of investigation and their findings, particularly because these techniques are becoming ever more sophisticated and because their full potential can be realized only by strong theoretical backing. Physical chemistry also has an essential role to play in the understanding of the complex processes and molecules characteristic of biological systems and modern materials.

Physical chemistry is traditionally divided into a number of disciplines, but the boundaries between them are imprecise. Thermodynamics is the study of transformations of energy. Although this study might seem remote from chemistry, in fact it is vital to the study of how chemical reactions yield work and heat. The bridge between thermodynamics and structural studies is called statistical thermodynamics, in which maximum properties of substances are interpreted in terms of the properties of their constituent molecules.

Physical chemistry is essential to understanding the other branches of chemistry. It provides a basis for understanding the thermodynamic influences that drive chemical reactions forward. Theoretical chemistry is a branch of physical chemistry in which quantum mechanics and statistical mechanics are used to calculate properties of molecules and bulk systems. The greater part of activity in quantum chemistry, as the former is commonly termed, is the computation of the electronic structures of molecules and, often, their graphical representation.

This book, *Physical Chemistry*, is divided into five units which will help to understand the basic concepts of physical chemistry, quantum chemistry, exact quantum mechanical results, approximate methods, angular momentum, electronic structure of atoms, molecular orbital theory, thermodynamics, classical thermodynamics, non-ideal systems, application of phase rule to three component systems, second order phase transitions, statistical thermodynamics, partition functions, heat capacity behaviour of solids, non-equilibrium thermodynamics, chemical dynamics, dynamic chain, dynamics of reactions, surface chemistry, adosorption, micelles, macromolecules, electrochemistry, semiconductor interfaces. The book follows the Self-Instruction Mode or the SIM format wherein each unit begins with an 'Introduction' to the topic followed by an outline of the 'Objectives'. The content is presented in a simple and structured form interspersed with Answers to 'Check Your Progress' for better understanding. A list of 'Summary' along with a 'Key Terms' and a set of 'Self-Assessment Questions and Exercises' is provided at the end of each unit for effective recapitulation.

UNIT 1 QUANTUM CHEMISTRY

NOTES

Structure

1.0 INTRODUCTION

Quantum chemistry, also sometimes termed as molecular quantum mechanics, is a specific branch of chemistry that focuses on the applications of quantum mechanics to chemical systems. Fundamentally, the 'Quantum Chemistry' helps to understand the electronic structure and molecular dynamics with the help of the Schrödinger equations.

Quantum mechanics is a fundamental theory in physics that provides a description of the physical properties of nature at the scale of atoms and subatomic particles. The Schrödinger equation is a linear partial differential equation that governs the wave function of a quantum mechanical system. It is a key result in quantum mechanics and its discovery was a significant landmark in the development of the subject.

Quantum chemistry studies the ground state of individual atoms and molecules, and the excited states, and transition states that occur during chemical reactions. Principally, the quantum chemistry studies the chemical reactions assuming that the nuclei are at rest as per the Born–Oppenheimer approximation. Most important objectives of quantum chemistry include increasing the accuracy of the results for small molecular systems and increasing the size of large molecules that can be processed.

The origin of the concept of quantum chemistry started in the year 1926 with the discovery of the Schrödinger equation and its application to the hydrogen atom. Even though, the article of Walter Heitler and Fritz London given in the year 1927 is acknowledged as the first milestone in the history of quantum chemistry.

This is considered as the first application of quantum mechanics to the diatomic hydrogen molecule and consequently to the phenomenon of the chemical bond.

In the subsequent years, considerable advancement was accomplished by the Robert S. Mulliken, Max Born, J. Robert Oppenheimer, Linus Pauling, Erich Hückel, Douglas Hartree and Vladimir Fock. The history of quantum chemistry also goes through the 1838 discovery of cathode rays by Michael Faraday, the 1859 statement of the black-body radiation problem by Gustav Kirchhoff, the 1877 suggestion by Ludwig Boltzmann that the energy states of a physical system could be discrete, and the 1900 quantum hypothesis by Max Planck that any energy radiating atomic system can theoretically be divided into a number of discrete energy elements **e** such that each of these energy elements is proportional to the frequency **n** with which they each individually radiate energy and a numerical value called Planck's constant. Subsequently, in the year 1905 to explain the photoelectric effect (1839) Albert Einstein postulated the theory that light itself consists of individual quantum particles which was based on Planck's quantum hypothesis. These quantum particles were later termed as photons (1926). Further in the subsequent years, this theoretical basis gradually gained the recognition and was applied to chemical structure, reactivity and bonding. Probably the greatest contribution to the field was made by Linus Pauling.

The variational method is a mathematical method that is used to approximately calculate the energy levels of difficult quantum systems. It can also be used to approximate the energies of a solvable system and then obtain the accuracy of the method by comparing the known and approximated energies. In mathematics and applied mathematics, perturbation theory comprises methods for finding an approximate solution to a problem, by starting from the exact solution of a related, simpler problem.

In physics, angular momentum is the rotational equivalent of linear momentum. It is an important quantity in physics because it is a conserved quantity the total angular momentum of a closed system remains constant. Geometrically, an eigenvector, corresponding to a real non-zero eigenvalue, points in a direction in which it is stretched by the transformation and the eigenvalue is the factor by which it is stretched. If the eigenvalue is negative, the direction is reversed. In linear algebra and its application to quantum mechanics, a raising or lowering operator (collectively known as ladder operators) is an operator that increases or decreases the eigenvalue of another operator.

The Pauli exclusion principle is the quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously.

In atomic physics and quantum chemistry, the electron configuration is the distribution of electrons of an atom or molecule in atomic or molecular orbitals. In atomic spectroscopy, Russell–Saunders coupling, also known as LS coupling, specifies a coupling scheme of electronic spin- and orbital-angular momenta. The Slater–Condon rules express integrals of one-body and two-body operators over wave functions constructed as Slater determinants of orthonormal orbitals in terms of the individual orbitals. The Zeeman Effect is the effect of splitting of a spectral line into several components in the presence of a static magnetic field. In mechanics, the virial theorem provides a general equation that relates the average over time of the total kinetic energy of a stable system of discrete particles, bound by potential forces, with that of the total potential energy of the system.

In this unit, you will study about the, quantum chemistry, the Schrodinger equation, the postulates of quantum mechanics, particle in a box, the harmonic oscillator, the rigid rotor, the hydrogen atom, variation theorem, linear variation principle, perturbation theory, angular momentum, ordinary and generalized angular momentum, eigen functions and eigenvalues for angular momentum, operator using ladder operators, Pauli exclusion principle, electronic structure of atoms, electronic configuration, Russell-Saunders terms and coupling schemes, Slater-Condon parameters, magnetic effects, spin-orbit coupling and Zeeman splitting, molecular orbital theory, Hückel theory of conjugated systems, bond order and charge density calculations, and extended Hückel theory.

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the quantum chemistry
- Know about the postulates of quantum mechanics
- Interpret the variation theorem
- State the Perturbation theory
- Comprehend the ordinary angular momentum
- Calculate the eigen functions and eigenvalues of angular momentum
- Discuss the Ladder operators
- Elaborate on the addition of angular momenta
- Explain the antisymmetry and Pauli exclusion principle
- Analyse the molecular orbital theory
- Determine the bond order or calculations of charge density
- Analyse the applications to Ethylene, Cyclopropenyl Radical
- Introduce to extended Hückel theory

1.2 THE POSTULATES OF QUANTUM MECHANICS

Quantum Mechanics (QM) is also known as quantum physics, quantum theory, the wave mechanical model, or matrix mechanics. It includes quantum field theory, the fundamental theory in physics which describes nature at the smallest scales of energy levels of atoms and subatomic particles. Quantum mechanics differs from classical physics in that energy, momentum, angular momentum and other quantities of a bound system are restricted to discrete values (quantization); objects have characteristics of both particles and waves (wave-particle duality); and there are limits to the precision with which quantities can be measured (uncertainty principle). Early quantum theory was profoundly re-conceived in the mid-1920s by Erwin Schrödinger, Werner Heisenberg, Max Born and others. The modern theory is formulated in various specially developed mathematical formalisms. A mathematical function, the wave function, provides information about the probability amplitude of position, momentum, and other physical properties of a particle. In quantum mechanics, the Schrödinger equation is a mathematical equation that describes the changes over time of a physical system in which quantum effects, such as wave–particle duality, are significant.

Schrodinger used de Broglie's idea of matter waves and developed it into rigorous mathematical theory. The basic idea of Quantum theory is that matter can be regarded as wave. Wave function Ψ is a sort of amplitude function. It is not an observable quantity but Ψ^2 is probability of finding the electron within a given volume. These systems are referred to as quantum (mechanical) systems.

Quantum mechanics is an axiomatic theory because it is well-grounded on few principles or axioms or postulates, all of these words meaning the same thing. Following are the six postulates of quantum mechanics.

Postulate 1. Associated with any particle moving in a conservative field of force is a wave function which determines everything that can be known about the system.

Postulate 2. With every physical observable **q** there is associated an operator **Q**, which when operating upon the wave function associated with a definite value of that observable will yield that value times the wave function.

Postulate 3. Any operator **Q** associated with a physically measurable property **q** will be Hermitian.

Postulate 4. The set of eigenfunctions of operator **Q** will form a complete set of linearly independent functions.

Postulate 5. For a system described by a given wave function, the expectation value of any property **q** can be found by performing the expectation value integral with respect to that wave function.

Postulate 6. The time evolution of the wave function is given by the time dependent Schrodinger equation.

The Wave Function Postulate

It is one of the postulates of quantum mechanics that for a physical system consisting of a particle there is an associated wave function. This wave function determines everything that can be known about the system. The wave function can be a single-valued function of position and time, since that is sufficient to guarantee an unambiguous value of probability of finding the particle at a particular position and time. Also the wave function may be a complex function, since it is its product with its complex conjugate which specifies the real physical probability of finding the particle in a particular state.

$$\Psi(x,t) = \text{single-valued probability amplitude at } (x,t)$$

$$\Psi^*(x,t)\Psi(x,t) = \text{probability of finding particle at } x \text{ at time } t$$
$$\text{provided the wavefunction is normalized.}$$

Schrodinger's Wave Equation

Schrodinger used de Broglie's idea of matter waves and developed it into rigorous mathematical theory. The relation of de Broglie is fused in to the classical wave equation. The basic idea of quantum theory is that matter can be regarded as wave and these waves can be described by the equation for a vibrating string, i.e.,

$$\psi = A \sin \frac{2\pi x}{\lambda} \qquad ...(1)$$

where ψ is called the wave function, and can be described mathematically in terms of trigonometric sine function of displacement x and the wavelength λ. Schrodinger assigned this sine wave equation to the electron with the object of describing the behaviour of the electron in terms of its kinetic energy and potential energy.

Differentiating Equation (1) we get,

$$\frac{d\psi}{dx} = \frac{2\pi A}{\lambda}\cos\frac{2\pi x}{\lambda} \qquad ...(2)$$

Differentiating Equation (2) second time, with respect to x,

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2 A}{\lambda^2}\sin\frac{2\pi x}{\lambda} \qquad ...(3)$$

Since $\psi = \text{A} \sin \frac{2\pi x}{\lambda}$

Equation (3) can be written as,

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2}{\lambda^2}\psi \qquad ...(4)$$

Kinetic energy of a particle of mass m, moving with the velocity v is given by,

$$\text{K.E.} = \frac{1}{2}mv^2 \qquad ...(5)$$

where m is its mass and v the velocity. On multiplying and dividing right hand side of Equation (5) by m,

$$\text{K.E.} = \frac{1}{2}\frac{m^2v^2}{m} \qquad ...(6)$$

de Broglie equation can be expressed as,

$$mv = \frac{h}{\lambda} \qquad ...(7)$$

On squaring both sides of Equation (7)

$$m^2v^2 = \frac{h^2}{\lambda^2} \qquad ...(8)$$

On comparing Equations (6) and (8) we get,

$$\text{K.E.} = \frac{1}{2m}\frac{h^2}{\lambda^2} \qquad ...(9)$$

From Equation (4),

$$\lambda^2 = -\frac{4\pi^2\psi}{\frac{d^2\psi}{dx^2}} \qquad ...(10)$$

On substituting the value of λ^2 from Equation (10) in Equation (9),

$$\text{K.E.} = -\frac{1}{2m}\frac{h^2}{4\pi^2\psi}\cdot\frac{d^2\psi}{dx^2}$$

$$\text{K.E.} = -\frac{h^2}{8\pi^2 m\psi}\cdot\frac{d^2\psi}{dx^2} \qquad ...(11)$$

The total energy E, of a particle is the sum of its kinetic and potential energy.

Thus, $$\text{K E} = (\text{E} - \text{V}) = \frac{-h^2}{8\pi^2 m\psi}\frac{d^2\psi}{dx^2} \qquad ...(12)$$

Rearrangement of this gives,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\ (E - V)\ \psi = 0 \qquad ...(13)$$

This is Schrodinger equation is one dimension. While dealing with atomic structure, it is expanded to three dimensions using the Cartesian coordinates, x, y, z. Equation (13) can be written in the form,

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi\ = 0 \qquad ...(14)$$

where ψ is called the wave function or the probability amplitude function, E is the total energy of the system which is constant for a given value of λ, V is potential energy which depends upon the position of the system. Since E is constant and V is variable, therefore$(E - V)$ is also a variable. The wave equation is a differential equation of second order.

The Schrodinger's equation can be expressed in polar coordinates r, θ and ϕ, where r is the radical distance of a point from the origin, 0 is the inclination of the radial line to the Z-axis and ψ is the angle made with the X-axis by projecting the radial line in the $X - Y$ plane, as shown in Figure 1.1.

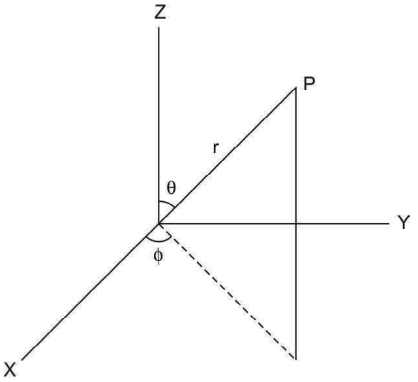


Fig. 1.1 *Polar coordinates*

The solutions for ψ are called wave functions and may be expressed as the product of three functions each of which depends only on one of the coordinates.

$$\psi\ (r, \theta, \varphi) = R\ (r)\ \Theta\ (\theta)\ \Phi\ (\phi) \qquad ...(15)$$

where R (r) is a function that depends on the distance r of the electron from the nucleus, which in turn depends on the quantum numbers n and l.

Θ (θ) is a function of θ, which depends on the quantum numbers l and m. Φ (ϕ) is a function of ϕ which depends on the quantum number m.

Nature of the Wave Function

The wave function ψ is a sort of amplitude function. It is not an observable quantity but $|\psi\psi^*|$ is observable where ψ^* is the conjugate of ψ. If the function is equal to its conjugate than ψ^2 gives the probability of finding the electron within a given volume.

The wave function ψ must obey certain mathematical conditions, the important ones are:

1. ψ must always be finite at any point.

If ψ were to become finite at any point in space this would correspond to a certainty of finding the particle there, which conflict with the uncertainty principle. This is shown Fig. 1.2.

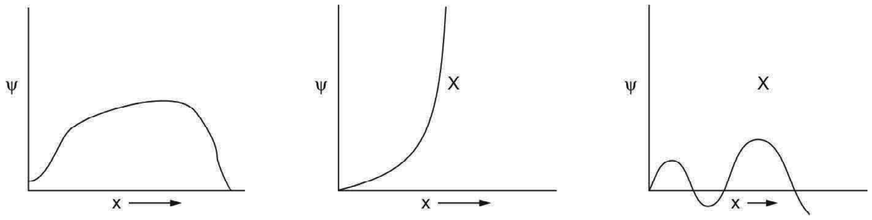


Fig. 1.2 *Finite Nature of* ψ

2. ψ must be single-valued at any point in space.

There can clearly be only one value of the probability of finding the particle at a given point in space. This is shown in Fig. 1.3.

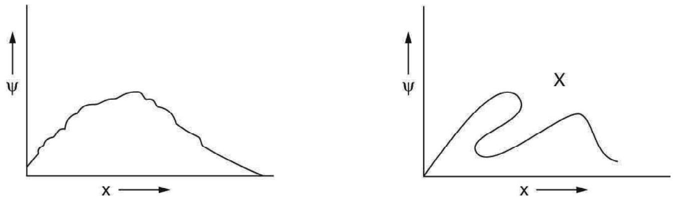


Fig. 1.3 ψ *Must be Single Valued*

3. ψ must be continuous.

If the probability of finding a particle at point x has a given value, that at $(x + \delta x)$ must be similar as $\delta x \rightarrow 0$. If this were not so, the double differentiation in the Schrodinger equation could not be performed. An important consequence of this condition is that y must become zero at infinity. This is shown in Figure 1.4.

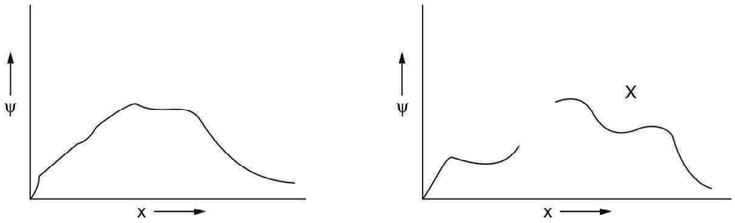


Fig. 1.4 *Continuity of* ψ

Operators

An operator is a rule that changes or transforms a given function into another function. In other words an operator changes one function into another according to some rule. The function is called an operand. Operator may be denoted by A,

B, etc., or with help of a circumflex, i.e., $\widehat{D}$ is the operator that differentiates, the result of operating on $f(x)$ with $\widehat{D}$ as $\widehat{D} = f'(x)$. For example, $\widehat{D}(x^2 + 3e^x) = 2x + 3e^x$. If $\hat{3}$ is the operator that multiplies a function by 3, i.e., $\hat{3}(2x^2 + 4e^x) = 4x + 4e^x$

Let illustrate it further with an example if $\widehat{D} = \frac{d}{dx}$ then

$$(\widehat{D} + \hat{5})(x^3 - 6) = \widehat{D}(x^3 - 6) + \hat{5}(x^3 - 6)$$

$$(\widehat{D} + \hat{5})(x^3 - 6) = 3x^2 + 5x^3 - 30$$

$$\widehat{Q}(\widehat{D} + \hat{5})(x^3 - 6) = 5x^3 + 3x^2 - 30$$

The sum and difference of two operators,

$$(\widehat{A} + \widehat{B})f(x) = \widehat{A}f(x) + \widehat{B}f(x)$$

$$(\widehat{A} - \widehat{B})f(x) = \widehat{A}f(x) - \widehat{B}f(x)$$

The product of two operators,

$$\widehat{A}\widehat{B}f(x) = \widehat{A}[\widehat{B}f(x)]$$

In other words we first operate on $f(x)$ with operator on the right of the operator product and then take the resulting function and operate it on the operator on the left of the operator product.

When more than one operator is applied in succession their symbols can be written together as in multiplication. For example ABf means that first the operator B is applied to a function f, then the operator A to the result. One must be cautious in such manipulations, since in general the order of operations can not be interchanged without affecting the result. For example if A means multiply by 3 and B means add 4. Then,

$$ABf = 3f + 4$$

If AB is equal to BA, then

$$ABf = BAf$$

or $$(AB - BA)f = 0 \qquad ...(16)$$

then we say that A and B commute. It is generally true that

$$Af + Bf = Bf + Af$$

Two operators A and B are said to be equal if $Af = Bf$ for all functions f. Some times we use a circumflex to indicate an operator as $\hat{A}$ or $\widehat{D}$. The operator $\hat{I}$ (multiplication by 1) is called the unit operator. The operator $\widehat{O}$ (multiplicat ion by O) is the null operator.

An operator is $\widehat{A}$ is linear operator if,

$$\widehat{A}(f + g) = \widehat{A}f + \widehat{A}g$$

Application of schrodinger equation particle in one-dimensional box

The most elementary application of Schrodinger equation is to study the effect of imposing a constraint upon the free particle by requiring that its motion be confined within fixed boundaries. In three dimensions, this is the problem of a particle enclosed in a box. The problem is further simplified if the box is a one dimensional box. In this case, a particle is required to move between set points on a straight line. The potential function that corresponds to such a condition is shown in Figure. 1.5 in which the electron is shown in a one-dimensional box which allow electron waves and energy levels.

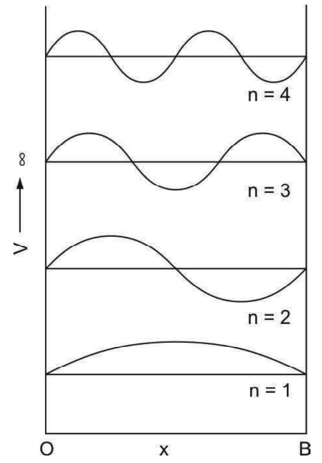


Fig. 1.5 *Electron in a One-Dimensional Box*

One-dimensional Schrodinger equation can be written as,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + V(x)\,\psi = E_n\,\psi \qquad ...(17)$$

One-dimensional box is defined by a potential that is zero for $0 \leq x \leq a$ and infinite elsewhere. Algebraically, the potential is given by

$$\begin{aligned} V(x) &= \infty & x &< 0 \\ V(x) &= 0 & 0 \leq x &\leq a \\ V(x) &= \infty & a &< x \end{aligned}$$

$$...(18)$$

Since, the particle cannot move outside the box, we have the following condition *i.e.*,

$$V(x) = 0x < 0 \text{ and } x > a \qquad ...(19)$$

The Schrodinger equation inside the box can be written as:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E_n\ \psi \qquad ...(20)$$

where E_n must be real and positive quantity. Let us introduce a new parameter l which is defined as:

$$\frac{8\pi^2 m E_x}{h^2} = \lambda^2 \qquad ...(21)$$

Now the Schrodinger equation can be written as

$$\frac{d^2\psi}{dx^2} = -\lambda^2\psi \qquad ...(22)$$

This is a differential equation and has two solutions, *i.e.*,

$$\psi_1(x) = \sin \lambda x \qquad ...(23)$$

And $$\psi_2\ (x) = \cos \lambda x \qquad ...(24)$$

NOTES

The general solution is a linear combination of the two solutions and can be written as

$$\psi(x) = A \sin \lambda x + B \cos \lambda x \qquad ...(25)$$

This expression contains three parameters, i.e., A, B and λ and satisfies Schrodinger equations for any values of these parameters,

Equation (20) must satisfy the criterion of a wave function. It is normalizable because it is non-zero only in the finite interval $0 \le x \le a$ and is finite every where within the interval. These results can be summarized as under,

$$\psi\ (x) = 0 \qquad x < 0 \quad ...(26)$$
$$\psi\ (x) = A \sin \lambda x + B \cos \lambda x \qquad 0 \le x \le a$$
$$\psi\ (x) = 0 \qquad a < x$$

The above function is continuous within any of the three intervals, but it is not necessarily continuous if we go from one interval to another, i.e., at the points $x = 0$ and $x = a$. On imposing the conditions of continuity at these points, we get

$$\psi\ (x) = \lim_{x \to 0}(A \sin \lambda x + B \cos \lambda x) = B = 0 \quad ...(27)$$

And $$\psi\ (x) = \lim_{x \to 0}(A \sin \lambda x + B \cos \lambda x) = 0$$

$$\psi\ (x) = A \sin \lambda a + B \cos \lambda a = 0 \qquad ...(28)$$

Since $B = 0$, Equation (23) can be written as,

$$A \sin \lambda a = 0 \qquad ...(29)$$

In the above equation the parameter A cannot be zero, as this would mean the value of wave function to be zero everywhere. This will lead to zero probability of finding the particle which does not make any sense, we have the conditions in,

$$\sin \lambda a = 0 \qquad ...(30)$$

This equation has infinite number of solutions, i.e.,

$$\lambda a = n\pi,\ n = 0, \pm 1, \pm 2, \pm 3.... \qquad ...(31)$$

$n = 0$, would mean the wave function to be zero everywhere, hence this is not allowed. Since $n = v$ and $n = -v$ lead to the same probability density function. Hence, the possible values of n are,

$$n = 1, 2, 3, 4$$

Squaring both sides of Equation (31),

$$\lambda^2 a^2 = n^2\pi^2 \qquad ...(32)$$

From Equation (21),

$$\lambda^2 = \frac{8\pi^2 m E_n}{h^2} \qquad ...(33)$$

On comparing Equations (27) and (28) we get,

$$E_n = \frac{n^2 h^2}{8ma^2} \qquad ...(34)$$

The first of these energy levels are shown in Figure 1.5. It follows from the above equation that the kinetic energy E_n decreases as the value of a increases. This means that more the room the electron has in which to move, the lower will be its kinetic energy which means greater stability of the system. Such a delocalization of the motion of the electron can occur in certain kinds of structures like conjugated and aromatic compounds. Equations (29) also leads to the concept of stationary states because only certain values are allowed. All other values are not allowed because they would lead to results that do not make sense from physical point of view.

Normalization of the Wave Function

The wave function,

$$\psi = A \sin\left(\frac{n\pi x}{a}\right)$$

contains an undetermined constant A. Its value can be determined using the total probability expression. Since, the particle remains inside the box, i.e., the probability of finding the particle with in the box is unity, i.e., from $x = 0$ to $x = a$

$$\int_0^a \psi\psi dx = A^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx = 1 \qquad \text{...(35)}$$

The integral $\int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx = a/2$ ...(36)

$$A^2 \left(\frac{a}{2}\right) = 1 \quad \text{or} \quad A = \sqrt{\frac{2}{a}}$$

Therefore, the normalized wave function is,

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \qquad \text{...(37)}$$

Orthogonality of Wave Function: Using the equation (21) a series of acceptable wave functions of a particle one dimensional box can be generated by assigning different permitted values to the quantum number n. Each eigen function is orthogonal to any other eigen value. By definition the two functions are orthogonal if the intergral,

$$\int_0^a \Psi^*{}_m \Psi_n d\tau = 0 \qquad \text{...(38)}$$

where m and n are two different quantum numbers. For the particle in a one dimensional box

$$\psi^*{}_m = \psi_m = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi}{a}x\right)$$

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

On applying the condition of orthogonality we have

$$\int_0^a \psi^*_m \psi_n dx = \frac{2}{a}\int_0^a \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx = 0$$

$$\left[\sin\alpha\sin\beta = \frac{1}{2}\left\{\cos\left(\alpha-\beta\right) - \cos(\alpha+\beta)\right\}\right]$$

$$\frac{1}{a}\int_0^a\left[\cos\left\{(m-n)\frac{x\pi}{a} - \cos\left\{(m+n)\frac{\pi x}{a}\right\}\right]dx \ = 0$$

$$\frac{1}{a}\left[\frac{\alpha}{(m-n)\pi}\sin\left\{(m-n)\frac{\pi x}{a}\right\} - \frac{a}{(m+n)\pi}\sin\left\{(m+n)\frac{\pi x}{a}\right\}\right]_0^1 = 0$$

...(39)

Since *m* and *n* are integers the above expression is numerically equal to zero.

Plot of ψ and ψ²

The probability of finding the particle at the point *x* is

$$\psi^2 = \frac{2}{a}\sin^2\left(\frac{n\pi x}{a}\right)$$

The Figure 1.6 gives the plot of wave function and the probability densities for some values of quantum numbers *n*.

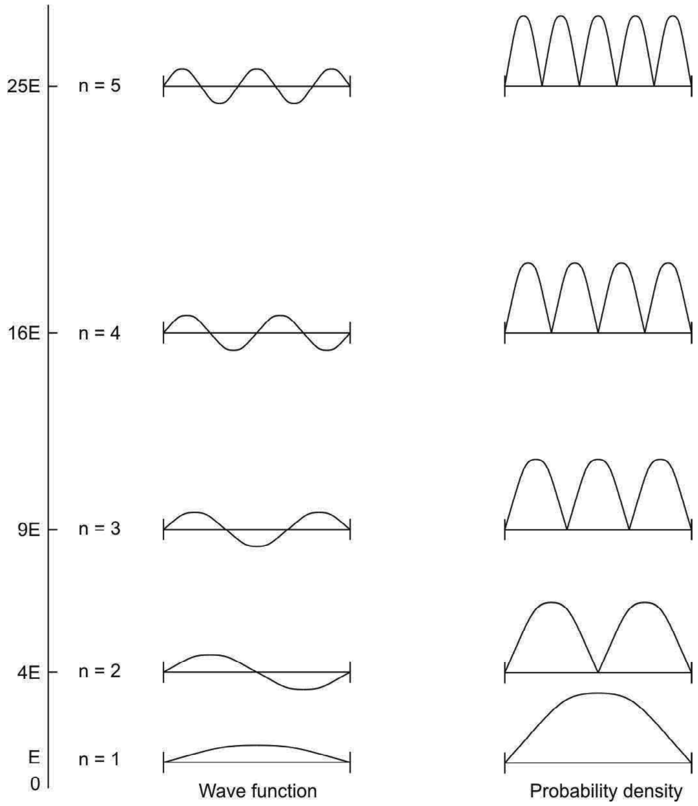


Fig. 1.6 *The Energy is Wave Function of Probability Densities*

Some Features of Particle in a Box

In order that the wave function must be zero at the walls. The length of the box must be an integral multiple of half wavelength, i.e.,

$$a = n\left(\frac{\lambda}{2}\right)$$

This can be shown as under

Since

$$E = n^2\left(\frac{h^2}{8ma^2}\right)$$

And $$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Also $$p = \frac{h}{\lambda}$$

$\therefore$ $$E = \frac{(h/\lambda)^2}{2m} = \frac{n^2h^2}{8ma^2}$$

Or $$= \frac{1}{\lambda^2}\frac{h^2}{2m} = \frac{n^2}{2m}\frac{h^2}{4a^2}$$

Or $$\lambda^2 = \frac{4a^2}{n^2}$$

$$a^2 = \frac{\lambda^2 n^2}{4}$$

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

Taking square root of both sides,

$$a = n\left(\frac{\lambda}{2}\right) \qquad ...(40)$$

Thus, the wave function besides being zero at the walls of the box also have zero values at various points within the box.

NOTES

Applications of Particle in a Box: The application of particle is a one dimensional box is in calculating the energies of conjugated system. The π electrons in a polyene may be regarded as the system of particle in a box. The length of the box may be taken as the end to end distance. The polyene is not a linear molecule but it is regarded as linear. The end to end distance is extended by a half C – C distance on either side of the molecule.

$$\Delta E = E_{n+1} - E_n$$

$$\Delta E = (n+1)^2\frac{h^2}{8ma^2} - \frac{n^2h^2}{8ma^2}$$

$$\Delta E = \left(n^2 + 2n + 1 - n^2\right)\frac{h^2}{8ma^2}$$

$$\Delta E = (2n+1)\ \frac{h^2}{8ma^2}$$

In case of butadiene molecule,

$$H_2C = CH - CH = CH_2$$

$$n = \frac{\text{Number of } \pi \text{ electrons } 4}{2} = 2$$

Length of the box, a

$$a = 1 \text{ (single bond)} + 2 \text{ (double bonds)} + 1 \text{ single bond}$$

$$= 154 \text{ pm} + 2 \times 135 \text{ pm} + 154 \text{ pm}$$

$$= 578 \text{ pm} = 5.78 \times 10^{10} \text{ m}$$

$$\Delta E = (2\,n + 1)\ \frac{h^2}{8ma^2}$$

$$\Delta E = (2 \times 2 + 1) \times \frac{6.626 \times 10^{-34} \text{ Js.}}{8\left(5.78 \times 10^{-10} \text{m}\right)^2 \left(9.1 \times 10^{-31} \text{kg}\right)}$$

$$\Delta E = 9.02 \times 10^{-19} \text{ J}$$

Wave number, $\bar{v} = \dfrac{\Delta E}{hc} = \dfrac{9.02 \times 10^{-19} \text{ J}}{\left(6.626 \times 10^{-34} \text{ Js}\right)\left(2.998 \times 10^{8} \text{ ms}^{-1}\right)}$

$$\bar{v} = 4.54 \times 10^6 \text{ m}^{-1} = 4.54 \times 10^4 \text{ cm}^{-1}$$

Particle in a Three-Dimensional Box

For a particle in a three-dimensional box of sides a, b and c, the Schrodinger equation can be written as,

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} E\psi = 0 \qquad \text{...(41)}$$

ψ is a three-dimensional variable in x, y and z. The Equation (41) can be solved by writing ψ as a product of three wave functions involving only one independent variable of x, y and z respectively, i.e.,

$$\psi\,(x, y, z) = X\,(x)\ Y(y)\ Z(z) \qquad \text{...(42)}$$

where $X(x)$, $Y(y)$ and $Z(z)$ are the three components of the wave function ψ. On substituting Equation (42) in Equation (41), we get,

$$\nabla^2\,(XYZ) + \frac{8\pi^2 m}{h^2}(E)XYZ = 0$$

$$\text{Or}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(XYZ) + \frac{8\pi^2 m}{h^2} EXYZ = 0 \qquad \text{...(43)}$$

$$YZ\left(\frac{\partial^2 X}{\partial x^2}\right) + XZ\left(\frac{\partial^2 Y}{\partial y^2}\right) + XY\left(\frac{\partial^2 Z}{\partial z^2}\right) + \frac{8\pi^2 m}{h^2} EXYZ = 0 \qquad \text{...(44)}$$

Dividing both sides of Equation (44) by XYZ, we get

$$\frac{1}{X}\left(\frac{\partial^2 X}{\partial x^2}\right) + \frac{1}{Y}\left(\frac{\partial^2 Y}{\partial y^2}\right) + \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial z^2}\right) + \frac{8\pi^2 m}{h^2} E = 0 \qquad \text{...(45)}$$

$$\frac{1}{X}\left(\frac{\partial^2 X}{\partial x^2}\right) + \frac{1}{Y}\left(\frac{\partial^2 Y}{\partial y^2}\right) + \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial z^2}\right) = -\frac{8\pi^2 m}{h^2} E = \alpha^2 \qquad \text{...(46)}$$

α^2 is a constant quantity.

If we change x (or y or z) keeping the other two constant. This is possible only when each term is independent of the other terms and each is equal to a constant quantity so that the sum of the constant is equal to α^2

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\alpha_x^2 \quad ...(47)$$

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\alpha_y^2 \quad ...(48)$$

$$\frac{1}{Y}\frac{\partial^2 Z}{\partial z^2} = -\alpha_z^2 \quad ...(49)$$

Where $$\alpha_x^2 = \frac{8\pi^2 m}{h^2}E_x \quad ...(50)$$

$$\alpha_y^2 = \frac{8\pi^2 m}{h^2}E_y$$

$$\alpha_z^2 = \frac{8\pi^2 m}{h^2}E_z$$

$$\alpha^2 = \alpha_x^2 + \alpha_y^2 + \alpha_z^2$$

$$E = E_x + E_y + E_z$$

On solving the Equations (47) to (49), we get

$$X = \sqrt{\frac{2}{a}}\sin\frac{n_x \pi x}{a}$$

$$E_x = \frac{n_z^2 h^2}{8ma^2}$$

$$Y = \sqrt{\frac{2}{b}}\sin\frac{n_y \pi y}{b}$$

$$E_y = \frac{n_y^2 h^2}{8mb^2}$$

$$Z = \sqrt{\frac{2}{c}}\sin\frac{n_z \pi z}{c}$$

$$E_z = \frac{n_z^2 h^2}{8mc^2}$$

$$\psi = XYZ = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x \pi x}{a}\right)\sqrt{\frac{2}{b}}\sin\left(\frac{n_x \pi y}{b}\right)\sqrt{\frac{2}{c}}\sin\left(\frac{n_x \pi z}{c}\right)$$

$$\psi = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right)$$

$$E_{nx}n_y n_z = E_x + E_y + E_z = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$En_xn_yn_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$$

NOTES

n_x, n_y and n_z are three quantum numbers a, b and c are the sides of the box.

When $n_x = n_y = n_z = 1, \quad a = b = c$

$$E_{111} = \frac{h^2}{8m}\left(\frac{1}{a^2}+\frac{1}{a^2}+\frac{1}{a^2}\right) = 3\left(\frac{h^2}{8ma^2}\right) = 3 \times E$$

when $n_x = 2\ n_y = 1,\ n_z = 1$

$$E_{211} = \frac{h^2}{8m}\left(\frac{4}{a^2}+\frac{1}{a^2}+\frac{1}{a^2}\right) = 6\text{ E}$$

$n_x = 1 \quad n_y = 2 \quad n_z = 1 \quad E_{121} = 6\ E$

$n_x = 1 \quad n_y = 1 \quad n_z = 2 \quad E_{112} = 6E$

where $E = \dfrac{h^2}{8ma^2}$.

Quantum Mechanics – Degeneracy

In quantum mechanics, an energy level is degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement. The number of different states corresponding to a particular energy level is known as the degree of degeneracy of the level. It is represented mathematically by the Hamiltonian for the system having more than one linearly independent eigenstate with the same energy eigenvalue.

Degeneracy plays a fundamental role in quantum statistical mechanics. For an N-particle system in three dimensions, a single energy level may correspond to several different wave functions or energy states (Refer Figure 1.7). These degenerate states at the same level are all equally probable of being filled. The number of such states gives the degeneracy of a particular energy level.

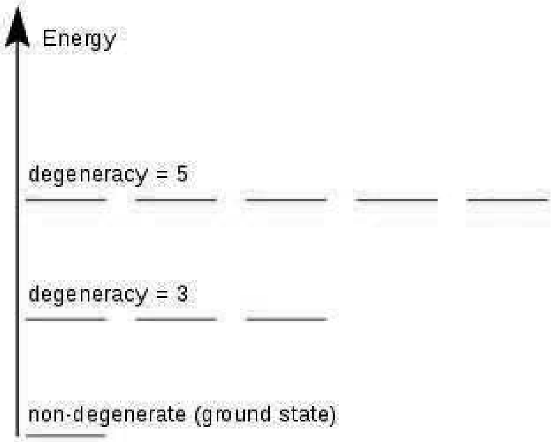


Fig. 1.7 *Degenerate States in a Quantum System*

Mathematically, the possible states of a quantum mechanical system may be treated as abstract vectors in a separable, complex Hilbert space, while the observables may be represented by linear Hermitian operators acting upon them. By selecting a suitable basis, the components of these vectors and the matrix elements of the operators in that basis may be determined.

If A is a $N \times N$ matrix, X a non-zero vector, and λ is a scalar, such that $AX = \lambda X$, then the scalar λ is said to be an eigenvalue of A and the vector X is said to be the eigenvector corresponding to λ. Together with the zero vector, the set of all eigenvectors corresponding to a given eigenvalue λ form a subspace of $\mathbf{C}^n$, which is called the **eigenspace** of λ.

An eigenvalue λ which corresponds to two or more different linearly independent eigenvectors is said to be **degenerate**, i.e., $AX_1 = \lambda X_1$ where $X_1$and $X_2$are linearly independent eigenvectors. The dimensionality of the eigenspace corresponding to that eigenvalue is known as its **degree of degeneracy**, which can be finite or infinite. An eigenvalue is said to be non-degenerate if its eigenspace is one-dimensional. The eigenvalues of the matrices representing physical observables in quantum mechanics give the measurable values of these observables while the eigenstates corresponding to these eigenvalues give the possible states in which the system may be found, upon measurement. The measurable values of the energy of a quantum system are given by the eigenvalues of the Hamiltonian operator, while its eigenstates give the possible energy states of the system. A value of energy is said to be degenerate if there exist at least two linearly independent energy states associated with it. Moreover, any linear combination of two or more degenerate eigenstates is also an eigenstate of the Hamiltonian operator corresponding to the same energy eigenvalue.

The term 'Degeneracy' refers to the fact that two or more stationary states of the same quantum-mechanical system may have the same energy even though their wave functions are not the same. In this case the common energy level of the stationary states is degenerate.

1.2.1 Hydrogen Atom

The Hydrogen Atom: The hydrogen atom characterises or symbolizes the simplest atom because it contains only one proton and one electron. The potential energy is because of the electrostatic force between the positively charged proton and the negatively charged electron. The potential energy curve in a hydrogen atom along with the first three probability density functions ($r^2|\psi|^2$) of the wavefunctions, which are radially symmetric, are illustrated in the following Figure 1.8. Characteristically, the probability densities are illustrated for curve $n = 1$ and $l = 0$, the curve $n = 2$ and $l = 0$ and the curve $n = 3$ and $l = 0$. The probability densities can be shifted or moved by means of the corresponding electron energy.

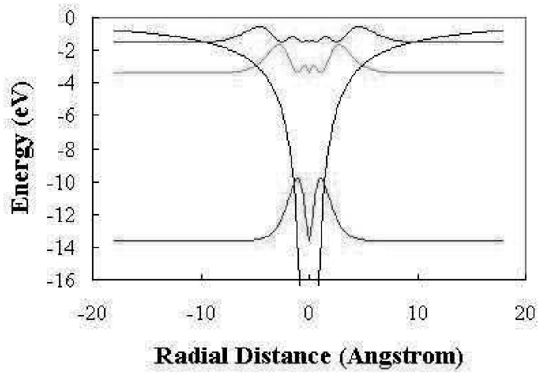


Fig. 1.8 *Potential Energy Curve in a Hydrogen Atom and the Probability Densities*

The possible or probable energy levels of the electron in the hydrogen atom are expressed by the following equation:

$$E_n = -\frac{m_0 q^4}{8\varepsilon_0^2 h^2 n^2}, \text{ with } n = 1, 2, \ldots$$

Where,

m_0 = Reduced Mass of the Electron

n = Primary Quantum Number

Figure 1.9 illustrates the energy levels and possible or probable electronic transitions in a hydrogen atom. The first six energy levels equivalent to $n = 1, 2, 3, 4, 5$ and 6 are illustrated in the Figure 6 in addition to the possible or probable transitions including the lowest energy level ($n = 1$). The transitions are indicated and specified as 5 arrows (Left side in the Figure 1.9) which typically represent or signify the first five transitions of the Lyman series. The arrow (Right side in the Figure 1.9) indicates and characterises the largest possible energy difference between the two bound states and is equivalent to 13.6 eV, also sometimes termed as one Rydberg.

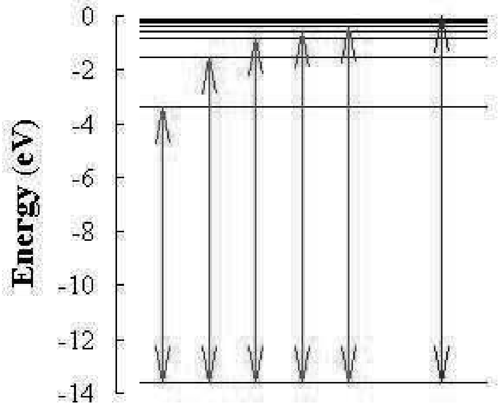


Fig. 1.9 *Energy Levels and Possible Electronic Transitions in a Hydrogen Atom Showing the Possible or Probable Transitions*

Remember that all the possible or probable energy values are negative in nature. Electrons having a positive energy do not bound to the proton and behave as free electrons.

Wave Functions: In one dimension, the wave functions are typically represented by means of the symbol $\psi\ (x, t)$, which are the functions of the coordinate x and the time t. However $\psi\ (x, t)$ is not a real function, but it is a complex function, consequently the Schrödinger equation does not have real solutions, but it has complex solutions. At a specific time, the wave function of a particle holds all the information about that particle. There is no physical interpretation of the wave function, hence it cannot be measured. However, the square of the absolute value of the wave function has a physical interpretation which is measurable. In one dimension, interpret $|\psi\ (x, t)|^2$ as a probability density function, i.e., a probability per unit length to find the particle at a specific time t at position x.

1.2.2 Hamiltonian Operator

In quantum mechanics, a '**Hamiltonian**' is an operator that corresponds or relates to the sum of the kinetic energies plus the potential energies for all the particles in the system, the addition of the total energy of the system is specifically required for studying analysis. Generally it is denoted by ***H***, but also sometimes denoted by ***H*** or ***H*** for highlighting its function as an operator. When the total energy of a system is measured then its spectrum is defined as the set of possible outcomes. Since it is closely related to the time-evolution of a system, therefore Hamiltonian operator is very significant and fundamental in most of the formulations of quantum theory.

The name Hamiltonian is given after William Rowan Hamilton, who generated a revolutionary reformulation of 'Newtonian Mechanics', nowadays termed as the 'Hamiltonian Mechanics', which is also significant and essential in quantum physics.

Definition: The Hamiltonian is the sum of the kinetic energies of all the particles, plus the potential energy of the particles associated with the system.

The expression or appearance of the Hamiltonian can have different types and the simplifications or the interpretations are done on the basis of concrete existing characteristics of the system under analysis, i.e., single or several particles in the system, interaction between particles, type of potential energy, time varying potential or time independent one, etc.

The Hamiltonian operator, when operated on an appropriate quantity, specifically the wavefunction in the context of quantum mechanics, then it provides the total energy of the system, i.e., the sum of the kinetic (denoted as K or as T) and the potential energy (denoted as U or as V).

Expressions for the Hamiltonian

Following are typical expressions for the Hamiltonian operator. Characteristic methods to classify or categorise the expressions are the number of particles, number of dimensions, and the nature of the potential energy function significantly the space and the time dependence. Masses are denoted by m, and Charges by q.

General Forms for One Particle

Free Particle: The particle is not bound by any potential energy, so the potential is zero and this Hamiltonian is the simplest. For one dimension, the Hamiltonian expression is,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

In higher dimensions, the Hamiltonian expression is,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

Constant-Potential Well: For a particle in a region of constant potential $V = V_0$ (no dependence on space or time), in one dimension, the Hamiltonian operator expression is,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0$$

In three dimensions, the Hamiltonian operator expression is,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_0$$

This expression can be specifically applied to the elementary or fundamental problem, such as 'particle in a box' and step potentials.

Simple Harmonic Oscillator: For a simple harmonic oscillator in one dimension, the potential varies with position only but not time, and accordingly due to this the expression is given as,

$$V = \frac{k}{2}x^2 = \frac{m\omega^2}{2}x^2$$

Where the angular frequency 'ω', effective spring constant 'k', and mass 'm' of the oscillator satisfy the notation,

$$\omega^2 = k / m$$

Consequently the Hamiltonian operator expression is,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2}x^2$$

For three dimensions, this becomes,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{m\omega^2}{2}r^2$$

Where the three-dimensional position vector **r** using the Cartesian coordinates is (*x*, *y*, *z*), and its magnitude is,

$$r^2 = \mathbf{r}\cdot\mathbf{r} = |\mathbf{r}|^2 = x^2 + y^2 + z^2$$

Characteristically, the Hamiltonian obtainable in complete displays that it is basically the sum of the one-dimensional Hamiltonians in each direction, as given below:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+\frac{m\omega^2}{2}(x^2+y^2+z^2)\\ &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{m\omega^2}{2}x^2\right)+\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}+\frac{m\omega^2}{2}y^2\right)+\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+\frac{m\omega^2}{2}z^2\right)\end{aligned}$$

Hamiltonian Operators for Molecules - Density Functional Theory

The Hamiltonian Operator (= Total Energy Operator) is a sum of two operators, namely the kinetic energy operator and the potential energy operator,

$$\hat{H} = \hat{T} + \hat{V}$$

Kinetic energy can be defined considering the momentum operator,

$$T = \frac{1}{2}mv_x^2 = \frac{(mv_x)^2}{2m}$$

$$\hat{T} = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

The potential energy operator can be defined as,

$$\hat{V} = V(x)$$

The Hamiltonian operator expression thus becomes,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

Expectation Values of Operators

- Experimental measurements of physical properties are average values.
- Quantum mechanics postulates that the result of any such measurement can be calculated by 'Averaging' the appropriate operator and the wavefunction as follows:

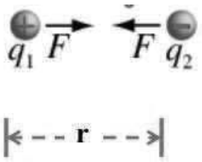
$$\langle x\rangle = \frac{\int_{-\infty}^{\infty}\Psi^*(x)\,\hat{x}\,\Psi(x)dx}{\int_{-\infty}^{\infty}\Psi^*(x)\Psi(x)dx}$$

The above example notation gives the expectation value (average value) of the position along the X-axis.

Force Between Two Charges: Coulomb's Law

Like charges repel,

Unlike charges attract,



Coulomb's Law

$$F = \frac{kq_1q_2}{r^2} = \frac{q_1q_2}{4\pi\varepsilon_0 r^2}$$

Energy of Two Charges

Energy of two charges can be given as,

$$E_{q_1q_2} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\mathbf{r}|}$$

$$|\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}$$

$$|\mathbf{r}| = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2} = |\mathbf{r}_2 - \mathbf{r}_1|$$

Coulomb Potential Energy or Operator

$$E_{q_1q_2} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\mathbf{r}|} = q_1\boxed{\frac{q_2}{4\pi\varepsilon_0|\mathbf{r}|}}$$

Following are the example expressions of the Coulomb potential energy in three different dimensions:

In One Dimension

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{|x|}$$

In Two Dimensions

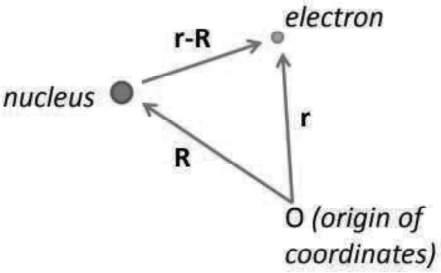
$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{\sqrt{x^2 + y^2}}$$

In Three Dimensions

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{\sqrt{x^2+y^2+z^2}}$$

Hamiltonian for Hydrogen Atom

Following is the Hamiltonian structure for Hydrogen atom:



The following Hamiltonian expression gives the nuclear kinetic energy, the electronic kinetic energy and the electron-nucleus attraction:

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

Nuclear Kinetic Energy   Electronic Kinetic Energy   Electron-Nucleus Attraction

Therefore,

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

Atomic Units

Atomic Units are typically used as they help to simplify the quantum chemistry expressions. The following are the standard notations:

In SI Units

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

In Atomic Units

$$\hat{H} = -\frac{1}{2M}\nabla^2_{\mathbf{R}} - \frac{1}{2}\nabla^2_{\mathbf{r}} - \frac{1}{|\mathbf{r}-\mathbf{R}|}$$

NOTES

Following is the standard values for energy, charge and length of Hydrogen atom:

Quantity	Atomic Unit	Value in SI
Energy	$\hbar^2/m_e a_0$ (Hartree)	4.36×10^{-18} J
Charge	e	1.60×10^{-19} C
Length	a_0	5.29×10^{-11} m
Mass	m_e	9.11×10^{-31} kg

1.2.3 Rigid Rotator

A rigid rotator consists of two mass points attached at the two ends of a massless rod. The system is capable of rotating about an axis passing through its centre of mass and perpendicular to the length of the rod. If the rotator is constrained to rotate in plane, it can be described by an angle coordinate q at any instant of time. The potential energy of the rotator is zero because the masses are rigidly connected to the ends of the rod of constant length. The kinetic energy of the rotator is given by

$$T = \frac{1}{2} I\omega^2 = \frac{1}{2} I\dot{\theta}^2$$

where *I* is the moment of inertia of the rotator about the axis of rotation and $\omega = \theta$ is the angular velocity of rotation. Clearly, the total energy of the classical rotator is

$$E = T = \frac{1}{2} I\dot{\theta}^2 = \frac{1}{2} I\omega^2 \qquad \text{...(51)}$$

The phase integral of the rotator can be written in terms of the total angular momentum P_θ and the angular coordinate θ as

$$J = \oint p_\theta d_\theta \qquad \text{...(52)}$$

According to Wilson–Sommerfeld quantization rule we have

$$J = nh, \quad n = 0, 1, 2, \ldots \qquad \text{...(53)}$$

Using above equations we obtain,

$$\oint p_\theta d_\theta = nh$$

Since the total angular momentum $P_\theta = I\omega$ is a constant of motion, the above equation gives

$$p_\theta \int_0^{2\pi} d\theta = nh$$

$$\text{or} \qquad p_\theta = I\omega = \frac{nh}{2\pi} \qquad \text{...(54)}$$

The above equation gives

$$\omega = \frac{nh}{2\pi I} = \frac{n\hbar}{I} \qquad ...(55)$$

Substituting the value of w in above equations we obtain

$$E = \frac{1}{2} I \frac{n^2\hbar^2}{I^2}$$

$$\text{or} \qquad E = \frac{1}{2} \frac{n^2\hbar^2}{I} \qquad ...(56)$$

We find that the energy of the rigid rotator is discrete and not continuous.

Problem of Rigid Rotator

Rigid rotator is a system of two spherical particles separated by a fixed distance. The system can rotate about an axis through the centre of mass and perpendicular to the plane containing the particles. If the plane containing the particles can take any arbitrary orientation, the axis of rotation can assume any orientation in space and the system is then referred to as a rigid rotator with free axis. On the other hand, if the particles are confined within a given plane then the axis of rotation has a fixed direction in space and the system is then referred to as a rigid rotator with fixed axis. A quantum mechanical treatment of rigid rotator with free axis is helpful in understanding the behaviour of a diatomic molecule which can be considered as a rigid rotator with free axis at least as a first approximation.

Schrödinger Equation for a Rigid Rotator with Free-Axis

In order to arrive at the Schrödinger equation, let us first calculate the total energy of the oscillator which is the sum of the kinetic energies of the two particles constituting the rotator and the potential energy of the system.

Let the rotator consist of two particles of masses $m1$ and $m2$ separated by a fixed distance ro. Let the system of particles rotate with an angular velocity 'w' about the axis XY passing though the centre of mass O and normal to the line joining the particles as shown in the Figure (1.10).

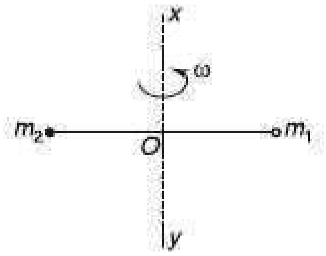


Fig. 1.10 *Rigid Rotator*

Let for any arbitrary position of the plane containing the particles, i.e., for an arbitrary orientation of the axis XY in space, the Cartesian coordinates of m_1 and m_2 with respect to O which is considered as the origin of a rectangular coordinate

NOTES

system be respectively (x_1, y_1, z_1) and (x_2, y_2, z_2). Let (r_1, q, f) and (r_2, q + p, f + p) be respectively the spherical polar coordinates of m_1 and m_2. We then have the transformation equations given by

$$\left.\begin{aligned} x_1 &= r_1 \sin\theta \cos\phi \\ y_1 &= r_1 \sin\theta \sin\phi \\ z_1 &= r_1 \cos\theta \end{aligned}\right\}$$

and

$$\left.\begin{aligned} x_2 &= r_2 \sin(\theta+\pi)\cos(\phi+\pi) = r_2 \sin\theta\cos\phi \\ y_2 &= r_2 \sin(\theta+\pi)\sin(\phi+\pi) = r_2 \sin\theta\sin\phi \\ z_2 &= r_2 \cos(\theta+\pi) = -r_2 \cos\theta \end{aligned}\right\} \quad ...(57)$$

...(58)

The kinetic energy of the particle of mass m_1 is

$$T_1 = \frac{1}{2} m_1(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) \quad ...(59)$$

Obtaining the time derivatives $\dot{x}_1, \dot{y}_1$ and $\dot{z}_1$ from above equation, substituting them in above equation and simplifying we obtain

$$T_1 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2) \quad ...(60)$$

Similarly, the kinetic energy of the particle of mass m_2 is found to be

$$T_2 = \frac{1}{2} m_2(\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) = \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) \quad ...(61)$$

The total kinetic energy of the rotator is thus

$$T = T_1 + T_2 = \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2\right)(\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2) \quad ...(62)$$

Since for the rigid rotator the distance r0 between the two particles is fixed (r_0 = constant), we can say that there exists no mutual force between the particles. As a consequence, the potential energy of the rotator is zero ($V = 0$).

The total energy of the rotator is the moment of inertia of the rotator about the axis of rotation XY.

$$E = T = \frac{1}{2}(m_1 r_1^2\ m_2 r_2^2)(\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2)$$

$$E = \frac{1}{2} I (\dot{\theta}^2 + \sin^2\theta\, \dot{\phi}^2) \quad ...(63)$$

where, $$I = m_1 r_1^2 + m_2 r_2^2$$

...(64)

NOTES

To gain physical insight into the rotator problem, we now express Equation (51) in a different form using the definition of centre of mass of a system of particles. Let with respect to the origin $O, \vec{r}_1$ and $\vec{r}_2$ be respectively the position vectors of the particles of masses m_1 and m_2. The position vector of the centre of mass with respect to the origin is then given by

$$\vec{r} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \qquad ...(65)$$

Since the origin has been chosen as the centre of mass itself we have $\vec{r} = 0$, $\vec{r}_1$ and $\vec{r}_2$ oppositely directed

We thus obtain from Equation (65)

$$O = \frac{m_1 r_1 - m_2 r_2}{m_1 + m_2}$$

The above gives

$$m_1 r_1 = m_2 r_2$$

We may write Equation (5.49) as

$$m_1 r_1 = m_2 (r_0 - r_1) \qquad ...(66)$$

or

$$r_1 = \frac{m_2}{m_1 + m_2} r_0$$

...(67)

Similarly, we obtain

$$r_2 = \frac{m_1}{m_1 + m_2} r_0$$

Substituting Equations (67) and (68) in Equation (64) we get

$$I = m_1\left(\frac{m_2}{m_1 + m_2}\right)^2 r_0^2 + m_2\left(\frac{m_1}{m_1 + m_2}\right)^2 r_0^2$$

or

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 \qquad ...(68)$$

or

$$I = \mu r_0^2$$

Where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ in the reduced mass of the two particles.

Using Equation (68) in Equation (60) we get the total energy of the rotator as

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$$E = \frac{1}{2}\mu r_0^2(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) \qquad ...(69)$$

If for convenience, we set the distance between the particles equal to unity, i.e., $r_0 = 1$, we get

$$\mu r_0^2 = \mu = I_0(\text{say}) \qquad ...(70)$$

We can then write the total energy of the rotator as

$$E = \frac{1}{2}I_0(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) \qquad ...(71)$$

which is the kinetic energy of a particle of mass $m = I0$ moving on the surface of a sphere of radius unity.

Thus the motion of the rigid rotator is the same as that of a single particle of mass I_0, equal to the reduced mass of the two particles forming the rotator, over the surface of a sphere of radius unity.

The wavefunction $y(x, y, z)$ describing the state of a particle of mass m having a total energy E moving in a potential field V satisfies the Schrödinger equation,

$$\Delta^2\psi(x, y, z) + \frac{2m}{\hbar^2}[E - V]\psi(r, \theta, \phi) = 0 \qquad ...(72)$$

In spherical polar coordinates the above becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)$$

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial\psi(r,\theta,\phi)}{\partial\phi^2} + \frac{2m}{\hbar^2}[E - V]\psi(r,\theta,\phi) = 0 \qquad ...(73)$$

As seen above, the rigid rotator behaves as a single particle of mass $m = I0$ over a sphere of unit radius. We thus have $r = 1$ so that we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial\phi^2}\right) = 0 \qquad ...(74)$$

Equation (73) then becomes

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\phi}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2I_0}{\hbar^2}[E - V]\psi = 0 \qquad ...(75)$$

Further for the rigid rotator V = 0, so that Equation (75) reduces to

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2I_0}{\hbar^2}E\psi = 0 \qquad ...(76)$$

In the above, ψ is a function of only θ and ϕ since r = constant, i.e., $\psi = \psi(\theta, \phi)$.

1.3 VARIATION THEOREM

The variational method is the key approximate method/technique typically used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it is hard to determine a good unperturbed Hamiltonian, i.e., one which makes the perturbation small but is still solvable. On the other hand, in cases where there is a good unperturbed Hamiltonian, perturbation theory can be more efficient than the variational method.

The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions, such as molecular orbitals. The basis for this method is the variational principle. The method consists of choosing a 'trial wavefunction' depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.

Basically the 'trial wavefunction' for the problem consists of some adjustable parameters called termed as the 'variational parameters'. These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.

Suppose we are given a Hilbert space and a Hermitian operator over it called the Hamiltonian, *H*. Ignoring complications about continuous spectra, consider the discrete spectrum of *H* and the corresponding eigenspaces of each eigenvalue »:

$$\langle\psi_{\lambda_1} \mid \psi_{\lambda_2}\rangle = \delta_{\lambda_1\lambda_2}$$

Where $\delta_{i,j}$ is the Kronecker delta,

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j, \\ 1 & \text{if } i = j. \end{cases}$$

And the Hamiltonian is related to » through the typical eigenvalue relation,

$$\hat{H}\left|\psi_\lambda\right\rangle = \lambda\left|\psi_\lambda\right\rangle$$

Physical states are normalized, meaning that their norm is equal to 1. Once again ignoring complications involved with a continuous spectrum of H, suppose it is bounded from below and that its greatest lower bound is E_0. Suppose also that we know the corresponding state |Èé'. The expectation value of H is then,

$$\begin{aligned}\langle\psi \mid H \mid \psi\rangle &= \sum_{\lambda_1,\lambda_2 \in \mathrm{Spec}(H)} \langle\psi|\psi_{\lambda_1}\rangle \langle\psi_{\lambda_1}|H|\psi_{\lambda_2}\rangle \langle\psi_{\lambda_2}|\psi\rangle \\ &= \sum_{\lambda \in \mathrm{Spec}(H)} \lambda|\langle\psi_\lambda \mid \psi\rangle|^2 \geq \sum_{\lambda \in \mathrm{Spec}(H)} E_0|\langle\psi_\lambda \mid \psi\rangle|^2 = E_0\end{aligned}$$

Evidently, in order to vary over all possible states with norm 1 trying to minimize the expectation value of H, the lowest value would be E_0 and the corresponding state would be an eigenstate of E_0. Varying over the entire Hilbert space is usually too complicated for physical calculations, and a subspace of the entire Hilbert space is chosen, parametrized by some (real) differentiable parameters $\pm_i$ (i = 1, 2, ..., N). The choice of the subspace is called the ansatz. Some choices of ansatzes lead to better approximations than others, therefore the choice of ansatz is important.

Assume that there is some overlap between the ansatz and the ground state (otherwise, it is a bad ansatz). We still wish to normalize the ansatz, so we have the constraints,

$$\langle\psi(\alpha) \mid \psi(\alpha)\rangle = 1$$

And to minimize,

$$\varepsilon(\alpha) = \langle\psi(\alpha)|H|\psi(\alpha)\rangle$$

If ψ (α) is expressed as a linear combination of other functions (α_i being the coefficients), as in the Ritz method, there is only one minimum and the problem is straightforward.

Although generally limited to calculations of the ground state energy, this method can be applied in certain cases to calculations of excited states as well. If the ground state wavefunction is known, either by the method of variation or by direct calculation, a subset of the Hilbert space can be chosen which is orthogonal to the ground state wavefunction.

$$|\psi\rangle = |\psi_{\mathrm{test}}\rangle - \langle\psi_{\mathrm{gr}} \mid \psi_{\mathrm{test}}\rangle\,|\psi_{\mathrm{gr}}\rangle$$

The resulting minimum is usually not as accurate as for the ground state, as any difference between the true ground state and ψ_{gr} results in a lower excited energy. This defect is worsened with each higher excited state.

In another formulation,

$$E_{\text{ground}} \leq \langle\phi|H|\phi\rangle$$

This holds for any trial Æ since, by definition, the ground state wavefunction has the lowest energy, and any trial wavefunction will have energy greater than or equal to it.

Proof: φ can be expanded as a linear combination of the actual eigenfunctions of the Hamiltonian (which we assume to be normalized and orthogonal):

$$\phi = \sum_n c_n \psi_n$$

Then, to find the expectation value of the Hamiltonian,

$$\begin{aligned}
&\langle\phi|H|\phi\rangle \\
&= \left\langle \sum_n c_n \psi_n |H| \sum_m c_m \psi_m \right\rangle \\
&= \sum_n \sum_m \langle c_n^* \psi_n | E_m | c_m \psi_m \rangle \\
&= \sum_n \sum_m c_n^* c_m E_m \left\langle \psi_n \mid \psi_m \right\rangle \\
&= \sum_n |c_n|^2 E_n .
\end{aligned}$$

Now, the ground state energy is the lowest energy possible, i.e., $E_n \geq E_g$. Therefore, if the guessed wave function Æ is normalized:

$$\langle\phi|H|\phi\rangle \geq E_g \sum_n |c_n|^2 = E_g$$

For a Hamiltonian H that describes the studied system and any normalizable function ψ with arguments appropriate for the unknown wave function of the system, we define the functional,

$$\varepsilon[\Psi] = \frac{\left\langle \Psi | \hat{H} | \Psi \right\rangle}{\left\langle \Psi \mid \Psi \right\rangle}$$

The variational principle states that,

- $\varepsilon \geq E_0$, where E_0 is the lowest energy eigenstate (ground state) of the Hamiltonian.
- $\varepsilon = E_0$ if and only if Ψ is exactly equal to the wave function of the ground state of the studied system.

The variational principle formulated above is the basis of the variational method used in quantum mechanics and quantum chemistry to find approximations to the ground state.

Another feature in variational principles in quantum mechanics is that since ψ and Ψ^+ can be varied separately (a fact arising due to the complex nature of the wave function), the quantities can be varied in principle just one at a time.

Helium Atom Ground State

The helium atom consists of two electrons with mass ***m*** and electric charge **–e**, around an essentially fixed nucleus of mass $M >> m$ and charge +2e. The Hamiltonian for it, neglecting the fine structure, is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

where $\hbar$ is the reduced Planck constant, ε_0 is the vacuum permittivity, r_i (for $i = 1, 2$) is the distance of the ith electron from the nucleus, and $|\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the two electrons.

If the term $V_{ee} = e^2/(4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|)$, representing the repulsion between the two electrons, were excluded, the Hamiltonian would become the sum of two hydrogen-like atom Hamiltonians with nuclear charge $+2e$. The ground state energy would then be $8E_1 = -109$ eV, where E_1 is the Rydberg constant, and its ground state wavefunction would be the product of two wavefunctions for the ground state of hydrogen-like atoms:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$$

Where a_0 is the Bohr radius and $Z = 2$, Helium's nuclear charge. The expectation value of the total Hamiltonian H (including the term V_{ee}) in the state described by ψ_0 will be an upper bound for its ground state energy. $<V_{ee}>$ is $-5E_1/2 = 34$ eV, so $<H>$ is $8E_1 - 5E_1/2 = -75$ eV.

A tighter upper bound can be found by using a better trial wavefunction with 'tunable' parameters. Each electron can be thought to see the nuclear charge partially 'shielded' by the other electron, so we can use a trial wavefunction equal with an 'effective' nuclear charge $Z < 2$: The expectation value of H in this state is:

$$\langle H \rangle = \left[-2Z^2 + \frac{27}{4}Z\right]E_1$$

This is minimal for Z = 27/16 implying shielding reduces the effective charge to ~1.69. Substituting this value of Z into the expression for H yields $729E_1/128 = -77.5$ eV, within 2% of the experimental value, –78.975 eV.

Deuteron Ground State

Deuterium or hydrogen-2, symbol D or ^{2}H, also known as heavy hydrogen, is one of two stable isotopes of hydrogen (the other being protium, or hydrogen-1). The nucleus of deuterium, called a deuteron, contains one proton and one neutron, whereas the far more common protium has no neutron in the nucleus.

Deuterium has a natural abundance in Earth's oceans of about one atom in 6420 of hydrogen. Thus deuterium accounts for approximately 0.02% (or, on a mass basis, 0.03%) of all the naturally occurring hydrogen in the oceans, while protium accounts for more than 99.98%.

The deuteron has spin +1 'triplet state' and is thus a boson. The NMR frequency of deuterium is significantly different from common light hydrogen. Infrared spectroscopy also easily differentiates many deuterated compounds, due to the large difference in IR absorption frequency seen in the vibration of a chemical bond containing deuterium, versus light hydrogen. The two stable isotopes of hydrogen can also be distinguished by using mass spectrometry.

The triplet deuteron nucleon is barely bound at $E_B = 2.23$ MeV, and none of the higher energy states are bound. The singlet deuteron is a virtual state, with a negative binding energy of ~60 keV. There is no such stable particle, but this virtual particle transiently exists during neutron-proton inelastic scattering, accounting for the unusually large neutron scattering cross-section of the proton.

Variation method – ground state of helium atom – ground state of Deuteron.

Check Your Progress

1. Give the uses of Schrodinger equation.
2. Define the postulate of wave function.
3. What is Ψ?
4. Define operator.
5. When energy level is degenerate?
6. Define the Eigen value.
7. State the variation method.
8. State the perturbation theory.

1.4 PERTURBATION THEORY

In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a 'small' term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated. This is only approximate because the sum of a Coulomb potential with a linear potential is unstable (has no true bound states) although the tunneling time (decay rate) is very long.

The expressions produced by perturbation theory are not exact, but they can lead to accurate results as long as the expansion parameter, say α, is very small. Typically, the results are expressed in terms of finite power series in α that seem to converge to the exact values when summed to higher order. After a certain order n ~ 1/α however, the results become increasingly worse since the series are usually divergent (being asymptotic series). There exist ways to convert them into convergent series, which can be evaluated for large expansion parameters, most efficiently by the variational method.

Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence. The time independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In this paper Schrödinger referred to earlier work of Lord Rayleigh, who investigated harmonic vibrations of a string perturbed by small inhomogeneities. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.

First Order Corrections

Consider an unperturbed Hamiltonian, H_0, which is also assumed to have no time dependence. It has known energy levels and eigenstates, arising from the time independent Schrödinger equation of the form:

$$H_0 \left|n^{(0)}\right\rangle = E_n^{(0)} \left|n^{(0)}\right\rangle, \qquad n = 1, 2, 3, \cdots$$

For simplicity, assume that the energies are discrete. The (0) superscripts denote that these quantities are associated with the unperturbed system. Note the use of bra–ket notation.

We now introduce a perturbation to the Hamiltonian. Let V be a Hamiltonian representing a weak physical disturbance, such as a potential energy produced by an external field. Thus, V is formally a Hermitian operator. Let λ be a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (the full perturbation). The perturbed Hamiltonian is represented as,

$$H = H_0 + \lambda V$$

The energy levels and eigenstates of the perturbed Hamiltonian are again given by the Schrödinger equation:

$$(H_0 + \lambda V) |n\rangle = E_n |n\rangle$$

The objective is to express E_n and $|n\rangle$ in terms of the energy levels and eigenstates of the old Hamiltonian. If the perturbation is sufficiently weak, we can write them as a (Maclaurin) power series in λ:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$
$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \cdots$$

Where,

$$E_n^{(k)} = \frac{1}{k!} \frac{d^k E_n}{d\lambda^k}\bigg|_{\lambda=0}$$

$$\left|n^{(k)}\right\rangle = \frac{1}{k!} \frac{d^k |n\rangle}{d\lambda^k}\bigg|_{\lambda=0}$$

When $k = 0$, these reduce to the unperturbed values, which are the **first term** in each series. Since the perturbation is weak, the energy levels and eigenstates should not deviate too much from their unperturbed values, and the terms should rapidly become smaller as we go to higher order.

Substituting the power series expansion into the Schrödinger equation, we obtain,

$$(H_0 + \lambda V)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \cdots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \cdots\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \cdots\right)$$

Expanding this equation and comparing coefficients of each power of λ results in an infinite series of simultaneous equations. The zeroth-order equation is simply the Schrödinger equation for the unperturbed system. The first order equation is,

$$H_0\left|n^{(1)}\right\rangle + V\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(1)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle$$

Operating through by $\langle n^{(0)}|$, the first term on the left-hand side cancels the first term on the right-hand side as per the unperturbed Hamiltonian is Hermitian. This leads to the first order energy shift:

$$E_n^{(1)} = \left\langle n^{(0)}\right| V \left|n^{(0)}\right\rangle$$

This is simply the expectation value of the perturbation Hamiltonian while the system is in the unperturbed state.

The Stark Effect for n = 2 Hydrogen

The Stark effect for the $n = 2$ states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of E_0. That is $H_0\phi_{2\ell m} = E_0\phi_{2\ell m}$.

The degenerate states are $\phi200$, $\phi211$, $\phi210$ and $\phi21(-1)$.

The perturbation due to an electric field in the z direction is $H_1 = +e\mathcal{E}z$.

So the first order degenerate state perturbation theory equation is,

$$\sum_i \alpha_i \left\langle \phi^{(j)} \left| H_0 + e\mathcal{E}z \right| \phi^{(i)} \right\rangle = (E_0 + E^{(1)})\alpha_j.$$

This is essentially a 4 x 4 matrix eigenvalue equation. There are 4 eigenvalues $(E_0 + E^{(1)})$, distinguished by the index n.

Because of the exact degeneracy $(H_0\phi^{(j)} = E_0\phi^{(j)})$, the H_0 and E_0 can be eliminated from the equation.

$$\begin{aligned} \sum_i \alpha_i (E_0\delta_{ij} + \left\langle \phi^{(j)} \left| e\mathcal{E}z \right| \phi^{(i)} \right\rangle) &= (E_0 + E^{(1)})\alpha_j \\ E_0\alpha_j + \sum_i \alpha_i \left\langle \phi^{(j)} \left| e\mathcal{E}z \right| \phi^{(i)} \right\rangle &= E_0\alpha_j + E^{(1)}\alpha_j \\ \sum_i \alpha_i \left\langle \phi^{(j)} \left| e\mathcal{E}z \right| \phi^{(i)} \right\rangle &= E^{(1)}\alpha_j \end{aligned}$$

This is just the eigenvalue equation for H_1 which we can write in (pseudo) matrix form as follows,

$$\begin{pmatrix} \\ H_1 \\ \\ \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

Now, in fact, most of the matrix elements of H_1 are zero. We can define that because $[L_z, z] = 0$, hence all the matrix elements between states of unequal m are zero. Another way of saying this is that the operator z does not 'change' m. Here is a little proof.

$$\langle Y_{lm} \left| [L_z, z] \right| Y_{l'm'} \rangle = 0 = (m - m') \langle Y_{lm} \left| z \right| Y_{l'm'} \rangle$$

This implies that $\langle Y_{lm} \left| z \right| Y_{l'm'} \rangle = 0$ unless $m = m'$.

Let us define the one remaining nonzero (real) matrix element to be γ.

$$\gamma = e\mathcal{E} \langle \phi_{200} \left| z \right| \phi_{210} \rangle$$

The equation that is labelled with the basis states to define the order is.

$$\begin{array}{c} \phi_{200} \\ \phi_{211} \\ \phi_{210} \\ \phi_{21-1} \end{array} \begin{pmatrix} 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & 0 \\ \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

We can see by inspection that the eigenfunctions of this operator are $\phi211$, $\phi21-1$, and $\frac{1}{\sqrt{2}}(\phi_{200} \pm \phi_{210})$ with eigenvalues (of H_1) of 0, 0, and $\pm\gamma$.

What remains is to compute γ. Recall $Y_{00} = \frac{1}{\sqrt{4\pi}}$ and $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$.

$$
\begin{aligned}
\gamma &= e\mathcal{E}\int (2a_0)^{-3/2}\,2\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}Y_{00}z\,(2a_0)^{-3/2}\,\frac{1}{\sqrt{3}}\left(\frac{r}{a_0}\right)e^{-r/2a_0}Y_{10}d^3r \\
&= 2e\mathcal{E}\,(2a_0)^{-3}\,\frac{1}{\sqrt{3}}\int r^3d^3r\left(1-\frac{r}{2a_0}\right)\left(\frac{r}{a_0}\right)e^{-r/a_0}\int\frac{1}{\sqrt{4\pi}}\cos\theta Y_{10}d\Omega \\
&= 2eE(2)^{-3}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\int_0^\infty\left(\frac{r^4}{a_0^4}-\frac{r^5}{2a_0^5}\right)e^{-r/a_0}dr \\
&= \frac{a_0e\mathcal{E}}{12}\left[\int_0^\infty x^4e^{-x}dx-\frac{1}{2}\int_0^\infty x^5e^{-x}dx\right] \\
&= \frac{a_0e\mathcal{E}}{12}\left[4\cdot3\cdot2\cdot1-\frac{5\cdot4\cdot3\cdot2\cdot1}{2}\right] \\
&= \frac{a_0e\mathcal{E}}{12}(-36) \\
&= -3e\mathcal{E}a_0 \qquad\Rightarrow\qquad E^{(1)}=\mp3e\mathcal{E}a_0
\end{aligned}
$$

This is first order in the electric field, as we would expect in first order (degenerate) perturbation theory.

If the states are not exactly degenerate, we have to leave in the diagonal terms of H_0. Assume that the energies of the two (mixed) states are $E_0 \pm \Delta$, where Δ comes from some other perturbation, like the hydrogen fine structure. The $\phi 211$ and $\phi 21\,(-1)$ are still not mixed by the electric field.

$$
\begin{pmatrix} E_0-\Delta & \gamma \\ \gamma & E_0+\Delta \end{pmatrix}\begin{pmatrix}\alpha_1\\ \alpha_2\end{pmatrix}=E\begin{pmatrix}\alpha_1\\ \alpha_2\end{pmatrix}
$$

$$
E=E_0\pm\sqrt{\gamma^2+\Delta^2}
$$

This is correct in both limits, $\Delta \gg \gamma$, and $\gamma \gg \Delta$. It is also correct when the two corrections are of the same order.

1.5 ORDINARY ANGULAR MOMENTUM

NOTES

In physics, **angular momentum**, also termed as moment of momentum or rotational momentum, is the rotational equivalent of linear momentum. It is an important quantity in physics because it is a conserved quantity—the total angular momentum of a closed system remains constant.

In three dimensions, the angular momentum for a point particle is a pseudovector **r** × **p**, the cross product of the particle's position vector **r** (relative to some origin) and its momentum vector; the latter is **p = mv** in Newtonian mechanics. Unlike momentum, angular momentum depends on where the origin is chosen, since the particle's position is measured from it.

There are two special types of angular momentum of an object, namely the spin angular momentum is the angular momentum about the object's centre of mass, while the orbital angular momentum is the angular momentum about a chosen center of rotation. The total angular momentum is the sum of the spin and orbital angular momenta. The orbital angular momentum vector of a point particle is always parallel and directly proportional to its orbital angular velocity vector ω, where the constant of proportionality depends on both the mass of the particle and its distance from origin. The spin angular momentum vector of a rigid body is proportional but not always parallel to the spin angular velocity vector **Ω**, making the constant of proportionality a second-rank tensor rather than a scalar.

The total angular momentum of any composite system is the sum of the angular momenta of its constituent parts. For a continuous rigid body or a fluid, the total angular momentum is the volume integral of angular momentum density, i.e., angular momentum per unit volume in the limit as volume shrinks to zero, over the entire body.

Torque can be defined as the rate of change of angular momentum, analogous to force. The net external torque on any system is always equal to the total torque on the system; in other words, the sum of all internal torques of any system is always 0, this is the rotational analogue of Newton's Third Law. Therefore, for a closed system, i.e., where there is no net external torque, the total torque on the system must be 0, which means that the total angular momentum of the system is constant.

Angular momentum is subject to the Heisenberg uncertainty principle, implying that at any time, only one projection, also called 'component' can be measured with definite precision.

Orbital Angular Momentum in Two Dimensions

Angular momentum is defined as a vector quantity, more precisely, a pseudovector, that represents the product of a body's rotational inertia and rotational velocity (in radians/sec) about a particular axis. Angular momentum can be considered a rotational analog of linear momentum. Therefore, where linear momentum p is proportional to mass m and linear speed v,

$$p = mv$$

Angular momentum L is proportional to moment of inertia I and angular speed ω measured in radians per second.

$$L = I\omega$$

Orbital angular velocity is always measured with respect to a fixed origin. Therefore, L should be referred to as the angular momentum relative to that center.

Generalized Angular Momentum

Angular momentum in higher dimensions can be defined by application of Noether's theorem to rotation groups of higher order. Generalization beyond three dimensions is best treated using differential forms. A set of commuting generalized orbital angular momentum operators in $\boldsymbol{n}$-dimensional polar coordinates can be defined and also their eigenvalues and simultaneous eigenfunctions.

The angular momentum of a particle of mass m with respect to a chosen origin is given by,

$$L = mvr \sin \theta$$

By the vector product,

$$L = r \times p$$

For an orbit, angular momentum is conserved, and this leads to one of Kepler's laws. For a circular orbit, L becomes,

$$L = mvr$$

1.5.1 Eigen Functions and Eigenvalues of Angular Momentum

Abstract Operator Method

The Schrödinger method for solving the energy eigenvalue problem of linear harmonic oscillator as presented in the previous sections consists in replacing the position x and the linear momentum p in the expression for total energy by the corresponding Hermitian operator $\hat{x} \int x$ and $\hat{p} = -i\hbar \frac{d}{dx}$, respectively, to obtain the Hamiltonian operator $\hat{H}$ for the oscillator and then to solve for the energy eigenvalue equation,

$$\hat{H}\psi = E\psi$$

We may, however, note that one of the fundamental features of quantum mechanics is that operators $\hat{x} = x$ and $\hat{p}$ satisfy the commutation relation,

$$[\hat{x}, \hat{p}] = i\hbar \qquad \text{...(77)}$$

There exist many problems which can be exactly and elegantly solved using the method of abstract operator algebra, i.e., using the commutation relations between operators without considering specific forms for the operators.

In the following, we use this method to solve the energy eigenvalue problem for linear harmonic oscillator. As we shall see, the method allows us to find, with simplicity not only the expectation values of various physical quantities for the oscillator but also the energy eigenfunctions of the oscillator.

The Hamiltonian operator of a harmonic oscillator of mass m oscillating along the x-axis under a force constant k is,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} k x^2 \qquad \text{...(78)}$$

Let us introduce two operators and † according to,

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\, x + i\sqrt{\frac{1}{2m\hbar\omega_0}}\, \hat{p} \qquad \text{...(79)}$$

And

$$\hat{a}^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}}\, x - i\sqrt{\frac{1}{2m\hbar\omega_0}}\, \hat{p} \qquad \text{...(80)}$$

In the above $\hat{a}^\dagger$ is the Hermitian adjoint of $\hat{a}$ and ω_0 is the natural angular frequency of the oscillator. From Equations (79) and (80) we obtain

$$\hat{a}\hat{a}^\dagger = \left(\sqrt{\frac{m\omega_0}{2\hbar}}\, x + i\sqrt{\frac{1}{2m\hbar\omega_0}}\, \hat{p}\right)\left(\sqrt{\frac{m\omega_0}{2\hbar}}\, x - i\sqrt{\frac{1}{2m\hbar\omega_0}}\, \hat{p}\right)$$

$$= \frac{m\omega_0}{2\hbar}x^2 + \frac{1}{2m\hbar\omega_0}\hat{p}^2 + \frac{i}{2\hbar}(\hat{p}x - x\hat{p})$$

Using Equation (81) in the above we obtain

$$\hat{a}\hat{a}^{\dagger} = \frac{m\omega_0}{2\hbar}x^2 + \frac{1}{2m\hbar\omega_0}\hat{p}^2 + \frac{i}{2\hbar}(-i\hbar)$$

or $$\hat{a}\hat{a}^{\dagger} = \frac{1}{\hbar\omega_0}\left[\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right] + \frac{1}{2}$$

or $$\hat{a}\hat{a}^{\dagger} = \frac{\hat{H}}{\hbar\omega_0} + \frac{1}{2} \text{ [using Equation (81)]} \qquad ...(81)$$

Similarly, we obtain

$$\hat{a}^{\dagger}\hat{a} = \frac{\hat{H}}{\hbar\omega_0} - \frac{1}{2} \qquad ...(82)$$

Adding Equations (82) and (83) we obtain,

$$2\frac{\hat{H}}{\hbar\omega_0} = \hat{a}\hat{a}^{\dagger} + \hat{a}\hat{a}^{\dagger}$$

or $$\hat{H} = \frac{1}{2}\hbar\omega_0(\hat{a}\hat{a}^{\dagger} + \hat{a}^{\dagger}\hat{a}) \qquad ...(83)$$

Subtracting Equation (84) from Equation (85) we get,

$$\hat{a}\hat{a}^{\dagger} - \hat{a}^{\dagger}\hat{a} = 1$$

Clearly, the operators and $\hat{a}^{\dagger}$ satisfy the commutation relation,

$$[\hat{a}, \hat{a}^{\dagger}] = 1 \qquad ...(84)$$

We may also express the Hamiltonian operator as,

$$\hat{H} = \hbar\omega_0\left(\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right) \qquad ...(85)$$

We observe that the Hamiltonian operator $\hat{H}$ and the operator $\hat{a}^{\dagger}$ are related to each other by numbers only. Clearly, the eignvalues $\hat{H}$ and that of $\hat{a}^{\dagger}\hat{a}$ bear the same relationship.

Eigenvalues of $\hat{a}^{\dagger}\hat{a}$

We have

$$[\hat{a}^{\dagger}\hat{a}, a] = \hat{a}^{\dagger}\hat{a}\hat{a} - \hat{a}\hat{a}^{\dagger}\hat{a} = (\hat{a}^{\dagger}\hat{a}$$

1.5.2 Operator using Ladder Operators

If with each ket $|a\rangle$ in the ket space we can associate another ket $|b\rangle$, then this association may be used to define an operator say $\hat{\alpha}$ which we may write in the form

$$|b\rangle = \hat{\alpha}|a\rangle \qquad \ldots(86)$$

$\hat{\alpha}$ in the above might mean multiplication, differentiation, integration, etc., operations.

NOTES

An operator always appears to the left of the ket on which it operates.

A class of operators used extensively in the formulation of quantum mechanics is the *linear operators*. A linear operator in ket space is defined as given in the following; if $|a_1\rangle$, $|a_2\rangle$ and $|a\rangle$ are any three kets in the space and *C* is a number then an operator $\hat{\alpha}$ is said to be linear if

$$\hat{\alpha}\,(\,|a_1\rangle + |a_2\rangle\,) = \hat{\alpha}\,|a_1\rangle + \hat{\alpha}\,|a_2\rangle \qquad \ldots(87)$$

And $$\hat{\alpha}(C\,|\,a\rangle) = C\,\hat{\alpha}|\,a\rangle$$

$$\ldots(88)$$

Equal Linear Operators

A linear operator is completely defined when its effect on every ket in the ket space is known. Hence, two linear operators $\hat{\alpha}_1$ *and* $\hat{\alpha}_2$ are equal $(\hat{\alpha}_1 = \hat{\alpha}_2)$ if

$$\hat{\alpha}_1\,|a\rangle = \hat{\alpha}_2\,|a\rangle \quad \text{for all } |a\rangle \qquad \ldots(89)$$

Null Operator

A linear operator a is a *null operator* if

$$\hat{\alpha}|a\rangle = 0 \quad \text{for all } |a\rangle \qquad \ldots(90)$$

Identity operator

A linear Operator $\hat{\alpha}$ is said to be an *identity operator* if

$$\hat{\alpha}\,|a\rangle = |a\rangle \quad \text{for all } |\,a\rangle \qquad \ldots(91)$$

Algebra of Linear Operators

(i) **Sum** of two linear operators $\hat{\alpha}_1$ and $\hat{\alpha}_2$, i.e., $(\hat{\alpha}_1 + \hat{\alpha}_2)$ is defined according to

$$(\hat{\alpha}_1 + \hat{\alpha}_2)\,|\,a\rangle = \hat{\alpha}_1\,|\,a\rangle + \hat{\alpha}_2\,|a\rangle \qquad \ldots(92)$$

(ii) **Product** of two linear operators α_1 and $\hat{\alpha}_2$, i.e., $(\hat{\alpha}_1\ \hat{\alpha}_2)$ is defined according to

$$(\hat{\alpha}_1\ \hat{\alpha}_2)\,|\,a\rangle = \hat{\alpha}_1\,(\hat{\alpha}_2\,|\,a\rangle\,) \qquad \ldots(93)$$

From Equation (42) it is possible to define powers of a linear operator.

We further find the following relations to hold

$$(\hat{\alpha}_1 + \hat{\alpha}_2)\,|\,a\rangle = (\hat{\alpha}_2 + \hat{\alpha}_1)\,|\,a\rangle \qquad \ldots(94)$$

$$[(\hat{\alpha}_1 + \hat{\alpha}_2) + \hat{\alpha}_3]\,|\,a\rangle = [\hat{\alpha}_1 + (\hat{\alpha}_2 + \hat{\alpha}_3)]\,|\,a\rangle \qquad \ldots(95)$$

$$[\hat{\alpha}_1\,(\hat{\alpha}_2 + \hat{\alpha}_3)]\,|\,a\rangle = \hat{\alpha}_1\,\hat{\alpha}_2\,|\,a\rangle + \hat{\alpha}_1\,\hat{\alpha}_3\,|\,a\rangle \qquad \ldots(96)$$

(iii) **Commutator** of two linear operators $\hat{\alpha}_1$ and $\hat{\alpha}_2$ is written as $[\hat{\alpha}_1, \hat{\alpha}_2]$ and is defined as

$$[\hat{\alpha}_1, \hat{\alpha}_2] = \hat{\alpha}_1 \hat{\alpha}_2 - \hat{\alpha}_2 \hat{\alpha}_1 \qquad \text{...(97)}$$

The operator $\alpha\hat{}_1$ and $\alpha\hat{}_2$ are said to be *non-commutative* if

$$\hat{\alpha}_1 \hat{\alpha}_2 \neq \hat{\alpha}_2 \hat{\alpha}_1, \text{ i.e., } [\hat{\alpha}_1, \hat{\alpha}_2] \neq 0 \qquad \text{...(98)}$$

We may note that the above properties hold with matrices.

It is seen that the algebra of *N*-dimensional square matrices is the same as the algebra of linear operators.

We may further note that the algebra of quantum mechanics is a non-commutative algebra.

Multiplication by a constant is linear operation. A constant operator commutes with all linear operators.

(iv) **Inverse of an Operator:** If two linear operators $\hat{\alpha}_1$ and $\hat{\alpha}_2$ satisfy the equation

$$\hat{\alpha}_1 \hat{\alpha}_2 = \hat{\alpha}_2 \hat{\alpha}_1 = \hat{I} \text{ (Identity operator)} \qquad \text{...(99)}$$

then $\hat{\alpha}_2$ is said to be the *inverse* of $\hat{\alpha}_1$ and vice-versa, provided the inverse exists and we write

$$\hat{\alpha}_2 = \hat{\alpha}_1^{-1}, \quad \hat{\alpha}_1 = \hat{\alpha}_2^{-1} \qquad \text{...(100)}$$

The inverse of a product of operators $(\hat{\alpha}_1, \hat{\alpha}_2, \hat{\alpha}_3)$ is

$$(\hat{\alpha}_1 \hat{\alpha}_2 \hat{\alpha}_3)^{-1} = \hat{\alpha}_3^{-1} \hat{\alpha}_2^{-1} \hat{\alpha}_1^{-1} \qquad \text{...(101)}$$

As mentioned earlier, the above properties of linear operators are common to finite square matrices. This fact allows us to *represent operators by matrices*.

Operation of Linear Operator on Bra

By operating a linear operator (say $\hat{\alpha}$) on a bra (say $\langle c|$) we obtain, in general, another bra (say $\langle d|$) in the same bra space. It is a convention to write the operator to the right of the bra on which it operates. Hence we write,

$$\langle d| = \langle c|\hat{\alpha} \qquad \text{...(102)}$$

The operation is defined through the equation,

$$\langle c|(\hat{\alpha}|a\rangle) = (\langle c|\hat{\alpha})|a\rangle. \qquad \text{...(103)}$$

Thus, $\hat{\alpha}$ may first operate on $\langle c|$ and the result applied to $|a\rangle$ or vice-versa.

We may note that operator properties given above are equally valid whether they are applied to kets or to bras.

An Example of a Linear Operator

A simple example of a linear operator that occurs frequently in quantum theory is,

$$|a\rangle\ \langle b| = \hat{P} \qquad \ldots(104)$$

$\hat{P}$ may operate as a ket, say, $|c\rangle$ to give

$$\hat{P}\ |c\rangle = |a\rangle\ \langle b|c\rangle$$

The above is the ket $|a\rangle$ multiplied by the number $\langle b|c\rangle$

$\hat{P}$ may operate on the bra $\langle c|$ to give

$$\langle c|\hat{P} = \langle ca\rangle\ \langle b. \qquad \ldots(105)$$

The above is the bra $\langle b|$ multiplied by the number $\langle c|a\rangle$.

The operator $\hat{p}$ defined above is seen to satisfy the requirements of a linear operator.

Hermitian Operators

As discussed earlier, the linear operators which represent dynamical variables of a quantum system are real linear operators. Such operators are said to be Hermitian. In the following we define Hermitian operator in the space of ket and bra vectors.

Consider the ket $|q\rangle$ to be the result of operation of the linear operator $\hat{\alpha}$ on a ket $|p\rangle$, i.e.,

$$|q\rangle = \hat{\alpha}\ |p\rangle$$

The bra associated with ket $|q\rangle$ is then given by,

$$\langle q| = \langle p|\ \hat{\alpha}^{\dagger} = \hat{\alpha}^{\dagger}\ |p\rangle^{\dagger} = (\ |q\rangle\ )^{\dagger}$$

The symbol $\hat{\alpha}^{\dagger}$ is called the Hermitian adjoint of $\hat{\alpha}$. Thus, the bra $\langle q|$ which is hermitian adjoint of $|q\rangle$ may be considered as the result of some linear operator operating on $\langle p|$ which is designated by $\hat{\alpha}^{\dagger}$.

If in Equation (28) we take /$\langle a| = \langle p|\ \hat{\alpha}^{\dagger}$ and $|a\rangle = \hat{\alpha}\ |p\rangle$, then we get

$$\langle p|\ \hat{\alpha}^{\dagger}\ |b\rangle = \langle b|\ \hat{\alpha}\ |p\rangle^{*} \qquad \ldots(106)$$

Equation (81) is a general result that applies to any two kets $|p\rangle$ and | $|b\rangle$ and any linear operator $\hat{\alpha}$.

We may replace $\hat{\alpha}$ by $\hat{\alpha}^{\dagger}$ in Equation (81) to obtain

$$\langle p|\ \hat{\alpha}^{\dagger\dagger}|b\rangle = \langle b|\ \hat{\alpha}^{\dagger}|p\rangle^{*} \qquad \ldots(107)$$

Let us now replace $|a\rangle$ in Equation by $|a\rangle = \hat{\alpha}^{\dagger} |p\rangle$

and $\langle a| = \langle p|\hat{\alpha}$. We then get

$$\langle p|\hat{\alpha}|b\rangle = \langle b|\hat{\alpha}^{\dagger}|p\rangle^{*} \qquad \ldots(108)$$

Comparing Equations (82) and (83) we obtain

$$\langle p|\hat{\alpha}^{\dagger}|b\rangle = \langle p|\hat{\alpha}|b\rangle. \qquad \ldots(109)$$

Since in Equation (84) ket $|b\rangle$ and bra $\langle p|$ are arbitrary, we find that

$$\hat{\alpha}^{\dagger\dagger} = \hat{\alpha} \qquad \ldots(110)$$

If the linear operator $\hat{\alpha}$ is self adjoint, i.e., if

$$\hat{\alpha} = \hat{\alpha}^{\dagger}$$

then $\hat{\alpha}$ is said to be Hermitian. From Equation (81) we find that if $\hat{\alpha}$ is Hermitian, it must satisfy

$$\langle p|\hat{\alpha}^{\dagger}|b\rangle = \langle b|\alpha^{\wedge}|p\rangle^{*} \qquad \ldots(111)$$

for arbitrary $|b\rangle$ and $|p\rangle$.

Eigenvalue Problem for Operators in Ket and Bra Space

Let us consider a linear operator $\hat{\alpha}$. In general, $\hat{\alpha}$ operating as a ket gives another ket in the same space.

However, for every linear operator there exists a set of kets such that the result of operation of the operator on any such ket is the same ket multiplied by a number. If $|a\rangle$ be such a ket for the operator $\hat{\alpha}$ then we obtain

$$\hat{\alpha}|a\rangle = \alpha_a|a\rangle \qquad \ldots(112)$$

α_a being a number.

Equation (87) is referred to as the eigenvalue problem for the operator $\hat{\alpha}$. $|a\rangle$ is said to be the eigen ket of $\hat{\alpha}$ and α_a the associated eigenvalue.

It is customary to label an eigenket with the associated eigenvalue. With this convention, we may rewrite the eigenvalue problem (eigenvalue equation) as

$$\hat{\alpha}|\alpha_a\rangle = \alpha_a|\alpha_a\rangle \qquad \ldots(113)$$

If $|\alpha_a\rangle$ is an eigenket of $\hat{\alpha}$, then by Equation (88) any constant *c* times $|\alpha_a\rangle$ is also an eigenket of $\hat{\alpha}$ with the same eigenvalue α_a. The states represented by $|\alpha_a\rangle$ and $c|\alpha_a\rangle$ are one and the same state.

Eigenvalue problem formulated in terms of bras is

$$\langle \beta_a | \hat{\beta} = \beta_a \langle \beta_a | \qquad \text{...(114)}$$

In the above $\langle \beta_a |$ is an eigenbra of the linear operator $\hat{\beta}$ belonging to the eigenvalue β_a.

Theorems Valid for All Linear Hermitian Operators

Earler we discussed the following two theorems related to linear Hermitian operators. We once again state the theorems and prove them using Dirac's bra and ket notations.

Theorem 1: The eigenvalues of a linear Hermitian operator are real.

Proof: Consider a linear hermitian operator $\hat{\alpha}$. The eigenvalues of $\hat{\alpha}$ satisfy the equation

$$\hat{\alpha} \, | \alpha_k \rangle = \alpha_k \, | \alpha_k \rangle$$

Forming scalar product of both sides of the above equation with $\langle \alpha_k |$, we get

$$\langle \alpha_k | \hat{\alpha} | \alpha_k \rangle = \alpha_k \langle \alpha_k | \alpha_k \rangle \qquad \text{...(115)}$$

Taking complex conjugate of both sides we obtain

$$\langle \alpha_k | \hat{\alpha} | \alpha_k \rangle^* = \langle \alpha_k | \hat{\alpha}^\dagger | \alpha_k \rangle = \alpha_{k^*} \langle \alpha_k | \alpha_k \rangle \qquad \text{...(116)}$$

But since $\hat{\alpha}^\dagger = \hat{\alpha}$ and $\langle \alpha_k | \alpha_k \rangle \neq 0$, comparing Equations (89) we get

$$\alpha_k = \alpha_k^* \qquad \text{...(117)}$$

Clearly the eigenvalue α_k is real.

Theorem 2: Two eigenvectors of a linear Hermitian operator belonging to different eigenvalues are orthogonal.

Proof: Consider a linear Hermitian operator $\hat{\alpha}$.

Let $| \alpha_j \rangle$ be the eigenvector of $\hat{\alpha}$ belonging to eigenvalue α_j and $| \alpha_k \rangle$ be the eigenvector of α belonging to eigenvalue α_k.

We then have according to our considerations

$$\left. \begin{array}{l} \hat{\alpha} = \hat{\alpha}^\dagger \\ \alpha_j = \alpha_j^* \;\; ; \;\; \alpha_k = \alpha_k^* \end{array} \right\} \qquad \text{...(118)}$$

Let $\langle \alpha_k |$ be the eigenbra associated with the eignket $| \alpha_k \rangle$.

We then have the eigenvalue equations

$$\hat{\alpha}|\alpha_j\rangle = \alpha_j|\alpha_j\rangle \qquad \ldots(119)$$

$$\langle\alpha_k|\hat{\alpha} = \alpha_k\langle\alpha_k| \qquad \ldots(120)$$

Forming scalar product of Equation (91) with $\langle\alpha_k|$, we get

$$\langle\alpha_k|\hat{\alpha}|\alpha_j\rangle = \alpha_j\langle\alpha_k|\alpha_j\rangle \qquad \ldots(121)$$

Similarly, forming scalar product of Equation (67) with $|\alpha_j\rangle$ we obtain

$$\langle\alpha_k|\hat{\alpha}|\alpha_j\rangle = \alpha_k\langle\alpha_k|\alpha_j\rangle \qquad \ldots(122)$$

Subtracting Equation (69) from Equation (68), we get

$$(\alpha_j-\alpha_k)\langle\alpha_k|\alpha_j\rangle = 0 \qquad \ldots(123)$$

Since α_j and α_k are two different eigenvalues, Equation (70) gives

$$\langle\alpha_k|\alpha_j\rangle = 0 \qquad \ldots(124)$$

Clearly, the eigenvectors $|\alpha_j\rangle$ and $|\alpha_k\rangle$ are orthogonal to each other.

We may note from Equations (92) and (93) that the eigenvalues associated with eigenkets are the same as those associated with the corresponding bras.

Physical Interpretation to Eigenvalues; Completeness, Expansion in Eigenkets

Any dynamical variable of a system that can be measured is called an observable of that system.

According to a basic postulate of quantum mechanics, with every observable there is associated a Hermitian operator and the result of measurement of an observable is an eigenvalue of the corresponding operator.

Consider an observable $\hat{\alpha}$ of a quantum system. Let $\hat{\alpha}$ be the corresponding Hermitian operator. If the system is in a particular eigen state of $\hat{\alpha}$, say $|\alpha_k\rangle$, then if we measure α we obtain the value α_k. We assume that if we measure α and in each measurement we obtain the value α_k with certainty, that is, if we measure α for a large number of systems each prepared in an identical way and always get the value α_k then we say that the system is in the state |/ $|\alpha_k\rangle$.

Furthermore, when a single measurement of α is made on the system in an arbitrary state, we obtain one of the eigen values of $\hat{\alpha}$. In such a measurement the measurement process disturbs the system and causes it to jump into one of the eigen states of $\hat{\alpha}$.

The eignekets of the operator $\hat{\alpha}$ corresponding to the observable α form an orthonormal set,

$$\langle l_1 | l_j\rangle = \delta_{ij} \qquad \ldots(125)$$

where δ_{ij} is the Kronecker delta,

$$\left.\begin{aligned}\delta_{ij} &= 0 \quad \text{if} \quad i \neq j \\ &= 1 \quad \text{if} \quad i = j\end{aligned}\right\} \qquad \ldots(126)$$

It is postulated that any state of the system is linearly dependent on the eigenkets $|\alpha_k\rangle$. In after words eigenkets of form a complete set. Any arbitrary state described by the ket $|P\rangle$ can thus be written in terms of the eigenkets of $\hat{\alpha}$ as

$$|P\rangle = \Sigma_k \quad a_k|\alpha_k\rangle \qquad \ldots(127)$$

If a measurement of α is made in the state described by $|P\rangle$ then $|a_k|^2$ gives the probability of obtaining the value α_k.

If the system is in a state described by the normalized ket

$$|P\rangle = a_1|\alpha_1\rangle + a_2|\alpha_2 \qquad \ldots(128)$$

then a measurement of α gives either the value α_1 with probability $|a_1|^2$ or the value α_2 with probability $|a_2|^2$. Since $\langle P|P\rangle = 1$, we obtain

$$|P\rangle = \Sigma_k \quad a_k|\alpha_k\rangle \ \ldots(7.74) \qquad |a_1|^2 + |a_2|^2 = 1. \qquad \ldots(129)$$

We know that the eigenkets of □ˆ form an orthonormal set so that

$$\langle\alpha_i|\alpha_j\rangle = \delta_{ij}$$

We have

$$\langle\alpha_i|P\rangle = \Sigma k \quad C_k\langle\alpha_i|\alpha_k\rangle = \Sigma k \quad C_k\,\delta_{ik} = C_i \qquad \ldots(130)$$

Thus, $|P\rangle = \Sigma|\alpha_k\rangle\ C_k = \{\Sigma k \quad |\alpha_k\rangle\ \langle\alpha_k\}|P\rangle$

$(\because C_k = \langle\alpha_k|P\rangle$ from Equation (76)

Since the above result holds for all arbitrary kets we must have

$$\Sigma_k \quad |\alpha_k\rangle\ \langle\alpha_k| = 1. \qquad \ldots(131)$$

The above equation is referred to as the completeness condition of eigenkets of the operator corresponding to an observable of a quantum system.

Classical Definition of Angular Momentum

Let us first consider the angular momentum classically. For this, let us consider a particle of mass *m* moving along a path *AB* about some fixed point *O* as shown in the Figure (1.11). Let at some instant of time, the particle be at the position *P*. The position *P* of the particle with respect to the point *O* is defined by the position vector $\overrightarrow{OP}$ or $\vec{r}$. Let the linear momentum of the particle at the position *P* be $\vec{p}$. The direction of $\vec{p}$ is along the tangent to the path *AB* at *P*.

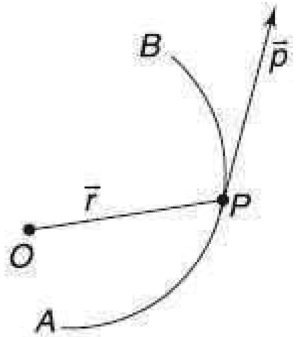

Fig. 1.11 *Angular Momentum*

Classically, the angular momentum (which is a vector quantity) of the particle about the point *O* when it is at *P* is defined as

$$\vec{L} = \vec{r} \times \vec{p} \quad \text{...(132)}$$

With the point *O* as the origin, let us consider a rectangular coordinate system (*XYZ*). If *x*, *y*, *z* be the coordinates of the point *P* then

$$\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z \quad \text{...(133)}$$

Further, if p_x, p_y and p_z be respectively the components of $\vec{p}$ along *X*, *Y* and *Z* axes then

$$\vec{p} = \hat{i}p_x + \hat{j}p_y + \hat{k}p_z \quad \text{...(134)}$$

If $L_{x,}$ L_y and L_z be respectively the *X*, *Y* and *Z* components of $\vec{L}$, then using equations (106) and (107) in Equation (105), we get

$$\hat{i}L_x + \hat{j}L_y + \hat{k}L_z = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

Evaluating the right hand side of the above equation and comparing the coefficients of $\hat{i}$, $\hat{j}$ and $\hat{k}$ on both sides we obtain

$$L_x = yp_z - zp_y \quad \text{...(135)}$$
$$L_y = zp_x - xp_z \quad \text{...(136)}$$
$$L_z = xp_y - yp_x \quad \text{...(137)}$$

NOTES

Quantum Mechanical Description of Angular Momentum

In order to treat angular momentum quantum mechanically, we replace the physical quantities $\vec{L}$, $\vec{r}$, $\vec{p}$, L_x, L_y, L_z, x, y, z, p_x, p_y and p_z by corresponding linear Hermitian operators,

$$x \to \hat{x} = x$$
$$y \to \hat{y} = y$$
$$z \to \hat{z} = z$$
$$p_x \to \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$
$$p_y \to \hat{p}_y = -i\hbar\frac{\partial}{\partial y}$$
$$p_z \to \hat{p}_z = -i\hbar\frac{\partial}{\partial z} \quad \text{...(138)}$$

Substituting the above in Equations (105), (108), (110) and (138) we obtain the quantum mechanical operators corresponding to the quantities $\vec{L}$, L_x, L_y, L_z as

$$\hat{\vec{L}} = -i\hbar\vec{r} \times \vec{\nabla} \quad \text{...(139)}$$
$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad \text{...(140)}$$
$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad \text{...(141)}$$
$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad \text{...(142)}$$

Step-Up (Raising) and Step-Down (Lowering) Operators or Ladder Operators

Instead of $\hat{L}_x$ and $\hat{L}_y$ it is often convenient and more instructive to use their complex combinations $\hat{L}_x \pm i\hat{L}_y$.

The operator $\quad L_+ = \hat{L}_x + i\hat{L}_y \quad$ ...(143)

is called the step-up operator.

The operator $\quad L_- = L_x - iL_y \quad$ ...(144)

is called the step-down operator.

We find $\quad L_zL_+ = L_z(L_x + iL_y) = L_zL_x + iL_zL_y \quad$ ...(145)

Using the commutation relations Equation (92) becomes

$$\hat{L}_z\hat{L}_+ = \hat{L}_x\hat{L}_z + i\hat{L}_y + i(\hat{L}_y\hat{L}_z - i\hat{L}_x)$$
$$= (\hat{L}_x + i\hat{L}_y)\,\hat{L}_z + (\hat{L}_x + i\hat{L}_y)$$
$$= \hat{L}_+\hat{L}_z + \hat{L}_+$$

or

$$\hat{L}_z\hat{L}_+ = \hat{L}_+\,(\hat{L}_z + 1) \qquad \ldots(146)$$

Similarly, we obtain

$$\hat{L}_z\hat{L}_- = \hat{L}_-\,(\hat{L}_z + 1) \qquad \ldots(147)$$

Let Y_{im} be a simultaneous eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ belonging to eigenvalue m of $\hat{L}_z$. We obtain

$$\hat{L}_z\hat{L}_+Y_{lm} = \hat{L}_+(\hat{L}_z + 1)\;Y_{lm} \qquad \text{[using Equation (119)]}$$
$$= \hat{L}_+\hat{L}_zY_{lm} + \hat{L}_+Y_{lm}$$
$$= \hat{L}_+mY_{lm} + \hat{L}_+Y_{lm}$$

or

$$\hat{L}_z(\hat{L}_+Y_{lm}) = (m + 1)\;(\hat{L}_+Y_{lm}) \qquad \ldots(148)$$

Similarly, we get

$$\hat{L}_z(\hat{L}_-Y_{lm}) = (m - 1)\;(\hat{L}_-Y_{lm}) \qquad \ldots(149)$$

Equation (121) shows that $\hat{L}_+Y_{lm}$ is an eigenfunction of $\hat{L}_z$ belonging to eigenvalue $(m+1)$, i.e., an eigenvalue one unit greater while Equation (122) shows that $\hat{L}_-Y_{lm}$ is an eigenfunction of $\hat{L}_z$ with eigenvalue $(m-1)$, i.e., an eigenvalue one unit less than the eigenvalue m belonging to the eigenfunction Y_{lm}. For the above reasons, the operators $\hat{L}_+$ and $\hat{L}_-$ are Respectively, called the step-up and step-down operators or ladder operators.

1.5.3 Antisymmetry and Pauli Exclusion Principle

Formation of Energy Bands in Solids

In the case of a single isolated atom, the electron in any orbit as shown in Figure 1.12 have a definite energy. As a result, they occupy discrete energy levels, as shown in Figure 1.13(a).

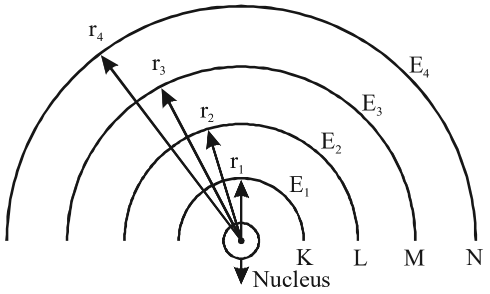

Fig. 1.12 *The energy levels of a single isolated atom*

The pauli exclusion principle allows each energy level to contain only two electrons. For example, the 2s level of a single atom contains one energy level with two electrons and 2p level contains 3 energy levels with two electrons in each level thus, with a total of six electrons as shown in Figure 1.13(a).

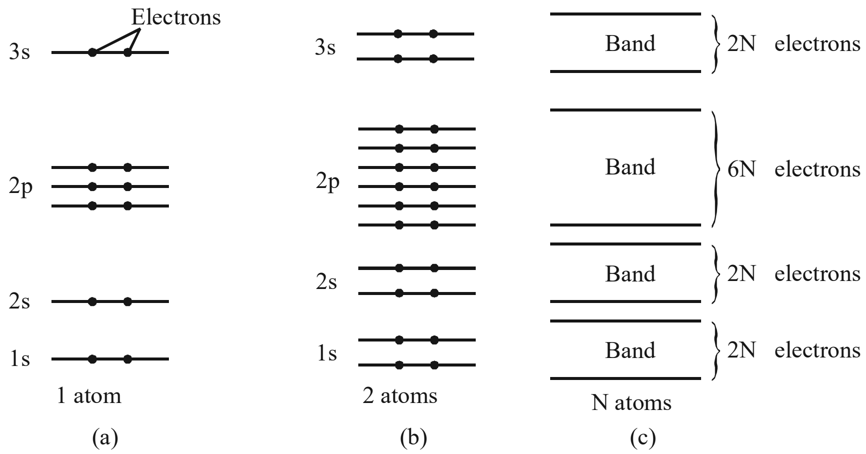

Fig. 1.13 *The energy levels broaden into energy bands*

Band Structure in Solid

Let us consider the formation of bands in a solid sodium.

The single energy level of an isolated sodium (Z = 11) based on the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$ is shown in Figure 1.13(a).

When an another sodium is brought close to it, the electrons will be subjected to the effect of an additional field. As a result, each energy level is split in to two as shown in Figure 1.13(b). Similarly, when three atoms come close together, the original level splits into three levels and so on.

More generally, when a solid is formed by bringing N atoms together, the Pauli principle still demands that only two electrons in the entire solid should have the same energy. Hence, in a solid the different split energy levels of electrons come together to form continuous bands of energies as shown in Figure 1.13(c).

Consequently, the 2s band in a solid sodium contain N discrete energy levels and 2N electrons, two in each energy level. Similarly, each of the 2p level contain N energy levels and 2N electrons. Hence, a broad 2p band will contain 3N energy levels and 6N electrons since the three 2p bands overlap.

Hence in general, each energy band has a total of N individual levels and each energy band can hold a maximum of $2(2l + 1)$ N electrons.

[Each energy level can hold $2\ (2l + 1)$ electrons. 2 corresponds to the electrospin and $(2l + 1)$ corresponds to the orientation of the electron orbital angular momentum].

The result is that, electrons in any orbit of atom within a solid can have a range of energies rather than a single value. *Thus, the range of energies possessed by an electron in a solid is known as energy band.* i.e., Each energy level of an isolated atom becomes a band in a solid as shown in Figure 1.16(c).

Antisymmetry

The term 'Antisymmetry' can be defined using the Pauli exclusion principle of the quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously. This principle was formulated by Austrian physicist Wolfgang Pauli in 1925 for electrons, and later extended to all fermions with his spin–statistics theorem of 1940.

In the case of electrons in atoms, it is impossible for two electrons of a polyelectron atom to have the same values of the four quantum numbers, we state that:

n, the principal quantum number.

$-l$, the azimuthal quantum number.

m_{-l}, the magnetic quantum number.

m_s, the spin quantum number.

For example, if two electrons reside in the same orbital, then their n, $-l$, and m_{-l} values are the same, therefore, their m_s must be different, and thus the electrons must have opposite half-integer spin projections of 1/2 and –1/2.

Concerning the exchange of two identical particles, the total (many-particle) wave function is **antisymmetric** for fermions, and symmetric for bosons. This means that if the space and spin coordinates of two identical particles are interchanged, then the total wave function changes its sign for fermions and does not change for bosons.

If two fermions were in the same state, for example the same orbital with the same spin in the same atom, then interchanging them would change nothing and the total wave function would be unchanged. The only way the total wave function can both change sign as required for fermions and also remain unchanged is that this function must be zero everywhere, which means that the state cannot exist. This reasoning does not apply to bosons because the sign does not change.

The Pauli exclusion principle with a single-valued many-particle wavefunction is equivalent to requiring the wavefunction to be antisymmetric with respect to exchange. If $|x\rangle$ and $|y\rangle$ range over the basis vectors of the Hilbert space describing a one-particle system, then the tensor product produces the basis vectors $|x, y\rangle = |x\rangle \otimes |y\rangle$ of the Hilbert space describing a system of two such particles. Any two-particle state can be represented as a superposition, i.e., sum, of these basis vectors:

$$|\psi\rangle = \sum_{x,y} A(x,y)|x,y\rangle$$

Where each $A(x,y)$ is a (complex) scalar coefficient. **Antisymmetry** under exchange means that $A(x,y) =$ “$A(y,x)$. This implies $A(x,y) = 0$ when $x = y$, which is Pauli exclusion. It is true in any basis since local changes of basis keep antisymmetric matrices antisymmetric.

Conversely, if the diagonal quantities $A(x,x)$ are zero in every basis, then the wavefunction component,

$$A(x,y) = \langle\psi|x,y\rangle = \langle\psi|\Big(|x\rangle \otimes |y\rangle\Big)$$

is necessarily antisymmetric.

Check Your Progress

9. What is null operator?
10. Define (LCAO).
11. What is bond angle?
12. Define the stability of molecules.

1.6 ELECTRONIC CONFIGURATION

The atomic structure and quantum mechanics are used to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom. The energy of atomic orbitals increases as the principal quantum number, *n*, increases. The **electron configuration** is the distribution of electrons of an atom or molecule (or other physical structure) in atomic or molecular orbitals. For example, the electron configuration of the neon atom is $1s^2\ 2s^2\ 2p^6$, meaning that the 1s, 2s and 2p subshells are occupied by 2, 2 and 6 electrons, respectively.

Russell-Saunders Coupling Schemes

In atomic spectroscopy, Russell–Saunders coupling, also known as LS coupling, specifies a coupling scheme of electronic spin- and orbital-angular momenta. The coupling scheme is named after H. N. Russell and F. A. Saunders (1925). Russell-Saunders coupling is useful mainly for the lighter atoms, roughly for atoms with atomic number less than 57. For heavier atoms j-j coupling gives a better approximation for atomic wave function.

Term Symbol and Coupling

Each energy level of an atom with a given electron configuration is described by not only the electron configuration but also its own **term symbol**, as the energy level also depends on the total angular momentum including spin. The usual atomic term symbols assume LS coupling, also known as **Russell–Saunders coupling** or **spin-orbit coupling**. The ground state term symbol is predicted by Hund's rules.

For light atoms, the **spin–orbit interaction** (or coupling) is small so that the total orbital angular momentum L and total spin S are good quantum numbers. The interaction between L and S is known as LS coupling, or spin-orbit coupling, Russell–Saunders coupling, named after Henry Norris Russell and Frederick Albert Saunders, who described this in 1925. Atomic states are then well described by term symbols of the form,

$$^{2S+1}L_J$$

Where,

- S is the total spin quantum number. $2S + 1$ is the spin multiplicity, which represents the number of possible states of J for a given L and S, provided that L e” S. (If $L < S$, the maximum number of possible J is $2L + 1$). This is easily proven by using $J_{max} = L + S$ and J_{min} = |L ” S|, so that the number of possible J with given L and S is simply J_{max} ” J_{min} + 1 as J varies in unit steps.
- J is the total angular momentum quantum number.
- L is the total orbital quantum number in spectroscopic notation.

The nomenclature (S, P, D, F) is derived from the characteristics of the spectroscopic lines corresponding to (*s*, *p*, *d*, *f*) orbitals which refers to sharp, principal, diffuse, and fundamental; the rest being named in alphabetical order from G onwards, except that J is omitted. When used to describe electron states in an atom, the term symbol usually follows the electron configuration. For example, one low-lying energy level of the carbon atom state is written as $1s^22s^22p^2\,{}^3P_2$. The superscript 3 indicates that the spin state is a triplet, and therefore $S = 1$ ($2S + 1 = 3$), the P is spectroscopic notation for $L = 1$, and the subscript 2 is the value of J. Using the same notation, the ground state of carbon is $1s^22s^22p^2\,{}^3P_0$.

Small letters refer to individual orbitals or one-electron quantum numbers, whereas capital letters refer to many-electron states or their quantum numbers.

Slater-Condon Parameters

The **Slater–Condon rules** express integrals of one- and two-body operators over wavefunctions constructed as Slater determinants of orthonormal orbitals in terms of the individual orbitals. The original integrals involving N-electron wavefunctions are reduced to sums over integrals involving at most two molecular orbitals, or in other words, the original $3N$ dimensional integral is expressed in terms of many three- and six-dimensional integrals.

The rules are used in deriving the working equations for all methods of approximately solving the Schrödinger equation that employ wavefunctions constructed from Slater determinants. These include Hartree–Fock theory, where the wavefunction is a single determinant, and all those methods which use Hartree–Fock theory as a reference, such as Møller–Plesset perturbation theory, and Coupled cluster and Configuration interaction theories.

In 1929 John C. Slater derived expressions for diagonal matrix elements of an approximate Hamiltonian while investigating atomic spectra within a perturbative approach. The following year Edward Condon extended the rules to non-diagonal matrix elements. In 1955 Per-Olov Löwdin further generalized these results for wavefunctions constructed from non-orthonormal orbitals, leading to what are known as the **Löwdin rules**.

In terms of an antisymmetrization operator (***A***) acting upon a product of *N* orthonormal spin-orbitals (with *r* and σ denoting spatial and spin variables), a determinantal wavefunction is denoted as,

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$$|\Psi\rangle = \mathcal{A}(\phi_1(\mathbf{r}_1\sigma_1)\phi_2(\mathbf{r}_2\sigma_2)\cdots\phi_m(\mathbf{r}_m\sigma_m)\phi_n(\mathbf{r}_n\sigma_n)\cdots\phi_N(\mathbf{r}_N\sigma_N))$$

A wavefunction differing from this by only a single orbital (the *m*th orbital) will be denoted as,

$$|\Psi_m^p\rangle = \mathcal{A}(\phi_1(\mathbf{r}_1\sigma_1)\phi_2(\mathbf{r}_2\sigma_2)\cdots\phi_p(\mathbf{r}_m\sigma_m)\phi_n(\mathbf{r}_n\sigma_n)\cdots\phi_N(\mathbf{r}_N\sigma_N))$$

A wavefunction differing by two orbitals will be denoted as,

$$|\Psi_{mn}^{pq}\rangle = \mathcal{A}(\phi_1(\mathbf{r}_1\sigma_1)\phi_2(\mathbf{r}_2\sigma_2)\cdots\phi_p(\mathbf{r}_m\sigma_m)\phi_q(\mathbf{r}_n\sigma_n)\cdots\phi_N(\mathbf{r}_N\sigma_N))$$

Zeeman Splitting

The Zeeman effect is the effect of splitting of a spectral line into several components in the presence of a static magnetic field. It is named after the Dutch physicist Pieter Zeeman, who discovered it in 1896 and received a Nobel prize for this discovery. It is analogous to the Stark effect, the splitting of a spectral line into several components in the presence of an electric field. Also similar to the Stark effect, transitions between different components have, in general, different intensities, with some being entirely forbidden (in the dipole approximation), as governed by the selection rules.

Since the distance between the Zeeman sub-levels is a function of magnetic field strength, this effect can be used to measure magnetic field strength, for example that of the Sun and other stars or in laboratory plasmas. The Zeeman effect is very important in applications, such as nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, Magnetic Resonance Imaging (MRI) and Mössbauer spectroscopy. It may also be utilized to improve accuracy in atomic absorption spectroscopy. A theory about the magnetic sense of birds assumes that a protein in the retina is changed due to the Zeeman effect. When the spectral lines are absorption lines, the effect is called inverse Zeeman effect.

Self-Consistent Field and Virial Theorem

The **virial theorem** provides a general equation that relates the average over time of the total kinetic energy of a stable system of discrete particles, bound by potential forces, with that of the total potential energy of the system. Mathematically, the theorem states,

$$\langle T\rangle = -\frac{1}{2}\sum_{k=1}^{N}\langle \mathbf{F}_k \cdot \mathbf{r}_k\rangle$$

For the total kinetic energy è'*T*é' of *N* particles, where $\mathbf{F}_k$ represents the force on the *k*th particle, which is located at position $\mathbf{r}_k$, and angle brackets represent the average over time of the enclosed quantity. The word **virial** for the right-hand side of the equation derives from ***vis***, the Latin word for 'force' or 'energy', and was given its technical definition by Rudolf Clausius in 1870.

The significance of the virial theorem is that it allows the average total kinetic energy to be calculated even for very complicated systems that defy an exact solution, such as those considered in statistical mechanics; this average total kinetic energy is related to the temperature of the system by the equipartition theorem. However, the virial theorem does not depend on the notion of temperature and holds even for systems that are not in thermal equilibrium. The virial theorem has been generalized in various ways, most notably to a tensor form.

1.7 MOLECULAR ORBITAL THEORY

1. When nuclei of two atoms come close to each other, there election cloud interact and result in the formation of molecular orbitals.
2. Each molecular orbital can be described by a wave function ψ^2, known as molecular orbital wave function ψ^2 represent the probability density or election density.
3. Each ψ^2 is associated with a definite set of quantum numbers which describes the shape and energy of the molecular orbital.
4. Each ψ is associated with a discrete value of energy.
5. The total energy of the molecule is the sum of the energies of the occupied molecular orbitals.
6. Elections tend to fill in molecular orbitals in similar way as they do in atomic orbitals by obeying Afbau's principle, Pauli's exclusion principle and Hund's rule.
7. Each election in a molecular orbital belong to all the nuclei present in the molecule.
8. Each election in as molecular orbital is either having clockwise $\left(+\frac{1}{2}\right)$ or anticlock wise $\left(-\frac{1}{2}\right)$ spin.

According to Linear Combination of Atomic Orbitals (LCAO) method, there are two ways of linear combination of atomic orbitals or their wave functions forming bonding and anti-bonding molecular orbitals. Suppose that the wave functions of two atomic orbitals on two atoms A and B of AB type molecule (hetero-diatomic molecule) are represented as ψ_A and ψ_B respectively. There are two different ways in which ψ_A and ψ_B can combine linearly with each other. These two different ways are discussed below:

(a) **Additive Overlap (Also Called Positive Overlap of ++ Overlap) and Formation of Bonding Molecular Orbital**: In this type of linear combination, the positive lobe (i.e., the lobe having + sign) of ψ_A overlaps with the positive love of ψ_B and a molecular orbital is formed. This molecular orbital has lower energy than each of the two isolated atomic orbital wave functions viz. ψ_A and ψ_B (decrease in energy) and hence the formation of this molecular orbital produces attraction between the two nuclei of A and B atoms. This attraction results in the establishment of a stable chemical bond between A and B. Since this molecular orbital leads to the formation of a stable bond, it is called bonding molecular orbital which is represented as ψ^b.

(b) **Subtractive Overlap (Also Called Negative or + - Overlap) and Formation of Anti-Bonding Molecular Orbital:** In this type of linear combination the positive lobe of ψ_A overlaps with the negative lobe (i.e., the lobe having-sign) of ψ_B and a molecular orbital is formed. This molecular orbital has higher energy than each of the two atomic orbital wave functions (ψ_A and ψ_B) (increase in energy) and hence the formation of this molecular orbital produces repulsion between the two nuclei of A and B. This repulsion opposes the formation of any bond between the nuclei. Since this molecular orbital opposes the formation of any bond between the nuclei, it is called anti-bonding molecular orbital which is represented as ψ^*.

Here, it should be understood clearly than (+) and (–) sings of the lobes are only geometric signs of the atomic orbital wave function and should not be confused with positive (+) and negative (–) charges.

Above discussion shows that the formation of bonding molecular orbital wave function (ψ^b) and anti-bonding molecular orbital wave function (ψ^*) by the linear combination of two atomic orbital wave functions, viz., ψ_A and ψ_B can be represented by the following equations:

$$\psi^b = +\psi_A + \psi_B \text{ (++ overlap)} \qquad \text{....(150)}$$

$$\psi^* = +\psi_A - \psi_B \text{ (+– overlap)} \qquad \text{....(151)}$$

When we show the contributions made by ψ_A and ψ_B in ψ^b and ψ^* molecular orbitals, Equations (151) and (151) are written as:

$$\psi^b = \frac{1}{\sqrt{2}}(\psi_A + \psi_B) \qquad \text{....(152)}$$

$$\psi^* = \frac{1}{\sqrt{2}}(\psi_A - \psi_B) \qquad \text{....(153)}$$

Obviously the sum of the squares of the coefficients of atomic orbital wave functions ψ_A and ψ_B appearing in the bonding molecular orbital wave function is equal to unity $\left[\left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2\right]$.

Similarly this sum for anti-bonding molecular orbital is also equal to unity.

The relative order of the energy of ψ_A, ψ_B, ψ^b and ψ^* can be shown pictorially in Figure 1.14.

NOTES

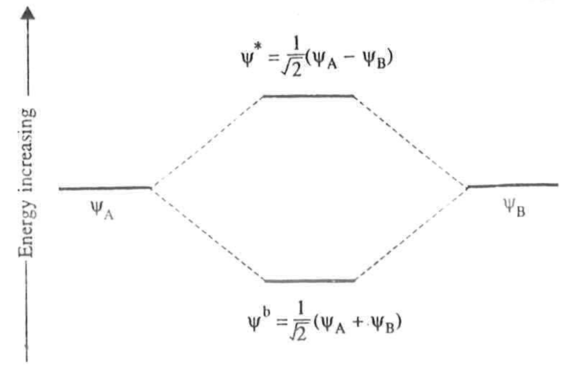


Fig. 1.14 *Relative Order of the Energy of* ψ_A, ψ_B, ψ^b *and* ψ^*.

Probability Density Variation with Internuclear Distance in H_2 Molecule

Consider two H-atoms H_A and H_B combine to form H_2 molecule let the wave function of these atoms may be represented by ψ_{H_A} and ψ_{H_B}. The positive overlap of ψ_{H_A} and ψ_{H_B} will give bonding molecular orbital $\psi^b_{H_2}$ and the negative overlap of ψ_{H_A} and ψ_{H_B} will produce anti-bonding molecular orbital, $\psi^*_{H_2}$ thus,

$$\psi^b_{H_2} = \psi_{H_A} + \psi_{H_B} \qquad \text{....(154)}$$

$$\psi^*_{H_2} = \psi_{H_A} - \psi_{H_B} \qquad \text{....(155)}$$

On squaring Equation (128), we get:

$$\left(\psi^b_{H_2}\right)^2 = \psi^2_{H_A} + \psi^2_{H_B} + 2\psi_{H_A}\psi_{H_B} \qquad \text{....(156)}$$

In Equation (156) $\left(\psi^*_{H_2}\right)^2$ denotes electron probability density or electron charge density in the bonding molecular orbital $\left(\psi^b_{H2}\right)$ while $\psi^2_{H_A}$ and $\psi^2_{H_B}$ indicate the electron charge density in the isolated (i.e., uncombined) atomic orbitals viz. ψ_{H_A} and ψ_{H_B}. From Equation (156), it is clear that $\left(\psi^b_{H_2}\right)^2$ is greater than $\left(\psi^2_{H_A} + \psi^2_{H_B}\right)$ by an amount equal to $2\psi_{H_A}\psi_{H_B}$. This means that the electron charge density in the bonding molecular orbital $\left(\psi^b_{H2}\right)$ is greater by $2\psi_{H_A}\psi_{H_B}$ than the sum of the electron charge densities of the isolated atomic orbitals, ψ_{H_A} and ψ_{H_B}. The excess or increase in electron charge density $\left(\psi 2\psi_{H_A}\psi_{H_B}\right)$ occurs in the region lying in between the two positively charged nuclei. The increase in electron charge density between the two positive nuclei shields (i.e., screens) the two nuclei from mutual repulsion, i.e., due to the increase in electron charge density, the two nuclei are attracted towards each other. Thus the formation of bonding molecular orbital produces attraction between the two nuclei and hence leads to the establishment of a stable chemical bond. The attraction between the nuclei (i.e., the formation of a stable bond) leads to a decrease in the energy of the bonding molecular orbital in the event of its being occupied by electrons. In other words, the bonding molecular orbital has lower energy than each of the isolated atomic orbitals from which this molecular orbital is derived.

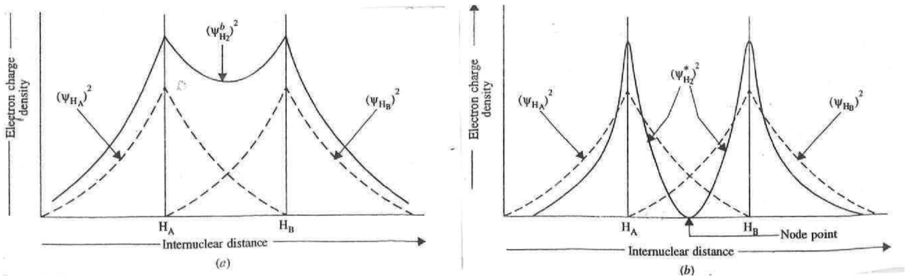


Fig. 1.15 *Inter Nuclear Distance and Electron Density Graph in H_2 Molecule*

At this stage it should be easy to understand since $\psi^b_{H_2}$ leads to the formation of a state bond, it is called bonding molecular orbital.

On squaring Equation (155), we get:

$$\left(\psi^*_{H_2}\right)^2 = \psi^2_{H_A} + \psi^2_{H_B} - 2\psi_{H_A}\psi_{H_B} \qquad .... (157)$$

In this Equation (157) $\left(\psi^*_{H_2}\right)^2$ represents the electron charge density in the anti-bonding molecular orbital $\left(\psi^*_{H_2}\right)$. As is evident from Equation (157), $\left(\psi^*_{H_2}\right)^2$ is smaller than $\left(\psi^2_{H_A} + \psi^2_{H_B}\right)$ by an amount equal to $2\psi_{H_A}\psi_{H_B}$. This means that electron charge density $\left(\psi^*_{H_2}\right)^2$ the anti-bonding molecular orbital $\left(\psi^*_{H_2}\right)$ is smaller by $2\psi_{H_A}\psi_{H_B}$ than the sum of the electron charge densities of the uncombined atomic orbitals, ψ_{H_A} and ψ_{H_B}. The decrease in the electron charge density $\left(= 2\psi_{H_A}\psi_{H_B}\right)$ occurs in the region lying in between the two positively charged nuclei. The decrease in electron charge density between the nuclei means that there is no shielding of the nuclei, i.e., due to the decrease in electron charge density between the nuclei, these are repelled from each other. Thus the formation of anti-bonding molecular orbital produces repulsion between the two nuclei and hence opposes the formation of any bond between the nuclei. The repulsion between the nuclei leads to an increase in the energy of the anti-bonding molecular orbital in the event of its being occupied by electrons. In other words, the anti-bonding molecular orbital has higher energy than each of isolated atomic orbitals from which this molecular orbital is derived (Refer Figure 1.16). Since $\psi^*_{H_2}$ molecular orbital opposes the formation of any bond, it is called anti-bonding molecular orbital.

1.7.1 Bond Order

For writing the electronic configuration of diatomic molecules, following two rules are to be applied.

(i) The number of electrons present in the two atoms are counted and then filled in the appropriate energy level diagram according to Aufbau's rule.

(ii) The pairing in π_{2p_x} and π_{2p_y} or $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ will take place only when each molecular orbital of identical energy has one electron.

NOTES

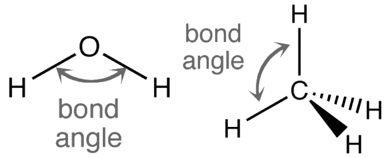
After writing the molecular orbital diagram for a molecule or ion, the under mentioned parameters about the molecule/ion may be predicted.

(i) **Bond Order:** It is defined as the number of covalent bonds by which the two atoms are joined in the molecule. It is calculated as given below.

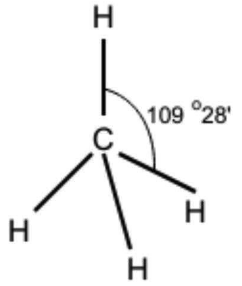
Bond Order $= \frac{1}{2}$ [Number of electrons in bonding M.O, i.e., N_b – Number of electrons in antibonding M.O, i.e., N_a]

$$\therefore \quad \text{Bond Order} = \frac{1}{2}[N_b - N_a]$$

(ii) **Bond Angle:** A bond angle is the angle between two bonds originating from the same atom in a covalent species. By definition, "Bond angle is simply the angle between two bonds or two bonded electron pairs in a compound". Geometrically, a bond angle is an angle between two converging lines. Following are examples of bond angles.



For example, in CH_4 the bond angle is 109 degrees.



A lone pair of electrons at the central atom always tries to repel the shared pair (bonded pair) of electrons. Due to this, the bonds are displaced slightly inside resulting in a decrease of bond angle. Electronegativity also effects bond angle. If the electronegativity of the central atom decreases, bond angle decreases.

(iii) **Bond Length:** Bond length is the distance between the centres of two bonded nuclei. It is inversely proportional to bond order, i.e., as bond order increases, bond length decreases.

$$\text{Bond Length} \propto \frac{1}{\text{Bond order}}$$

	Bond Order	Bond Length (A°)
F_2	1	1.43
O_2	2	1.21
N_2	3	1.10

(iv) **Stability of Molecules:** Stability of molecules is directly proportional to bond order.

$$\text{Stability} \propto \text{Bond Order of Molecule}$$

Higher the bond order of the molecule more will be the stability of molecule. When bond order is observed to be zero, the molecule does not exist at all.

(v) **Dissociation Energy:** Bond dissociation energy is the energy required to separate the two atoms. It is directly proportional to bond order.

$$\text{Bond Dissociation Energy} \propto \text{Bond Order}$$

So, bond dissociation energy increases with increase of bond order as evident from the following data

	Bond Order	Bond Dissociation Energy (kJ/mole)
F_2	1	151
O_2	2	493
N_2	3	940

(vi) **Magnetic Property of Molecule:** When all the electrons in molecular orbitals (bonding and anti-bonding) are paired, the molecule is repelled by the magnetic field. Such molecules are called diamagnetic. However, if molecular orbitals possess one or more unpaired electrons then the molecule is attracted by the magnetic field and termed as paramagnetic.

The magnetic moment shown by any atom, molecule or ion is calculated by the formula.

$$\mu = \sqrt{n(n+2)}$$

Where $\mu =$ Magnetic Moment

$n =$ Number of Unpaired Electrons

Check Your Progress

9. What is null operator?
10. Define (LCAO).
11. What is bond angle?
12. Define the stability of molecules.

1.8 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Schrodinger used de Broglie's idea of matter waves and developed it into rigorous mathematical theory. The basic idea of Quantum theory is that matter can be regarded as wave. Wave function Ψ is a sort of amplitude function. It is not an observable quantity but Ψ^2 is probability of finding the electron within a given volume. These systems are referred to as quantum (mechanical) systems.

2. It is one of the postulates of quantum mechanics that for a physical system consisting of a particle there is an associated wave function. This wave function determines everything that can be known about the system. The wave function can be a single-valued function of position and time, since that is sufficient to guarantee an unambiguous value of probability of finding the particle at a particular position and time.
3. ψ is called the wave function, and can be described mathematically in terms of trigonometric sine function of displacement x and the wavelength λ. Schrodinger assigned this sine wave equation to the electron with the object of describing the behaviour of the electron in terms of its kinetic energy and potential energy.
4. An operator is a rule that changes or transforms a given function into another function. In other words an operator changes one function into another according to some rule. The function is called an operand.
5. In quantum mechanics, an energy level is degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement.
6. An eigenvalue λ which corresponds to two or more different linearly independent eigenvectors is said to be **degenerate**, i.e., $AX_1 = \lambda X_1$ where X_1 and X_2 are linearly independent eigenvectors. The dimensionality of the eigenspace corresponding to that eigenvalue is known as its **degree of degeneracy**, which can be finite or infinite.
7 The variational method is the key approximate method/technique typically used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it is hard to determine a good unperturbed Hamiltonian, i.e., one which makes the perturbation small but is still solvable. On the other hand, in cases where there is a good unperturbed Hamiltonian, perturbation theory can be more efficient than the variational method.
8. In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a 'small' term to the mathematical description of the exactly solvable problem.
9. Null Operator A linear operator a is a *null operator* if

$$\hat{\alpha}_1 |a\rangle = \hat{\alpha}_2 |a\rangle \quad \text{for all } |a\rangle$$

10. According to Linear Combination of Atomic Orbitals (LCAO) method, there are two ways of linear combination of atomic orbitals or their wave functions forming bonding and anti-bonding molecular orbitals.
11. A bond angle is the angle between two bonds originating from the same atom in a covalent species. By definition, "Bond angle is simply the angle between two bonds or two bonded electron pairs in a compound". Geometrically, a bond angle is an angle between two converging lines.

1.9 SUMMARY

NOTES

- In quantum mechanics, the Schrödinger equation is a mathematical equation that describes the changes over time of a physical system in which quantum effects, such as wave–particle duality, are significant.
- Quantum mechanics is an axiomatic theory because it is well-grounded on few principles or axioms or postulates, all of these words meaning the same thing. Following are the six postulates of quantum mechanics.
- Associated with any particle moving in a conservative field of force is a wave function which determines everything that can be known about the system.
- The set of eigenfunctions of operator **Q** will form a complete set of linearly independent functions.
- The solutions for y are called wave functions and may be expressed as the product of three functions each of which depends only on one of the coordinates.
- If the probability of finding a particle at point x has a given value, that at $(x + dx)$ must be similar as dx ® 0. If this were not so, the double differentiation in the Schrodinger equation could not be performed.
- When more than one operator is applied in succession their symbols can be written together as in multiplication.
- The number of different states corresponding to a particular energy level is known as the degree of degeneracy of the level.
- Mathematically, the possible states of a quantum mechanical system may be treated as abstract vectors in a separable, complex Hilbert space, while the observables may be represented by linear Hermitian operators acting upon them.
- The term 'Degeneracy' refers to the fact that two or more stationary states of the same quantum-mechanical system may have the same energy even though their wave functions are not the same. In this case the common energy level of the stationary states is degenerate.
- The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian.
- Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In this paper Schrödinger referred to earlier work of Lord Rayleigh, who investigated harmonic vibrations of a string perturbed by small in-homogeneities. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.
- When nuclei of two atoms come close to each other, there election cloud interact and result in the formation of molecular orbitals.

- According to Linear Combination of Atomic Orbitals (LCAO) method, there are two ways of linear combination of atomic orbitals or their wave functions forming bonding and anti-bonding molecular orbitals.
- The number of electrons present in the two atoms are counted and then filled in the appropriate energy level diagram according to Aufbau's rule.
- The pairing in π_{2p_x} and π_{2p_y} or $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ will take place only when each molecular orbital of identical energy has one electron.
- A lone pair of electrons at the central atom always tries to repel the shared pair (bonded pair) of electrons. Due to this, the bonds are displaced slightly inside resulting in a decrease of bond angle. Electronegativity also effects bond angle. If the electronegativity of the central atom decreases, bond angle decreases.

1.10 KEY TERMS

- **Quantum Mechanics (QM):** It is also known as quantum physics, quantum theory, the wave mechanical model, or matrix mechanics, and includes quantum field theory, the fundamental theory in physics which describes nature at the smallest scales of energy levels of atoms and subatomic particles.
- **Wave function:** The wave function Ψ is a sort of amplitude function. It is not an observable quantity but Ψ^2 is probability of finding the electron within a given volume.
- **Variational principle**: It is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions.
- **Bond order:** It is defined as the number of covalent bonds by which the two atoms are joined in the molecule.
- **Bond length:** Bond length is the distance between the centres of two bonded nuclei. It is inversely proportional to bond order, i.e., as bond order increases, bond length decreases.
- **Bond dissociation energy:** Bond dissociation energy is the energy required to separate the two atoms. It is directly proportional to bond order.

1.11 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What are the postulates in quantum mechanics?
2. What is a wave function?
3. How particle in one and three dimensional boxes are defined?
4. Define the degeneracy in quantum mechanics.
5. What is variation method?

6. Define the ground state of helium atom.
7. What is ordinary angular momentum?
8. Calculate the Eigen value of angular momentum.
9. What is ladder operator?
10. State the Pauli exclusion principle.
11. What is spin orbit coupling?
12. Determine the LACO method.

Long-Answer Questions

1. Discuss the significance of the quantum mechanics. Briefly explain the various postulates of quantum mechanics.
2. Briefly explain the features and applications of particle in one and three dimensional boxes with reference to quantum mechanics.
3. Apply the Schrödinger wave equation for a particle in three dimensional box and obtain the expression for the energy of the same and explain the degeneracy of energy states.
4. Briefly discuss the variation method giving appropriate examples.
5. Drive the equation of Eigen value and Eigen vector of angular momentum.
6. Explain about the antisymmetriy and Pauli exclusion principle with appropriate examples.
7. Illustrate the electronic structure of an atom with examples.
8. Explain the basic criteria for forming M.O. from A.O. giving appropriate examples.
9. Interpret the formation of molecular orbitals in H_2 molecule by LCAO method.

1.12 FURTHER READING

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UNIT 2 THERMODYNAMICS

NOTES

Structure

2.0 INTRODUCTION

Thermodynamics is the study of the relations between heat, work, temperature, and energy. The laws of thermodynamics describe how the energy in a system changes and whether the system can perform useful work on its surroundings. The change in the free energy is the maximum amount of work that a thermodynamic system can perform in a process at constant temperature, and its sign indicates whether a process is thermodynamically favourable or forbidden. In thermodynamics, the chemical potential of a species is the energy that can be absorbed or released due to a change of the particle number of the given species.

The molar heat capacity of a chemical substance is the amount of energy that must be added, in the form of heat, to one mole of the substance in order to cause an increase of one unit in its temperature.

Phase transition is when a substance changes from a solid, liquid, or gas state to a different state. Every element and substance can transition from one phase to another at a specific combination of temperature and pressure.

In chemical thermodynamics, the fugacity of a real gas is an effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant. It is equal to the pressure of an ideal gas which has the same temperature and molar Gibbs free energy as the real gas.

Debye and Hückel developed a theory with which single ion activity coefficients could be calculated. By calculating the mean activity coefficients from them the theory could be tested against experimental data. The activity coefficient is a measure of how much a solution differs from an ideal solution.

Generalized statistical thermodynamics is a variational calculus of probability distributions. Most probable refers to having a large number of different ways of achieving the distribution. The primary goal of statistical thermodynamics (also known as equilibrium statistical mechanics) is to derive the classical thermodynamics of materials in terms of the properties of their constituent particles and the interactions between them. In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium.

Heat Capacity of an object can be calculated by dividing the amount of heat energy supplied (E) by the corresponding change in temperature (T). In a chemical reaction, chemical equilibrium is the state in which both the reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system. Such a state is known as dynamic equilibrium.

In general, non-equilibrium thermodynamic systems are spatially and temporally non-uniform, but their non-uniformity still has a sufficient degree of smoothness to support the existence of suitable time and space derivatives of non-equilibrium state variables.

Entropy production (or generation) is the amount of entropy which is produced in any irreversible processes such as heat and mass transfer processes including motion of bodies. Entropy flow is a core concept in non-equilibrium thermodynamics just as entropy is in classical thermodynamics and statistical physics. Heat flux or thermal flux is the rate of heat energy transfer through a given surface, per unit surface. The SI derived unit of heat rate is joule per second, or watt.

Phenomenological transport equations are expressed as relations between irreducible tensorial sets, using spherical tensor notation. The corresponding Onsager reciprocal relations then appear in a form independent of the specifically geometrical properties of the system. Electrokinetic phenomena are a family of several different effects that occur in heterogeneous fluids, or in porous bodies filled with fluid, or in a fast flow over a flat surface.

Non-equilibrium thermodynamics is a branch of thermodynamics that deals with physical systems that are not in thermodynamic equilibrium but can be described in terms of variables that represent an extrapolation of the variables used to specify the system in thermodynamic equilibrium.

In this unit, you will study about the laws of thermodynamics, entropy, free energy, chemical potential, molar heat capacity, phase transition, concept of fugacity and determination of fugacity, Debye–Hückel theory for activity coefficients, activity and activity co-efficeint, concept of distribution in statistical thermodynamic, partition function, heat capacity of solids, chemical equilibria, thermodynamic criteria for non-equilibrium states, entropy production and entropy flow, entropy balance equation for different irreversible process, fluxes and forces, phenomenological equations, electrokinetic phenomenon, irreversible thermodynamics for biological systems.

2.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the laws of thermodynamics
- Know about the entropy
- Interpret the free energy
- Comprehend the chemical potential
- Explain the molar heat capacity
- Understand the phase transition
- Discuss the concept of fugacity and determination of fugacity
- Elaborate on the Debye–Hückel theory for activity coefficients
- Explain the activity and activity co-efficeint
- Analyse the concept of distribution in statistical thermodynamic
- Determine the partition function
- Understand the heat capacity of solids
- Analyse the chemical equilibria
- Introduce to thermodynamic criteria for non-equilibrium states
- Know about the entropy production and entropy flow
- Elaborate on the entropy balance equation for different irreversible process
- Define the fluxes and forces
- Understand the phenomenological equations
- Introduce to electrokinetic phenomenon
- Know about the irreversible thermodynamics for biological systems

2.2 LAWS OF THERMODYNAMICS

The first law of thermodynamics has certain limitations as illustrated below:

The first law establishes definite relationship between the heat absorbed and the work performed by a system in a given process. But it pits no restriction on the direction of the flow of heat. According to the first law, for example, it is not impossible to extract heat from ice by cooling it to a low temperature and then use it for wanning water. But it is known from experience that such a transfer of heat from a lower to a higher temperature is not possible without expenditure of energy that is without doing some external work. It's known, on the other hand, that heat flows spontaneously, that is, of its own accord, from a higher to a lower temperature.

According to the first law, the total energy of an isolated system remains constant during a specified change of state. But it does not tell whether a specified change of or a process including a chemical reaction can occur spontaneously, whether it is feasible?

The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for another law, i.e., the second law of thermodynamics.

The second law of thermodynamics helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously, that is, its own accord. It also helps us to know the equilibrium conditions. The law is therefore, of great importance in chemistry.

It is known from experience that although various forms of energy can be completely transformed into one another, yet heat is a typical form of energy which cannot be transformed into work. The second law helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

The second law of thermodynamics is needed because the first law of thermodynamics does not define the energy conversion process completely. The first law is used to relate and to evaluate the various energies involved in a process. However, no information about the direction of the process can be obtained by the application of the first law. Early in the development of the science of thermodynamics, investigators noted that while work could be converted completely into heat, the converse was never true for a cyclic process. Certain natural processes were also observed always to proceed in a certain direction (for example, heat transfer occurs from a hot to a cold body). The second law was developed as an explanation of these natural phenomena.

The second law of thermodynamics is used to determine the maximum efficiency of any process. A comparison can then be made between the maximum possible efficiency and the actual efficiency obtained.

With the second law of thermodynamics, the limitations imposed on any process can be studied to determine the maximum possible efficiencies of such a process and then a comparison can be made between the maximum possible efficiency and the actual efficiency achieved. One of the areas of application of the second law is the study of energy-conversion systems. For example, it is not possible to convert all the energy obtained from a nuclear reactor into electrical energy. There must be losses in the conversion process. The second law can be used to derive an expression for the maximum possible energy conversion efficiency taking those losses into account. Therefore, the second law denies the possibility of completely converting into work all of the heat supplied to a system operating in a cycle, no matter how perfectly designed the system may be.

NOTES

The second law of thermodynamics can be stated in a number of ways. The original statements were concerned with the French engineer Sadi Carnot's analysis of performance of steam engines. There are two important statements of the second law; one is due to Lord Kelvin and other is due to Clausius. The statement due to Kelvin may be expressed as:

It is impossible for a cyclic process to take heat from a cold reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir.

The statement due to Clausius is:

It is impossible to construct a machine, which is able to convey heat by a cyclic process from one reservoir at a lower temperature to another at higher temperature unless work is done on the machine by some outside agency.

A cycle is a process in which a system returns to its original state after a succession of steps. A more useful statement of the second law can be given in terms of a quantity which is also a function of state called, *entropy*.

Principal and Applications of Thermodynamics

The laws of thermodynamics define a group of physical quantities, such as temperature, energy, and entropy that characterise thermodynamic systems in thermodynamic equilibrium. The laws also use various parameters for thermodynamic processes, such as thermodynamic work and heat, and establish relationships between them. They state empirical facts that form a basis of precluding the possibility of certain phenomena, such as perpetual motion. In addition to their use in thermodynamics, they are important fundamental laws of physics in general, and are applicable in other natural sciences.

Traditionally, thermodynamics has recognised three fundamental laws, simply named by an ordinal identification, the first law, the second law, and the third law. A more fundamental statement was later labelled as the zeroth law, after the first three laws had been established.

The ***zeroth law of thermodynamics*** defines thermal equilibrium and forms a basis for the definition of temperature: If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

The ***first law of thermodynamics*** states that, when energy passes into or out of a system (as work, heat, or matter), the system's internal energy changes in according with the law of conservation of energy.

The ***second law of thermodynamics*** states that in a natural thermodynamic process, the sum of the entropies of the interacting thermodynamic systems never decreases. Another form of the statement is that heat does not spontaneously pass from a colder body to a warmer body.

The ***third law of thermodynamics states*** that a system's entropy approaches a constant value as the temperature approaches absolute zero. With the exception of non-crystalline solids (glasses) the entropy of a system at absolute zero is typically close to zero.

The first and second law prohibit two kinds of perpetual motion machines, respectively: the perpetual motion machine of the first kind which produces work with no energy input, and the perpetual motion machine of the second kind which spontaneously converts thermal energy into mechanical work.

Zeroth Law of Thermodynamics

The zeroth law of thermodynamics provides for the foundation of temperature as an empirical parameter in thermodynamic systems and establishes the transitive relation between the temperatures of multiple bodies in thermal equilibrium. The law may be stated in the following form:

- If two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.
- Though this version of the law is one of the most commonly stated versions, it is only one of a diversity of statements that are labelled as the 'Zeroth Law'. Some statements go further, so as to supply the important physical fact that temperature is one-dimensional and that one can conceptually arrange bodies in a real number sequence from colder to hotter.
- These concepts of temperature and of thermal equilibrium are fundamental to thermodynamics and were clearly stated in the nineteenth century. The name 'Zeroth Law' was invented by Ralph H. Fowler in the 1930s, long after the first, second, and third laws were widely recognised. The law allows the definition of temperature in a non-circular way without reference to entropy, its conjugate variable. Such a temperature definition is said to be 'Empirical'.

First Law of Thermodynamics

The first law of thermodynamics is a related to the law of conservation of energy, adapted for thermodynamic processes. In general, the conservation law states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.

In a closed system (i.e. there is no transfer of matter into or out of the system), the first law states that the change in internal energy of the system (ΔU_{system}) is equal to the difference between the heat supplied to the system *(Q)* and the work *(W)* done by the system on its surroundings.

$$\Delta U_{system} = Q - W$$

When two initially isolated systems are combined into a new system, then the total internal energy of the new system, U_{system}, will be equal to the sum of the internal energies of the two initial systems, U_1 and U_2:

$$U_{system} = U_1 + U_2$$

The First Law Encompasses Several Principles:

- The Conservation of energy, which says that energy can be neither created nor destroyed, but can only change one form to another form. A particular consequence of this is that the total energy of an isolated system does not change.
- The concept of internal energy and its relationship to temperature. If a system has a definite temperature, then its total energy has three distinguishable components, termed kinetic energy (energy due to the motion of the system as a whole), potential energy (energy resulting from an externally imposed force field), and internal energy. The establishment of the concept of internal energy distinguishes the first law of thermodynamics from the more general law of conservation of energy.

  $$E_{\text{total}} = \text{KE}_{\text{system}} + \text{PE}_{\text{system}} + U_{\text{system}}$$

- Work is a process of transferring energy to or from a system in ways that can be described by macroscopic mechanical forces acting between the system and its surroundings. The work done by the system can come from its overall kinetic energy, from its overall potential energy, or from its internal energy.

  For example, when a machine (not a part of the system) lifts a system upwards, some energy is transferred from the machine to the system. The system's energy increases as work is done on the system and in this particular case, the energy increase of the system is manifested as an increase in the system's gravitational potential energy. Work added to the system increases the potential energy of the system:

  When matter is transferred into a system that masses associated internal energy and potential energy are transferred with it.

  $$(u\,\Delta M)_{\text{in}} = \Delta U_{system}$$

  Where u denotes the internal energy per unit mass of the transferred matter, as measured while in the surroundings; and ΔM denotes the amount of transferred mass.

- The flow of heat is a form of energy transfer. Heating is the natural process of moving energy to or from a system other than by work or the transfer of matter. In a diathermic system, the internal energy can only be changed by the transfer of energy as heat:

  $$\Delta U_{system} = Q$$

  Combining these principles leads to one traditional statement of the first law of thermodynamics: it is not possible to construct a machine which will perpetually output work without an equal amount of energy input to that machine. Or more briefly, a perpetual motion machine of the first kind is impossible.

Second Law of Thermodynamics

The second law of thermodynamics indicates the irreversibility of natural processes, and, in many cases, the tendency of natural processes to lead towards spatial homogeneity of matter and energy, and especially of temperature. It can be formulated in a variety of interesting and important ways. One of the simplest is the Clausius statement that heat does not spontaneously pass from a colder to a hotter body.

It implies the existence of a quantity called the entropy of a thermodynamic system. In terms of this quantity it implies that when two initially isolated systems in separate but nearby regions of space, each in thermodynamic equilibrium with itself but not necessarily with each other, are then allowed to interact, they will eventually reach a mutual thermodynamic equilibrium. The sum of the entropies of the initially isolated systems is less than or equal to the total entropy of the final combination. Equality occurs just when the two original systems have all their respective intensive variables (temperature, pressure) equal; then the final system also has the same values.

The second law is applicable to a wide variety of processes, both *reversible* and *irreversible*. According to the second law, in a reversible heat transfer, an element of heat transferred, δQ, is the product of the temperature (T), both of the system and of the sources or destination of the heat, with the increment (dS) of the system's conjugate variable, its entropy (S):

$$\delta Q = T\,dS$$

While reversible processes are a useful and convenient theoretical limiting case, all natural processes are irreversible. A prime example of this irreversibility is the transfer of heat by conduction or radiation. It was known long before the discovery of the notion of entropy that when two bodies, initially of different temperatures, come into direct thermal connection, then heat immediately and spontaneously flows from the hotter body to the colder one.

Entropy may also be viewed as a physical measure concerning the microscopic details of the motion and configuration of a system, when only the macroscopic states are known. Such details are often referred to as disorder on a microscopic or molecular scale, and less often as dispersal of energy. For two given macroscopically specified states of a system, there is a mathematically defined quantity called the difference of information entropy between them. This defines how much additional microscopic physical information is needed to specify one of the macroscopically specified states, given the macroscopic specification of the other often a conveniently chosen reference state which may be presupposed to exist rather than explicitly stated. A final condition of a natural process always contains microscopically specifiable effects which are not fully and exactly predictable from the macroscopic specification of the initial condition of the process. This is why entropy increases in natural processes the increase tells how much extra microscopic information is needed to distinguish the initial macroscopically specified state from the final macroscopically specified state. Equivalently, in a thermodynamic process, energy spreads.

Third Law of Thermodynamics

The third law of thermodynamics can be stated as: A system's entropy approaches a constant value as its temperature approaches absolute zero.

At zero temperature, the system must be in the state with the minimum thermal energy, the ground state. The constant value (not necessarily zero) of entropy at this point is called the *residual entropy* of the system. Note that, with the exception of non-crystalline solids (e.g. glasses) the residual entropy of a system is typically close to zero. However, it reaches zero only when the system has a unique ground state (i.e. the state with the minimum thermal energy has only one configuration, or microstate). Microstates are used here to describe the probability of a system being in a specific state, as each microstate is assumed to have the same probability of occurring, so macroscopic states with fewer microstates are less probable. In general, entropy is related to the number of possible microstates according to the Boltzmann principle:

$$S = k_B \ln \Omega$$

Where S is the entropy of the system, k_B Boltzmann's constant, and Ω the number of microstates. At absolute zero there is only 1 microstate possible ($\Omega=1$ as all the atoms are identical for a pure substance and as a result all orders are identical as there is only one combination) and $ln(1)=0$

Applications of Thermodynamics

- Sweating in a Crowded Room: In a crowded room, everybody (every person) starts sweating. The body starts cooling down by transferring the body heat to the sweat. Sweat evaporates adding heat to the room. Again, this happens due to the first and second law of thermodynamics in action. One thing to keep in mind, heat is not lost but transferred attaining equilibrium with maximum entropy.
- The first law of thermodynamics proclaims constancy of the total energy of isolated system for all changes, taking place in this system: energy cannot be created or destroyed. According to the second law of thermodynamics in isolated system entropy is always increasing or remaining constant. All processes in the Universe are oriented to the equilibrium state. Nevertheless, biological systems, and, consequently, ecological systems create order from disorder, they create and support chemical and physical non-equilibrium state the basis they live on.
- According to the second law, heat always flows from a body at a higher temperature to a body at the lower temperature. This law is applicable to all types of heat engine cycles including Otto, Diesel, etc., for all types of working fluids used in the engines. This law has led to the progress of present-day vehicles.
- Another application of second law is refrigerators and heat pumps based on the Reversed Carnot Cycle. If you want to move heat from a body at a lower temperature to a body at a higher temperature, then you have to supply external work. In the original Carnot cycle, heat produces work while in the Reversed Carnot cycle work is provided to transfer heat from lower temperature reservoir to a higher temperature reservoir.

- Removing heat from the food items in the refrigerator and throwing it away to the higher temperature atmosphere does not happen automatically. We need to supply external work via the compressor to make this happen in the refrigerator.
- Air conditioner and heat pump follow the similar law of thermodynamics. The air conditioner removes heat from the room and maintains it at a lower temperature by throwing the absorbed heat into the atmosphere. The heat pump absorbs heat from the atmosphere and supplies it to the room which is cooler in winters.
- Melting of Ice Cube: Ice cubes in a drink absorb heat from the drink making the drink cooler. If we forget to drink it, after some time, it again attains room temperature by absorbing the atmospheric heat. All this happens as per the first and second law of thermodynamics.

2.2.1 Entropy

Entropy has been derived from the Greek word entrope which means change. After the establishment of First Law of Thermodynamics, subsequent studies by Lord Kelvin, Carnot, and Clausius in about 1850 revealed hierarchy among the various forms of energy and an imbalance in their transformation. Although all kinds of energy can be completely converted into heat, the reverse is not true, i.e., there is always inevitable loss of energy in the form of irretrievable heat. The irreversible increase of this nondisposable energy in the universe is measured by the abstract dimension called entropy.

Entropy was introduced to help explain the Second Law of Thermodynamics. The change in this property is used to determine the direction in which a given process will proceed. It is a measure of the unavailability of heat to perform work. The actual entropy of a system is difficult to define and hence defined in terms of change of entropy during change of state. The change of entropy of a system is defined as the integral of all forms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process being carried reversibly or very simply as the heat transferred during a reversible process to the absolute temperature of the system. For infinitesimal change in state of a system at constant temperature T, $dS = \frac{dq_{\text{rev}}}{T}$.

For finite change of state of a system at constant temperature T,

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The reversible path taken by any system as it changes is the path in which the heat flow is minimum and the work flow is maximum. The actual heat flows and work flows although depend upon the path along which a system changes, the reversible heat flows and work flows do not depend upon the path of transformation. This is the reason the reversible flow of heat, which is a path-independent state function is used to define the thermodynamic state function entropy. Further, it must be mentioned that only reversible processes can be depicted on the $T - S$ diagram, the area of which represents the quantity of heat transferred during the process. Actual or irreversible processes cannot be drawn since they are not a succession of equilibrium conditions because only the initial and final conditions are known for such processes. For irreversible process the heat exchanged is indefinite and uncertain quantity and hence cannot be used to calculate ΔS.

Characteristics of Entropy Function

1. Like internal energy and enthalpy, entropy is an extensive function, i.e., mass dependent property.
2. Entropy is a state function whose magnitude depends on parameters like (P, V, T).
3. Entropy is a measure of disorderliness or randomness.
4. Entropy change dS is a perfect differential as its value depends only on the initial and final state of the system, independent of the path of change.
5. Entropy of the universe is increasing.
6. In a cyclic process entropy change ΔS is always zero.

Standard entropy of substance (S^o): The entropy of one mole of a substance in its pure state at 1 atm pressure and 25ºC is called the standard entropy of that substance and is denoted by S^o.

Units of Entropy: In C.G.S. units,

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\text{Calorie/mol}}{\text{Kelvin}} = \text{Cal mol}^{-1}\ \text{K}^{-1}$$

In S.I. units, $$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\text{Joules/mol}}{\text{Kelvin}} = \text{J mol}^{-1}\ \text{K}^{-1}$$

The Physical Significance of Entropy

Physically, entropy is a measure of molecular order. A change in entropy dS (infinitesimal change) or ΔS (finite change) corresponds to a change in the amount of molecular order of a system. When the entropy change is positive, the system becomes less orderly and vice versa. For example, when a gas is heated, q_{rev} is positive so is the ΔS and the intermolecular attraction between gas molecules and it will more chaotically distributed, i.e., randomness increases. Similarly, the melting of ice, q_{rev} is positive so is ΔS and the water molecules which had fixed position in ice now breaks up and water molecules began to move freely i.e., randomness increases. Thus it may be concluded that entropy change is a measure of randomness or disorder of a system. All the above example cited are all spontaneous process. As long as the spontaneous process in a system continues its randomness, i.e., entropy goes on increasing and when the process reaches the equilibrium state the entropy of the process becomes maximum and then no further increase in entropy is possible i.e., at equilibrium $\Delta S = 0$.

dq is not a Perfect Differential but dq/t is a Perfect Differential

When a system changes from a given state to another its thermal energy (dq) changes, depending on the path (reversible or irreversible) of transformation. Hence, dq is not a perfect differential.

Now let us take a mole of ideal gas undergoing transformation from state A to B, the volume changes from volume V_1 to V_2 and the temperature changes from T_1 to T_2. Then from the First Law of Thermodynamics

$$dq = dE + PdV$$

$$\text{or } \int_{\mathrm{A}}^{\mathrm{B}} dq = \int_{\mathrm{A}}^{\mathrm{B}} dE + \int_{\mathrm{A}}^{\mathrm{B}} PdV = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} RTd\ln V \quad ...(1)$$

$$\left[\because \left(\frac{\partial E}{\partial T}\right)_V = C_V \text{ and } P = \frac{RT}{V}\right]$$

$$= C_V(T_2 - T_1) + R\int_{V_1}^{V_2} Td\ln V \quad ...(2)$$

The integral $\int_{V_1}^{V_2} Td\ln V$ cannot be evaluated unless the relation between T and V is known.

For isothermal process T remains constant, for nonisothermal process, when T changes the integral, $\int_{V_1}^{V_2} T\ln V$ will have different values. Thus, the magnitude $\int_A^B dq$ depends on the way the expansion has been carried out.

Now dividing the equation (1) by T we have

$$\int_A^B \frac{dq}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} Rd\ln V = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

That is, $\int_A^B \frac{dq}{T}$ is now independent of the path of transformation because for the integral $\int_{V_1}^{V_2} Rd\ln V$ relationship between temperature and volume is not required.

Hence, $\int dq$ is path dependent but $\int \frac{dq}{T}$ is path independent. In this case, the heat change dq takes place in a reversible way.

For Carnot Cycle: In a Carnot cycle AB and CD are isothermals with temperature T_1 and T_2.

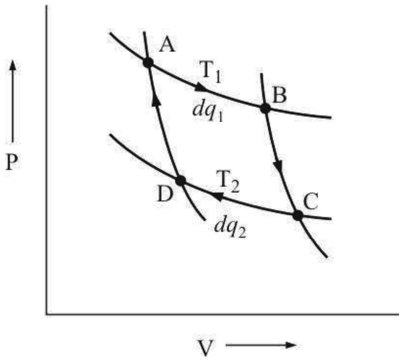


Fig. 2.1 The Carnot's cycle

BC and DA are the adiabatics.

NOTES

To reach the point C from A we can follow two paths either from A to C (ABC path) or A to C (ADC path) and in a Carnot cycle all the paths are reversible paths. (Fig. 2.1). Now let infinitesimal amount of heat (dq_1) be absorbed by the system from the source at T_1 and infinitesimal amount of heat (dq_2) is rejected to the sink at temperature T_2. Then from Carnot cycle ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$) equation

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_1}$$

or

$$\frac{dq_1}{T_1} = \frac{dq_2}{T_2} \qquad \text{...(3)}$$

Now, to reach point C along $A \rightarrow B \rightarrow C$

$$\frac{\text{Heat change}}{\text{Temp}} = \frac{dq_1}{T_1} + 0 = \frac{dq_1}{T_1}$$

and along $A \rightarrow D \rightarrow C$

$$\frac{\text{Heat change}}{\text{Temp}} = 0 + \frac{dq_2}{T_2} = \frac{dq_2}{T_2}$$

But from equation (3) $\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$.

Hence, the ratio of temperature $\frac{dq}{T}$ is same whatever path might have been followed by the system in the reversible change. Hence, we conclude that in a reversible process $\frac{dq}{T}$ is a perfect differential.

For the complete cyclic process in the Carnot cycle ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$), the sum of $\frac{dq}{T}$ will be

$$\sum \frac{dq}{T} = \frac{dq_1}{T_1} + 0 + \frac{(-dq_2)}{T_2} + 0$$

$$= \frac{dq_1}{T_1} - \frac{dq_2}{T_2} = 0$$

$$\left(\because \ \frac{dq_1}{T_1} = \frac{dq_2}{T_2}\text{; the negative sign implies heat rejected}\right)$$

Thus, in a Carnot cycle

$$\oint \frac{dq}{T} = 0$$

The above equation is obtained from the reversible change, hence $\frac{dq}{T}$ should be replaced by $\frac{dq_{\text{rev}}}{T}$ and what is known as entropy as discussed earlier. Hence,

$$dS = \frac{dq_{\text{rev}}}{T}$$

For heat change at different temperatures,

$$dS = \frac{dq_{1(\text{rev})}}{T_1} + \frac{dq_{2(\text{rev})}}{T_2} + \frac{dq_{3(\text{rev})}}{T_3} + \ldots = \sum \frac{dq_r}{T}$$

NOTES

or $$\int dS = \int \frac{dq_{\text{rev}}}{T}$$

Entropy Change in Reversible Cyclic Processes

We have seen that for a reversible Carnot cycle

$$\oint dS = 0$$

This is not only true for Carnot cycle but for any reversible cyclic process it holds good, i.e., $\oint dS = 0$. Suppose a reversible cyclic process as shown in Fig. 2.2 is taking place. In this cyclic process the complete cycle is from $A \rightarrow B \rightarrow A$. This reversible cycle can be divided into an infinite number of Carnot cycles. One of the carnot cycle chosen is *MNOP*, where *MP* and *NO* are the adiabatics. For isothermals (*MN*) heat change is considered as dq_1 at temperature T_1 and for *PO* be dq_2 at T_2. The heat change along adiabatic *MP* and *NO* is nil.

So for Carnot cycle *MNOP*

$$\frac{dq_1}{T_1} - \frac{dq_2}{T_2} = 0$$

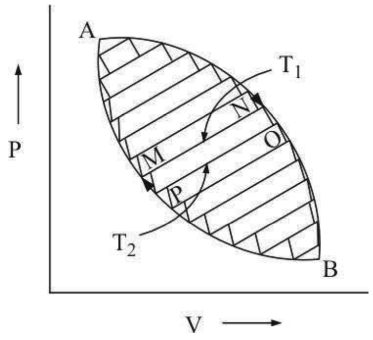


Fig. 2.2 *Entropy Change in a Reversible Cyclic Process*

Similarly, several Carnot cycles constructed and $\frac{dq_3}{T_3} - \frac{dq_4}{T_4} = 0$ and so on.

Hence, for the complete reversible cyclic process

$$\sum \frac{dq}{T} = 0 \quad \text{or,} \quad \oint \frac{dq}{T} = 0$$

i.e., $$\oint dS = 0$$

We thus conclude that for any reversible cyclic process, the net entropy of the system is zero.

Entropy Change of the Universe

In case of Carnot cycle only the entropy change of the system has been taken into account. But entropy change of the source or the sink has not been considered. But due to heat transfer either gain or lose whatever may be the case there is also change of entropy of both source and sink. The entropy change of the surroundings is the net change in entropy of source and the sink. The total change in entropy of the system and the surroundings is named entropy-change of the universe.

Hence, ΔS_{univ} or $\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

For Carnot cycle $\Delta S_{\text{system}} = 0$

Now,

Loss of entropy of the source = $-\frac{q_1}{T_1}$

and gain of entropy of the sink = $+\frac{q_2}{T_2}$

Hence, net entropy of the surroundings

$$\Delta S_{\text{surrounded}} = -\frac{q_1}{T_1} + \frac{q_2}{T_2}$$

Applying Carnot cycle equation $\frac{q_1}{T_1} = \frac{q_2}{T_2}$

or $\quad \Delta S_{\text{surround}} = 0$

Hence, for a reversible cyclic process

$$\Delta S_{\text{univ}} = 0 + 0 = 0$$

The net entropy change in a reversible cyclic process is zero i.e., neither gain nor loss of entropy.

Entropy Change in Irreversible Processes

Entropy or entropy change is always measured by considering reversible heat transfer and under that condition entropy is a state function, i.e., perfect differential. But for an irreversible process, we have to divide the whole system into infinitesimal numbers and under that conditions we may think that the infinitesimal systems are in virtual equilibrium.

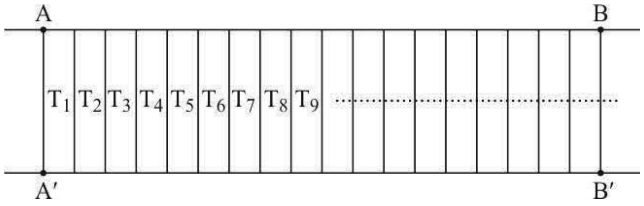


Fig. 2.3 *Entropy Change in Irreversible Process*

For a system undergoing changes from state A to B irreversibly, we have divided the system into several infinitesimal parts and the changes are occurring in reversible conditions. Hence

$$\Delta S = S_B - S_A$$

$$= \frac{dq_1}{T_1} + \frac{dq_2}{T_2} + \frac{dq_3}{T_3} + \ldots = \int_A^B \frac{dq_r}{T}$$

1. Irreversible Flow of Heat: Let a heat reservoir (A) at temperature T_1 be brought into contact with a second reservoir (B) at a lower temperature T_2. Let a small amount of heat q flow from A to B.

NOTES

The decrease in entropy of $A = \frac{-q}{T_1}$

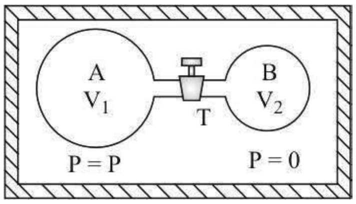
The increase in entropy of $B = \frac{+q}{T_2}$

$$\therefore \text{ Net entropy change } = \frac{q}{T_2} - \frac{q}{T_1} = q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= q\left(\frac{T_1 - T_2}{T_1 T_2}\right) = +\text{ve (as } T_1 > T_2)$$

Hence, irreversible process leads to an increase in entropy.

2. Irreversible isothermal expansion of an ideal gas: Suppose one mole of ideal gas is enclosed in vessel A with volume V_1 and is connected to another vessel B with volume V_2 by a stock cock. The vessel B is completely evacuated and the whole system is enclosed in a container and insulated and the temperature is TK.



Now as soon as the stop-cock is opened gas from A will rush to B till the volume becomes ($V_1 + V_2$). Now, the gas in A expands against zero pressure, work done is zero and as it is insulated heat supplied from surroundings is zero too. Thus ΔE is zero and temperature remains unaltered.

$$q = \Delta E + W = 0$$

Now, for reversible isothermal expansion at TK for volume to expand from V_1 to $V_1 + V_2$

$$q_{\text{rev}} = \Delta E + RT \ln \frac{V_1 + V_2}{V_1}$$

$$= 0 + RT \ln \frac{V_1 + V_2}{V_1}$$

$$\therefore \quad \Delta S_{\text{system}} = \frac{q_{rev}}{T} = R \ln \frac{V_1 + V_2}{V_1}$$

The surroundings has no thermal change, hence

$$\Delta S_{\text{surround}} = 0$$

To find out ΔS_{system}, the expansion should be carried out reversibly, i.e., all the time decreasing pressure by infinitesimal amount so that it becomes $p - dp$ then $p - 2dp$ ..., etc., till the volume from V_1 to $V_1 + V_2$ is reached.

In this case, the irreversible process for which entropy cannot be measured is divided into infinitesimal parts which are all in virtual equilibrium. Thus, ΔS_{system} measured under reversible condition is same as ΔS_{system} (irreversible).

Thus, in irreversible expansion of gas

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst.}} + \Delta S_{\text{surr.}}$$

$$= R \ln \frac{V_1 + V_2}{V_1} + 0 = R \ln \frac{V_1 + V_2}{V_1} = +\text{ve}$$

Hence, irreversible expansion of gas leads to increase in entropy.

3. Irreversible Cyclic Process: In the Carnot cycle, let us suppose that one of the process is irreversible i.e., from $A \rightarrow B$ irreversible process and hence heat absorbed by the system from source in an irreversible fashion amounting dq_1* at temperature T_1 and heat rejected to the sink under reversible condition is dq_2 at temperature T_2. It follows that

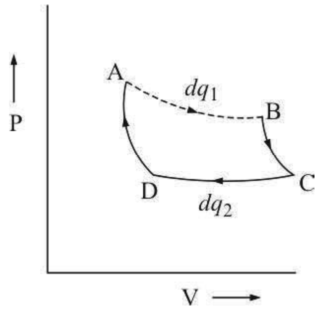


Fig. 2.4 Entropy Change in Irreversible Cyclic Process

$$\frac{dq_1^* - dq_2}{dq_1^*} < \frac{T_1 - T_2}{T_2}$$

or $$\frac{dq_2}{T_2} - \frac{dq_1^*}{T_1} > 0$$

When the system has completed the cycle, the engine has returned to the initial state and

$$\Delta S_{\text{system}} = 0$$

For the source

$$\Delta S_{\text{source}} = -\frac{dq_1^*}{T_1}$$

For the sink

$$\Delta S_{\text{sink}} = \frac{dq_2}{T_2}$$

Thus, for the surroudings

$$\Delta S_{\text{surroundings}} = \Delta S_{\text{source}} + \Delta S_{\text{Sink}} = -\frac{dq_1^*}{T_1} + \frac{dq_2}{T_2} = +\text{ve}$$

Thus, in the irreversible cyclic process

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0 + \Delta S_{\text{surrounding}} > 0$$

In an irreversible cyclic process, there would occur a net increase in entropy.

The spontaneous processes are irreversible. Hence, in a spontaneous process there should be net increase in entropy. Even if a system undergoes decrease in entropy the increase in entropy of surroundings will be such that the total change will be positive. If the net increase in entropy is negative then the process will not occur.

Irreversible Process and the Clausius Inequality

In an irreversible cyclic process, one in which friction occurs or as in case of mixing of non reacting gases, in all these cases the efficiency of an engine is reduced. The efficiency

$$\eta = \frac{dq_1^* - dq_2}{dq_1^*} < \frac{T_1 - T_2}{T_2}$$

or

$$\frac{dq^*_{1\,(\text{hot})} - dq_{2(\text{cold})}}{dq^*_{1\,(\text{hot})}} < \frac{T_{1(\text{hot})} - T_{2(\text{cold})}}{T_{2(\text{hot})}}$$

or rearranging

$$\frac{dq^*_{1\,(\text{hot})}}{T_{\text{hot}}} - \frac{dq_{2(\text{cold})}}{T_{\text{cold}}} < 0$$

and, in irreversible cycle

$$\oint \frac{dq}{T} < 0$$

This is known as Clausius inequality.

Entropy and the Second Law

For an irreversible process there is a net rise in entropy (ΔS_{univ} is positive). Natural processes are spontaneous and irreversible. Thus, natural process will take place in a direction in which entropy would increase or where there is no net increase in entropy process will not occur spontaneously. However, in all such changes the energy may be transferred but the total quantity remains constant. Thus,

First law: The energy of the universe remains constant,

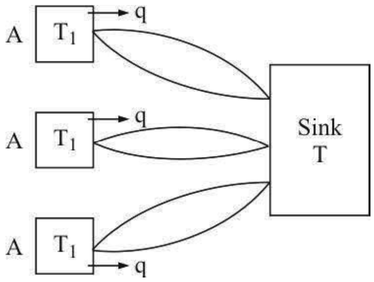
Second law: The net entropy of the universe tends to maximum.

Entropy and available work: Let there be three heat reservoirs *A*, *B* and *C* with temperature T_1, T_2 and T_3 and $T_1 > T_2 > T_3$. There is another heat reservoir the sink at temperature *T*. Now let there be a reversible heat engine working between *A* and the sink. If *q* be the amount of heat taken by the engine from the heat reservoir *A* at temperature T_1, the available work

$$W_1 = q\left[1 - \frac{T}{T_1}\right]$$

Now imagine that q amount of heat is flown irreversibly to heat reservoir B. Now, again the heat engine working reversibly between temperature T_2 and T, the maximum work is obtained.

NOTES



$$W_2 = q\left[1-\frac{T}{T_2}\right]$$

In the same way if Q amount of heat is flown to the third reservoir and the heat engine works in the similar fashion, maximum work obtainable is W_3

$$W_3 = q\left[1-\frac{T}{T_3}\right]$$

As $T_1 > T_2 > T_3$, $W_1 > W_2 > W_3$.

Thus, lower the temperature of the reservoir to which the heat q flows irreversibly, the lesser would be the yield of work.

If now q amount of heat flows to a reservoir at temperature T same as that of the sink at T, then maximum work obtainable

$$W = q\left[1-\frac{T}{T}\right] = 0$$

Thus, although the quantity of heat flow is the same amount (q), the work obtained is nil.

This is the reason we say

First law is the law of conservation of energy and

Second law is the law of degradation of energy.

Now, $\Delta W = W_1 - W_2$

$$= q\left[\frac{T}{T_2}-\frac{T}{T_1}\right] = qT\frac{T_1-T_2}{T_1T_2} = \text{a positive quantity}$$

Now, due to irreversible flow of heat, the entropy change

$$\Delta S = \frac{q}{T_2}-\frac{q}{T_1}$$

$$= q\frac{T_1-T_2}{T_1T_2} = \text{a positive quantity}$$

or $\Delta W = T\Delta S$

That means the energy rendered unavailable as work is proportional to the increase in entropy. The higher the increase in entropy, the lesser the availability of work. The entropy increment is a measure of unavailable work.

Entropy Change for Gases

From the first law of thermodynamics

$$dq = dE + dW = dE + PdV$$

NOTES

where PdV is the mechanical work.

For reversible process dq replaced by dq_{rev}, dE is a state function and hence it is same for both reversible and irreversible process

$$dq_{\text{rev}} = dE + PdV$$

or $$TdS = dE + PdV \qquad \left(\because dS = \frac{dq_{\text{rev}}}{T}\right)$$

For ideal gas $dE = nC_V dT$ and $P = \frac{nRT}{V}$

Hence, $$TdS = nC_V dT + \frac{nRT}{V} dV$$

or $$dS = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

Assuming, C_V is independent of temperature and volume changes from V_1 to V_2 when temperature changes from T_1 to T_2. Integrating between this limit

$$\int_1^2 dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

or $$S_2 - S_1 = \Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

For isothermal process

$$\Delta S = nC_V \ln 1 + nR \ln \frac{V_2}{V_1} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

For isochoric process

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln 1 = nC_V \ln \frac{T_2}{T_1}$$

In case of real gas

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Under condition of large volume it can be approximated to

$$P(V - nb) = nRT \quad \text{or} \quad P = \frac{nRT}{V - nb}$$

As before, $$dS = nC_V \frac{dT}{T} + \frac{PdV}{T} = nC_V \frac{dT}{T} + \frac{nRT}{V - nb} \cdot \frac{dV}{T}$$

$$= nC_V \frac{dT}{T} + \frac{nR}{V - nb} dV$$

or $$\int_1^2 dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + \int_{V_1}^{V_2} \frac{nR}{V - nb} dV$$

or $$S_2 - S_1 = \Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2 - nb}{V_1 - nb}$$

Entropy of Mixing

Two or more gases when brought in contact would immediately diffuse into one another and mix up irreversibly. Such a spontaneous irreversible process will lead to an increase in entropy. Now we wish to find out the entropy change in mixing of ideal gases which are non reacting.

Let n_1 mole of gas A and n_2 mole of gas B occupying volume V_1 and V_2 at constant pressure P and temperature T be kept in two bulbs separated by a stop cock (Fig. 2.5).

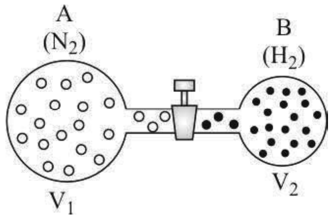


Fig. 2.5 *Before Mixing of Gases*

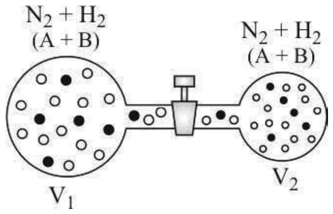


Fig. 2.6 *After Mixing of Gases*

After opening the stop cock the gas will mix spontaneously (Fig. 2.6) and the process will continue till they achieve equilibrium state. After mixing the gas A and B both occupy volume $(V_1 + V_2)$, i.e., the total volume of the container.

Hence, the entropy change ΔS for gas A due to isothermal volume expansion

$$\Delta S_A = n_1 R \ln\frac{V_1 + V_2}{V_1}$$

Similarly for gas B

$$\Delta S_B = n_2 R \ln\frac{V_1 + V_2}{V_1}$$

Since gases are ideal, each gas acts independently of the other. Thus, entropy change of mixing is equal to the sum of the entropy change due to their individual isothermal volume expansion.

$$\begin{aligned}\Delta S_{\text{mix}} &= \Delta S_A + \Delta S_B \\ &= n_1 R\ln\frac{V_1 + V_2}{V_1} + n_2 R\ln\frac{V_1 + V_2}{V_1} \\ &= -n_1 R\ln\frac{V_1}{V_1 + V_2} - n_2 R\ln\frac{V_2}{V_1 + V_2}\end{aligned}$$

NOTES

If x_1 and x_2 are the mole fractions of gas A and B in the mixture respectively then

$$x_1 = \frac{n_1}{n_1+n_2} = \frac{n_1}{n} = \frac{V_1}{V_1+V_2}$$

and $$x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n} = \frac{V_2}{V_1+V_2}$$

(n = total number of moles of A and $B = n_1 + n_2$)

Hence, entropy of mixing

$$\Delta S_{\text{mix}} = -n_1R \ln x_1 - n_2R \ln x_2$$

$$= -nR\left(\frac{n_1}{n}\ln x_1 + \frac{n_2}{n}\ln x_2\right)$$

$$= -nR\,(x_1 \ln x_1 + x_2 \ln x_2)$$

For more number of components the generalized equation can be given as

$$\Delta S_{\text{mix}} = -nR\sum_{i=1}^{N} x_i \ln x_i$$

Molar entropy of mixing

$$\Delta S_{m\,(\text{mix})} = -R\sum_{i=1}^{N} x_i \ln x_i$$

Since mole fraction of gas x_i is always less than unity, ln x_i will always be less than zero i.e., negative and hence, ΔS_{mix} will always be positive.

In case of binary mixture of ideal gas, if x_1 and x_2 are the mole fraction of component 1 and 2, then $x_1 + x_2 = 1$ and $x_2 = 1 - x_1$.

Hence, $\Delta S_{m\,(\text{mix})} = -R\,[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)]$

$\Delta S_{m\,(\text{mix})}$ is maximum when first derivative with respect to x_1 or x_2 is zero and second derivative is negative.

i.e., $$\frac{d(\Delta S_m(mix))}{dx_1} = 0 \quad \text{and} \quad \frac{d^2(\Delta S_m(mix))}{dx_1^2} = -ve$$

Now differentiating the equation, w.r.t. x_1

$$\frac{d(\Delta S_m(mix))}{dx_1} = -R\left\{\frac{x_1}{x_1} + \ln x_1 + \frac{1-x_1}{1-x_1}(-1) - \ln(1-x_1)\right\}$$

$$= -R\{\ln x_1 - \ln(1-x_1)\} = 0$$

or $$\ln x_1 = \ln(1-x_1)$$

Hence $$x_1 = 1 - x_1 \quad \text{or} \quad x_1 = \frac{1}{2}$$

$$\therefore \quad x_2 = 1 - x_1 = \frac{1}{2}$$

Now, $$\left\{\frac{d^2(\Delta S_m(mix))}{dx_1^2}\right\} = -R\left\{\frac{1}{x_1} + \frac{1}{1-x_1}\right\}$$

$$\text{or}\left\{\frac{d^2(\Delta S_m(mix))}{dx_1^2}\right\}_{x_1=\frac{1}{2}} = -R\left\{\frac{1}{\frac{1}{2}}+\frac{1}{1-\frac{1}{2}}\right\} = -4R = \text{negative}$$

NOTES

Hence, entropy of mixing of two ideal gases is maximum when the mole ratio in the mixture is 1 : 1.

In the similar way, it can also be shown that the free energy decrease is maximum when equimolar quantities of the two components are mixed.

Spontaneity in Terms of Entropy Change

In case of isolated systems there is neither exchange of energy nor matter with the surroundings. If two nonreacting gases, insulated and isolated in two different containers be allowed to mix by opening the stop-cock, the two gases mix spontaneously and there is an increase of randomness, i.e., entropy change is positive although there is no exchange of energy and matter with the surroundings and is an isolated system.

In such a case

$$\Delta S_{\text{universe}} \text{ or } \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{system}} + 0$$

$$\text{or} \qquad \Delta S_{\text{total}} = \Delta S_{\text{system}}$$

On the other hand, in case of open system there is both exchange of energy and matter, for example, spontaneous process like (*i*) Cooling down of hot water, (*ii*) Chemical reactions in open container like acid base reactions, reactions of sodium metal with water.

In such a case

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

As has been shown earlier that for the processes to be spontaneous, ΔS_{total} should be positive

'For any spontaneous process, the total entropy change (ΔS_{total}) must be positive.'

$$\text{i.e.,} \qquad \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surround}} > 0$$

It must also be noticed here that for a spontaneous process the entropy or randomness of a system keeps on increasing till equilibrium is reached, i.e., uniform distribution of gases after mixing is the final state what is achieved and is known as the state of equilibrium. Thus, the entropy of the system at equilibrium is maximum and once equilibrium is reached there is no further change of entropy, i.e., $\Delta S_{\text{total}} = 0$.

As has been seen that $\Delta S > 0$ for a process to be spontaneous then for $\Delta S_{\text{total}} < 0$ the process should be non-spontaneous. Thus, for change of state from X to Y.

$$X \rightarrow Y$$

For $X \rightarrow Y$ if it is spontaneous then $Y \rightarrow X$ will be non-spontaneous. Hence, we may conclude for a spontaneity in terms of entropy as (*i*) If ΔS_{total} is positive (i.e., $\Delta S_{\text{total}} > 0$), the process is spontaneous.

(*ii*) If ΔS_{total} is negative (i.e., $\Delta S_{\text{total}} < 0$), the forward process is non-spontaneous the backward process may be spontaneous.

(*iii*) If ΔS_{total} is zero, the process is in equilibrium.

2.2.2 Free Energy

From Second Law of Thermodynamics the criteria for reversible and irreversible processes

$$\Delta S = 0 \quad \text{for reversible change}$$

$$\Delta S > 0 \quad \text{for irreversible change.}$$

Although entropy provides criteria for spontaneity of a change in isolated system, it is inconvenient to use because entropy change referred to is that of the system and surroundings. Thus, if the criteria of spontaneity can be expressed in terms of system only, it would be much easy.

Again it is known that neither energy factor nor randomness factor (i.e., entropy) alone can decide the feasibility of a process. Thus, while deciding spontaneity or feasibility of a process, both ΔH and ΔS should be considered together. Again in thermodynamics we are interested to set up criteria for availing maximum work. To accomplish these, we need to define new function of states. The two other new thermodynamic function of state defined are called Helmholtz free energy A and Gibbs free energy G. Earlier it was called as Helmholtz free energy and Gibbs free energy but according to IUPAC system, now it is simply called as Helmholtz energy or Helmholtz function and Gibbs energy or Gibbs function. However, the use of the term 'free energy' has not yet been completely stopped.

The free energy of a system is defined as the maximum energy available to a system which can be converted into useful work. The above definition of free energy can be defined by considering 'Gibbs Free Energy'. However if Helmholtz free energy is considered it will not be in terms of useful work but 'maximum work'. Hence, Helmholtz free energy is termed as 'Work function' and Gibb's Free energy as 'Free Energy'.

Work Function, *A*

Mathematically it is given as

$$A = E - TS$$

E is internal energy of the system,

T is the absolute temperature at which process is carried out,

S is the entropy of the system,

For an isothermal change of the system (finite change).

$$\Delta A_T = \Delta E - T\Delta S \qquad (\because \quad \Delta T = 0)$$

Now as entropy changes $\Delta S = \frac{q_{rev}}{T}$ or $q_{\text{rev}} = T\Delta S$

or $$\Delta A_T = \Delta E - q_{\text{rev}} \qquad ...(4)$$

Now from First Law of Thermodynamics

$$q = \Delta E + W$$

For reversible change

$$q_{\text{rev}} = \Delta E + W_{\text{rev}}$$

or $\quad \Delta E - q_{\text{rev}} = - W_{\text{rev}}$ ...(5)

Comparing (1) and (2)

$$\Delta A_T = - W_{\text{rev}}$$

or $\quad - \Delta A_T = W_{\text{rev}}$

as W_{rev} is the maximum work available.

Thus A is such a thermodynamic property of the system that its decrease gives the maximum amount of work available during the isothermal transformation of the system. The work W_{rev} includes all type of work involving PV and non PV work. This may also be purely mechanical or purely non-mechanical or partly mechanical and partly external.

For irreversible process

$$- \Delta A_T > W$$

If the change be not isothermal, the change in work function will not be equivalent to maximum work.

$$A = E - TS$$

$\therefore \quad dA = dE - TdS - SdT$ (for infinitesimal change)

or $\quad dA = dE - dq_{rev} - SdT$

or $\quad dA = - PdV - SdT$ (W is taken as the PV work)

Thus, for an isochoric process

$$\left(\frac{\partial A}{\partial T}\right)_V = - S$$

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

If W is not purely mechanical PV work, then

$$dA = - W_{\text{max}} - SdT$$

or $\quad - dA = W_{\text{max}} + SdT$

For dA to be negative SdT is negative, i.e., magnitude of SdT is greater than W_{max} and hence $- dA$ does not give the maximum work.

Gibbs Energy, *G*

In mathematical form Gibbs energy is given as:

$$G = H - TS$$

H= Enthalpy of the system,

S= Entropy of the system,

T= Absolute temperature in Kelvin.

Again $H = E + PV$

Hence, $G = E + PV - TS$

If the system undergoes an isothermal reversible change at constant pressure, then

NOTES

$$\Delta G = \Delta E + P\Delta V + V\Delta P - T\Delta S - S\Delta T \text{ (for finite change)}$$

or $\Delta G_{P,\,T} = \Delta E + P\Delta V - T\Delta S$ ...(6)

Now, $\Delta S = \frac{q_{rev}}{T}$ or $T\Delta S = q_{\text{rev}}$

Again from First Law of Thermodynamics

$$q = \Delta E + W$$

For reversible process

$$q_{\text{rev}} = \Delta E + W_{\text{rev}}$$

or $T\Delta S = \Delta E + W_{\text{rev}}$

or $\Delta E - T\Delta S = - W_{\text{rev}}$ ...(7)

Now putting (2) in (1)

$$\Delta G_{P,\,T} = P\Delta V - W_{\text{rev}}$$

or $-\Delta G_{P,\,T} = W_{\text{rev}} - P\Delta V$

As under reversible condition work obtained is maximum W_{rev} is the $W_{\max}$

Hence,$-\Delta G_{P,\,T} = W_{\max} - P\Delta V$

where $P\Delta V$ is the mechanical work involved in the system itself undergoing transformation. Thus $W_{\max} - P\Delta V$ is the maximum amount of work received for any external use.

Free energy, (G) is thus, a thermodynamic property of the system whose decrease is the measure of the external work available during the transformation of the system. It may, therefore, be generalised that the free energy, G, of a system is a measure of its capacity to do useful work. It is a part of the energy of the system which is free for conversion to useful work and is, therefore, called free energy.

The above relationship $-\Delta G_{P,\,T} = W_{\max} - P\Delta V$, holds good only when the process is carried out at constant temperature and pressure.

In general

$$dG = dE + PdV + VdP - SdT - TdS$$

(infinitesimal change)

In a reversible mechanical process

$$dq_{\text{rev}} = dE + (PdV)_{\text{rev}}$$

or $TdS = dE + (PdV)_{\text{rev}}$

Hence, $dG = TdS + VdP - SdT - TdS = VdP - SdT$

For isothermal process

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

For isobaric process

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

NOTES

Standard Values of Gibbs Free Energy

G is a state function. In order to assign numerical values to free energy of a system, it becomes necessary to put a standard value of the free energy of the system at a specified state. The standard state is usually taken at a constant temperature (25ºC) and 1 atm pressure for a pure substance.

Now we know for isothermal change,

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{or} \quad dG = VdP$$

For a system undergoing changes from state I to state II, i.e., from 1 atm to some other pressure and temperature 25ºC to some other temperature.

$$\int_I^{II} dG = \int_1^P VdP$$

or $$G^{II} - G^I = \int_1^P VdP$$

Now G^I is the standard state, i.e., state at 1 atm and 25ºC and is replaced by G^o, and G^{II} is presented as G for simplicity.

$$G - G^o = \int_1^P VdP$$

For n mole of perfect gas $V = \frac{nRT}{P}$

Hence, $$G - G^o = \int_1^P \frac{nRT}{P} dP$$

$$= nRT\int_1^P \frac{dP}{P} \qquad \text{(isothermal process } T \text{ constant)}$$

or $$G - G^o = nRT\int_1^P d\ln P = nRT \ln\frac{P\,\text{atm}}{1\,\text{atm}}$$

or $$G = G^o + nRT\ln P$$

or $$\frac{G}{n} = \frac{G^o}{n} + RT\ln P$$

or $$\bar{G} = \bar{G}^o + RT\ln P$$

where $\bar{G}$, $\bar{G}^o$ are the free energies for 1 mole of substance. Generally free energy for 1 mole of substance is represented by the symbol μ thus,

$$\mu = \mu^o + RT\ln P$$

The free energy for 1 mole of pure substance is called chemical potential of that substance.

Free Energy of Real Gases

As we have seen

$$G - G^o = \int_1^P V dP$$

or $$\frac{G}{n} - \frac{G^o}{n} = \int_1^P \frac{V}{n} dP \quad \text{(where } n \text{ is the number of mole of gas)}$$

or $$\mu - \mu^o = \int_1^P \bar{V}\, dP \qquad \left(\bar{V} = \frac{V}{n}, \text{ i.e., volume per mole of gas}\right)$$

where μ and μ^o are the molar free energies (free energy per mole of gas) at P atm and 1 atm.

$$\mu = \mu^o + \int_1^P RT \frac{dP}{P}$$

$$= \mu^o + \int_1^P RTd \ln P = \mu^o + RT \ln P$$

or $$\mu = \mu^o + RT \ln P \qquad \text{(under isothermal condition)}$$

For a change of pressure from P_1 to P_2

$$\mu_1 = \mu^o + RT \ln P_1 \qquad \text{...(8)}$$

$$\mu_2 = \mu^o + RT \ln P_2 \qquad \text{...(9)}$$

or (8) – (9) gives,

$$\Delta\mu = \mu_2 - \mu_1 = RT \ln P_2 - RT \ln P_1 = RT \ln \frac{P_2}{P_1}$$

or $$\Delta\bar{G} = \Delta\mu = RT \ln \frac{P_2}{P_1}$$

In case of real gas the relationship will be different. For real gas or Vander Waal's gas:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

or per mole of gas,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

or $$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

or $$PV = \left(\frac{RT}{V - b}\right)V - \frac{a}{V}$$

$$= RT\left(\frac{V}{V - b}\right) - \frac{a}{V}$$

$$= RT\left(\frac{1}{\frac{V - b}{V}}\right) - \frac{a}{V} = RT\left(\frac{1}{1 - \frac{b}{V}}\right) - \frac{a}{V}$$

or $$PV = RT\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V} = RT\left(1 + \frac{b}{V} + \frac{b^2}{V^2} + ...\right) - \frac{a}{V}$$

NOTES

Neglecting $\frac{b^2}{V^2}$ and other higher terms (as b is small the square or other higher terms become negligible and division of that by much higher value of V^2 or other higher terms becomes again very much negligible).

or $$PV = RT\left(1 + \frac{b}{V}\right) - \frac{a}{V}$$

$$= RT + \frac{bRT}{V} - \frac{a}{V}$$

$$= RT + \frac{1}{V}(bRT - a) = RT + RT\left(b - \frac{a}{RT}\right)\frac{1}{V} \qquad ...(10)$$

Now, from Kammerlingh equation which express PV in terms of power series of pressure,

$$PV = RT[1 + B_1P + C_1P^2 + D_1P^3 + ...]$$

or in terms of volume

or $$PV = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + ...\right] \qquad ...(11)$$

This is what is known as Virial Equation of state and B, C, D ... are the second, third, fourth virial coefficients. These coefficients are function of temperature and the nature of the gas, and the second virial coefficients B is most important. Now comparing equation (10) with (11), the second virial coefficient $B = \left(b - \frac{a}{RT}\right)$.

From equation (1) we have

$$PV = RT + RT\left(b - \frac{a}{RT}\right)\frac{1}{V} = RT + \frac{BRT}{V}$$

or $$V = \frac{RT}{P} + \frac{BRT}{PV} = \frac{RT}{P} + \frac{BRT}{RT}$$

(For simplicity we have used $PV = RT$
as used for ideal gas equation)

$$= \frac{RT}{P} + B$$

In this case, we have considered one mole of the gas, hence, the volume is volume per mole and hence it will be $\bar{V}$. The equation becomes

$$\mu = \mu^o + \int_1^P \bar{V}dP$$

$$= \mu^o + \int_1^P \left(\frac{RT}{P} + B\right)dP = \mu^o + \int_1^P RTd\ln P + \int_1^P B\,dP$$

$$= \mu^o + RT\ln P + B(P - 1)$$

Hence, as before, for transition from pressure P_1 to P_2

$$\Delta\bar{G} = \Delta\mu = RT \ln \frac{P_2}{P_1} + B(P_2 - P_1)$$

NOTES

Fugacity

According to G.N. Lewis, the free energy of one mole or 1 gm-mole of real gas is given by

$$\mu = \mu^o + RT \ln f$$

where 'f' is called the fugacity of the gas.

The relationship between 'f' and 'P' is

$$f = \gamma P$$

where γ is the fugacity coefficient.

For ideal gas there is no interaction between the gaseous molecules, under such conditions γ is unity and $f = P$. For non ideal gas there is interaction between the gaseous molecules and $f = \gamma P$. Only at low pressure, where the gaseous molecules are far apart there are no interactions and

$$(f/P) = 1$$

$$\lim P \to 0$$

or $$f = P$$

But for other pressures $f = \gamma P$.

Fugacity is thus a sort of idealised pressure. Now,

$$\mu = \mu^o + RT \ln \gamma P = \mu^o + RT \ln P + RT \ln \gamma$$

Now we know,

$$V_{\text{real}} = V_{\text{ideal}} + B \text{ (where } B \text{ is second virial coefficient)}$$

Again, $$\Delta\bar{G} = \Delta\mu = \mu_2 - \mu_1 = \int_1^2 VdP = \int_1^2 (V_{\text{ideal}} + B)dP$$

or $$RT \ln \frac{f_2}{f_1} = \int_1^2 \left(\frac{RT}{P} + B\right) dP = RT \ln \frac{P_2}{P_1} + \int_1^2 B\, dP$$

(For ideal gases, i.e., when only the pressure terms are used, $\Delta\bar{G} = \mu_2 - \mu_1$

$= RT \ln \frac{P_2}{P_1}$ and for real gas pressure is replaced by the fugacity term)

or $$RT \ln \frac{f_2}{f_1} - RT \ln \frac{P_2}{P_1} = \int_1^2 B\, dP$$

or $$RT \ln \frac{P_1 f_2}{f_1} = RT \ln P_2 + \int_1^2 BdP$$

At low pressure i.e., $P \to 0$ or fugacity equals to pressure, i.e., $f_1 = P_1$.

or $$RT \ln f_2 = RT \ln P_2 + \int_1^2 B\, dP$$

And if state 1 implies 0 pressure and state 2 some other pressure P then f_2 can be represented by f

$$RT\ln f = RT\ln P + \int_0^P BdP$$

$$= RT\ln P + BP$$

or $\quad RT\ln\dfrac{f}{P} = BP \qquad$ i.e., $f = Pe^{BP/RT}$

or $\quad \ln\gamma = \dfrac{BP}{RT}$

Mixture of Gases

For a mixture of gases (ideal gases) the molar free energy for the *i*th component whose partial pressure, i.e., P_i.

$$\mu_i = \mu_i^o + RT\ln P_i$$

In case of real gas mixture if f_i be the fugacity of the *i*th component,

$$\mu_i = \mu_i^o + RT\ln f_i$$

For ideal gas

$$\mu_i = \mu_i^o + RT\ln P_i = \mu_i^o + RT\ln x_i P$$

(where P is the total pressure and x_i is the mole fraction of *i*th component. Here $P_i/P = x_i$)

$$= \mu_i^o + RT\ln x_i + RT\ln P$$

$$= \mu_i^o + RT\ln P + RT\ln x_i = \mu_i^{\neq} + RT\ln x_i \qquad ...(4)$$

(For a pure ideal gas i.e., only one component of the pressure is P then $\mu_i^{\neq} = \mu_i^0 + RT\ln P$, $\neq$ implies ideal gas in its pure state, i.e., not mixed with other components.)

Let under the same conditions of temperature and pressure n_1, n_2, n_3 ... moles of different components are mixed and $\mu_1^{\neq}, \mu_2^{\neq}, \mu_3^{\neq}$ ... are the molar free energy in, pure state, i.e., when not mixed. Now after mixing if μ_1, μ_2, μ_3 ... be the molar free energy, then as G is an extensive property

$$G_i = n_1\mu_1^{\neq} + n_2\mu_2^{\neq} + n_3\mu_3^{\neq} + ...$$

$$G_M = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + ...$$

(G_i and G_M are the free energies at the initial state and after mixing.)

$$\Delta G_M = n_1(\mu_1 - \mu_1^{\neq}) + n_2(\mu_2 - \mu_2^{\neq}) + n_3(\mu_3 - \mu_3^{\neq}) + ...$$

$$= n_1 RT\ln x_1 + n_2 RT\ln x_2 + n_3 RT\ln x_3$$

(following equation (4))

$$= nRT\left[\left(\frac{n_1}{n}\right)\ln x_1 + \left(\frac{n_2}{n}\right)\ln x_2 + \left(\frac{n_3}{n}\right)\ln x_3 + ...\right]$$

$$= nRT\sum x_i\ln x_i$$ (n is the total number of moles = $n_1 + n_2 + n_3 + ...$)

As mole fraction is less than unity ln x_i is negative, which implies that when the gases are mixed there will be a decrease in free energy.

2.2.3 Chemical Potential

NOTES

So far our discussions were mainly confined to closed systems. Now our attention will be on open systems. An open system as defined is one where both exchange of energy and matter takes place. Gibbs free energy is a function of pressure, temperature and volume. Again these parameters are interrelated for a system of fixed composition and we can write $G = f(P, T)$; $G = f(V, T)$; $G = f(P, V)$ and $G = f(P, T)$ is more convenient. But for an open system quantities of components may also vary, so as free energy which is an extensive property will also be dependent on the amount of components. Let a system contain n_1 moles of A, n_2 moles of B, n_3 moles of C, etc., then its free energy

$$G = f(P, T, n_1, n_2, n_3, ...)$$

If all the variables undergo change, the total differential will be given by,

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, n_3, ...} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, n_3, ...} dT$$

$$+ \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, ...} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, n_3, ...} dn_2$$

$$+ \left(\frac{\partial G}{\partial n_3}\right)_{P, T, n_1, n_2, ...} dn_3 + ...$$

It is already known that

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, n_3 ...} = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, n_3 ...} = -S$$

Hence, the equation becomes

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, ...} dn_1 +$$

$$\left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, n_3, ...} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{P, T, n_1, n_2, ...} dn_3 + ... \qquad ...(12)$$

$\left[\left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, ...}\right.$ means except n_1 all other parameters, i.e., P, T, n_2, n_3 ··· have been kept constant during differentiation.$\left.\right]$

The change in free energy per mole addition of a component keeping other components fixed at a fixed temperature is called the partial molar free energy.

Hence, $\left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_J}$ for the ith component is the partial molar free energy of the ith component and also called its chemical potential and is denoted by the symbol μ_i.

The chemical potential (μ_i) is thus the rate of increase in Gibbs free energy per mole of the component added. But while measuring chemical potential one must take care of two things

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1. Suppose to a given solution containing several components we add very small amount of component *i* and measure its chemical potential. Again chemical potential can also be measured by adding large amount of component *i*. What makes the difference then? In the first case the composition is unaltered (i.e., concentration of components does not vary or if varies that too a negligible amount) but in the second case the composition is altered (i.e., large variations in concentrations of components due to increment in volume). Thus, chemical potential of the same component having same kind of other components vary. Thus, small amount of component should be added to a large amount of system so that the composition remains practically unaltered.

2. Suppose we want to measure chemical potential of water. This can be done by adding 1 mole water to 1 kg of pure water, 1 kg of sugar solution or 1 kg of salt solution and so on. In these cases the chemical potential of water will not however be the same because in all the three cases the composition is different. Although chemical potential is independent of masses but it is dependent on the composition of a system.

Now at constant temperature and pressure, the equation (12) can be rewritten as

$$dG_{P,\,T} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + ... = \sum_{i=1}^{N} \mu_i dn_i \qquad ...(13)$$

Now suppose at constant *P* and *T* we have increased the constituents in the same proportion Δx. That is, component *A* is increased by an amount $n_1 \Delta x$ moles, *B* by $n_2 \Delta x$ moles, *C* by $n_3 \Delta x$ moles. Hence, $dn_1 = n_1 \Delta x$, $dn_2 = n_2 \Delta x$, $dn_3 = n_3 \Delta x$ or in general $dn_i = n_i \Delta x$.

Now as *G* is an extensive property, it will also increase by an amount $G\Delta x$, i.e.,

$$dG = G\Delta x$$

Hence, Equation (13) under this condition

$$dG = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \mu_3 n_3 \Delta x + ... + \mu_i n_i \Delta x$$

$$\text{or} \quad G\Delta x = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \mu_3 n_3 \Delta x + ... + \mu_i n_i \Delta x$$

$$\text{Hence, } G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + ... + \mu_i n_i = \sum_{i=1}^{N} \mu_i n_i \qquad ...(14)$$

The complete differentiation of (14) will give,

$$\begin{aligned} dG &= \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \mu_3 dn_3 + n_3 d\mu_3 \\ &\qquad + ... + \mu_i dn_i + n_i d\mu_i + \\ &= (\mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + ...\ \mu_i\,.\, dn_i) \\ &\qquad + (n_1\, d\mu_1 + n_2\, d\mu_2 + n_3\, d\mu_3 + ...\ n_i\, d\mu_i) \end{aligned}$$

Now subtracting (3) from (4) we get,

$$n_1\, d\mu_1 + n_2\, \mathrm{d}\mu_2 + n_3\, d\mu_3 + \ldots\, n_i\, d\mu_i = 0$$

or, $$\sum_{i=1}^{N} n_i\, d\mu_i = 0$$

Thus, we have got three very useful relations for chemical potentials with the composition of the system.

(*i*) $G = \mu_1\, n_1 + \mu_2\, n_2 + \mu_3\, n_3 + \ldots = \sum_{i=1}^{N} \mu_i\, n_i$

(*ii*) $dG = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \ldots = \sum_{i=1}^{N} \mu_i\, dn_i$

(*iii*) $0 = n_1\, d\mu_1 + n_2\, d\mu_2 + n_3\, d\mu_3 + \ldots = \sum_{i=1}^{N} n_i\, d\mu_i$

These three equations are commonly known as *Gibbs–Duhem relations*.

For a pure substance obviously chemical potential $\mu = \frac{G}{n}$, i.e., free energy per mole.

One of the important application of Gibbs-Duhem equation is prediction of condition of equilibrium. For simplicity we consider the phase of a component in equilibrium having free energies $\bar{G}_1$ and $\bar{G}_2$. Now at equilibrium, if an intinitenimal amount (*dn*) gm-moles of a component passes from phase 1 to phase 2. Then from Gibbs-Duhem relationship

$$\mu_1\, dn_1 + \mu_2\, dn_2 = dG = 0 \qquad \text{or} \quad \mu_1(-\,dn) + \mu_2(dn) = 0$$

$$\text{or} \quad \mu_1 = \mu_2 \ \text{ or } \ \bar{G}_1 = \bar{G}_2$$

The chemical potential or partial molal free energy of a component in every phase must be the same under conditions of equilibrium.

Expression of D*A* and D*G*

$$A = E - TS$$

$$\text{or} \qquad dA = dE - Td\,S - SdT$$

$$= dE - dq_r - SdT \qquad \left(\because dS = \frac{d\,q_{rev}}{T}\right)$$

$$= -\,PdV - SdT \ \ (\because\ dq_r = dE + (PdV)_r)$$

$$\text{Hence,} \left(\frac{\partial A}{\partial V}\right)_T = -\,P \qquad \ldots (15)$$

$$\text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -\,S \qquad \ldots(16)$$

Now for ideal gas $P = \frac{nRT}{V}$ and total change of A under isothremal condition can be obtained by integrating equation (15) when the system undergoes change from state 1 to state 2 and volume changes from V_1 to V_2

$$\Delta A = \int_1^2 dA = -\int_1^2 PdV = -\int_1^2 \frac{nRT\,dV}{V}$$

$$= -nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{V_2}{V_1} = nRT\ln\frac{P_1}{P_2}$$

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For *n* moles of Van der Waal's gas

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

Hence, $\Delta A = \int_1^2 dA = -\int_1^2 PdV = -\int_1^2 \left\{\frac{nRT}{(V-nb)} - \frac{n^2a}{V^2}\right\}dV$

$$= -nRT\ln\frac{V_2-nb}{V_1-nb} - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

The Gibbs free energy

$$G = H - TS$$
$$= E + PV - TS$$
$$= A + PV\ (\because\ A = E - TS)$$

or $dG = dA + PdV + VdP$

$$= -PdV - SdT + PdV + VdP\ (\because\ dA = -PdV - SdT)$$
$$= VdP - SdT$$

$\therefore$ $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$

The total change of *G* under isothermal condition can be given as

$$\Delta G = \int_1^2 dG = \int_1^2 VdP$$

For ideal gas $V = \frac{nRT}{P}$

Hence, $\Delta G = \int_1^2 \frac{nRT}{P}dP = nRT\ln\frac{P_2}{P_1} = nRT\ln\frac{V_1}{V_2}$

For Van der Waal's gas

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

or $PV = \frac{nRTV}{V-nb} - \frac{n^2a}{V}$

Again, $\Delta PV = P_2V_2 - P_1V_1$

$$= nRT\left\{\frac{V_2}{(V_2-nb)} - \frac{V_1}{(V_1-nb)}\right\} - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

Hence, for Van der Waal's gas

$$\Delta G = \Delta A + \Delta PV$$

$$= -nRT\ln\frac{V_2-nb}{V_1-nb} - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

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$$+\,nRT\left\{\frac{V_2}{(V_2-nb)}-\frac{V_1}{(V_1-nb)}\right\} - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$= -nRT\ln\frac{V_2-nb}{V_1-nb} - 2n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right) + nRT\left\{\frac{V_2}{(V_2-nb)}-\frac{V_1}{(V_1-nb)}\right\}$$

2.2.4 Molar Heat Capacity

The amount of heat required to raise the temperature of one gram of a substance by 1ºC or 1 K is called the specific heat. The heat capacity (C) of a substance is the amount of heat required to raise the temperature by 1ºC or 1 K of one mole of substance.

If dq amount of heat is required for dT increase in temperature for one mole of the substance then

$$C = \frac{dq}{dT}$$

But dq is a path function and its value depends on the actual process followed. Therefore, two restrictions are imposed to obtain precise values of heat capacity. The restrictions are 'at constant pressure' and 'at constant volume'. Thus,

$$C_V = \frac{dq_V}{dT} \quad \text{and} \quad C_P = \frac{dq_P}{dT}$$

We know $dq_V = dE$ and $dq_P = dH$.

Hence, $$C_V = \left(\frac{\partial E}{\partial T}\right)_V \text{ and } C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

For finite process at constant volume, $\Delta E = C_V\Delta T$ and at constant pressure, $\Delta H = C_P\Delta T$ assuming C_V and C_P remain unaltered in the temperature range of investigation.

The two heat capacities C_P and C_V are not equal. In general, C_P is greater than C_V. Volume of a substance generally increases at constant pressure with rise in temperature. So a part of the heat is utilised to perform extra mechanical work while at constant volume all the heat is utilised in increasing the internal energy of the system as there is no work. This is the reason why C_P is greater than C_V.

The difference in two heat capacities may be expressed as

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left[\frac{\partial(E+PV)}{\partial T}\right]_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \qquad ...(17)$$

We know $E = f(V, T)$

$$\therefore \qquad dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

Hence, $\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V$

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Substituting these values in equation (1)

$$C_P - C_V = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

From Joule experiment we know $\left(\frac{\partial E}{\partial V}\right)_T = 0.$

Hence, $C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$

Again for one mole of an ideal gas $V = \frac{RT}{P}$

$$\therefore \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Thus, for ideal gas $C_P - C_V = \frac{R}{P} \times P = R.$

Alternative method of finding out the difference in two heat capacities: The amount of heat required or supplied to one mole of an ideal gas to increase its temperature by dT at constant volume is given by $1 \times C_V \times dT = C_V dT$ where C_V is the molar heat capacity at constant volume. As the gas is heated at constant volume, it will not perform external work and in accordance with first law of thermodynamics, the heat supplied will be equal to increase in internal energy of the gas. Hence

$$dE = C_V dT$$

Now, if the same gas be heated at constant pressure to increase its temperature by dT and dq be the heat supplied, then

$$dq = 1 \times C_P \times dT = C_P\, dT$$

where C_P is the molar heat capacity at constant pressure.

The heat supplied at constant pressure increases the temperature of the body by dT, i.e., increases the internal energy by dE as well as enables the gas to perform dW amount of work. If dV is increased in volume, then work performed by the gas

$$dW = PdV$$

Now, from First Law of Thermodynamics

$$dq = dE + PdV$$

or $\qquad C_P dT = C_V dT + PdV$

For one mole of ideal gas

$$PV = RT$$

Now, heat is supplied at constant pressure, thus taking P as constant

or $$\frac{d}{dT}(PV) = \frac{d}{dT}(RT) = R$$

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or $$P\frac{dV}{dT} = R$$

or $$PdV = RdT$$

$\therefore$ $$C_P dT = C_V dT + RdT$$

or $$C_P = C_V + R$$

or $$C_P - C_V = R$$

This relationship holds good when C_P, C_V and R are measured in same units (either heat or work). However, if C_P and C_V are measured in units of heat and R in units of work,

$$C_P - C_V = \frac{R}{J}$$

2.2.5 Phase Transition

A phase is a part of a system that is homogeneous in its composition and properties and is physically distinct from other parts of the system. Under equilibrium condition several phases can co-exist. By changing the conditions of a system (i.e., pressure, temperature and composition, etc.) the material might be transformed from one phase to another. At constant temperature and pressure the phase transition is accompanied by decrease in Gibbs free energy. Under equilibrium conditions the two phases have same Gibbs free energies. The Gibbs free energy is a measure of the stability of a phase.

The Clapeyron-Clausius equation expresses $\frac{dP}{dT}$ for a two-phase system containing one component at equilibrium in terms of some thermodynamic quantities.

Let a liquid and its vapour be in equilibrium at a pressure P and temperature T and $\bar{G}_1$, $\bar{G}_2$ are their corresponding molar Gibbs free energies under equilibrium condition.

$$\bar{G}_1 = \bar{G}_2$$

Now imagine a virtual change of a infinitesimal amount of liquid vapourising at equilibrium (infinitesimal phase change at equilibrium). The drop in molar free energy of the liquid is $-d\bar{G}_1$ and gain in same for the vapour is $+d\bar{G}_2$. Since the system is in equilibrium, net $dG = 0$.

Hence,

$$-d\bar{G}_1 + d\bar{G}_2 = 0 \qquad \text{or} \qquad d\bar{G}_1 = d\bar{G}_2$$

or $$\bar{V}_1 dP - \bar{S}_1 dT = \bar{V}_2 dP - \bar{S}_2 dT$$

(where $\bar{V}_1, \bar{V}_2$ and $\bar{S}_1, \bar{S}_2$ are the corresponding molar volume and molar entropies.)

or $(\bar{V}_1 - \bar{V}_2)dP = (\bar{S}_1 - \bar{S}_2)\,dT$

$$\text{or} \quad \frac{dP}{dT} = \left(\frac{\bar{S}_1 - \bar{S}_2}{(\bar{V}_1 - \bar{V}_2)}\right) = \frac{(\bar{S}_1 - \bar{S}_2)}{(\bar{V}_1 - \bar{V}_2)} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

$$\text{or} \quad \frac{dP}{dT} = \frac{T\Delta\bar{S}}{T\Delta\bar{V}} = \frac{q_{rev}}{T\Delta\bar{V}} = \frac{\Delta\bar{H}}{T\Delta\bar{V}} = \frac{L}{T\Delta\bar{V}} \qquad \text{...(18)}$$

where $\Delta\bar{H}$ is the molar enthalpy change of this phase change and L is the latent heat per gm-mole. This equation is known Clapeyron equation and is applicable to the phase-changes such as transformation of one phase to other, for example α-sulphur to β-sulphur, etc. The sign of $\frac{dP}{dT}$ depends on the signs of L and $\Delta\bar{V}$. When L is positive and $\bar{V}_2 > \bar{V}_1$, $\frac{dP}{dT}$ is positive, i.e., there would be a rise in pressure with increase in temperature. In case of evaporation of a liquid, the vapour pressure increases with rise in temperature. In melting of solid such as paraffin, L is positive and $V_l > V_S$, the melting temperature increases with pressure. In case of ice, L is positive but $V_l < V_S$ and in such case $\frac{dP}{dT}$ is negative, i.e., higher the pressure, lower the melting temperature.

The Clapeyron equation was simplified by Clausius for the vapourisation and sublimation process by assuming that vapour behaves as an ideal gas (for sublimation L will be latent heat of sublimation per gm-mole of substance).

In such a case the equation can be written as

$$\frac{dP}{dT} = \frac{L}{T(\bar{V}_g - \bar{V}_l)}$$

($\bar{V}_g$ = molar volume of gas
$\bar{V}_l$ = molar volume of liquid)

Since $\bar{V}_l << \bar{V}_g$, the equation becomes

$$\frac{dP}{dT} = \frac{L}{T\bar{V}_g} = \frac{L}{T\left(\frac{RT}{P}\right)} = \frac{LP}{RT^2}$$

(For ideal gas $P\bar{V}_g = RT$)

$$\text{or} \quad \frac{1}{P}\frac{dP}{dT} = \frac{L}{RT^2}$$

$$\text{or} \quad \frac{d\ln P}{dT} = \frac{L}{RT^2} \qquad \text{...(19)}$$

If we further assume that the latent heat practically remains constant in the temperature range T_1 to T_2, the integration of equation (19) gives

$$\ln P = -\frac{L}{RT} + C \text{ (Constant)} \qquad \text{...(20)}$$

or by integrating between limits, P_2 and T_2 and P_1 and T_1, assuming latent heat is constant over narrow range of temperature

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{L}{R}\int_{T_1}^{T_2} \frac{dT}{T^2}$$

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or $$\ln\frac{P_2}{P_1} = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \ln\frac{P_2}{P_1} = \frac{L(T_2 - T_1)}{RT_1T_2}$$

This equation is known as Clausius-Clapeyron equation.

2.3 CONCEPT OF FUGACITY AND DETERMINATION OF FUGACITY

In chemical thermodynamics, the fugacity of a real gas is an effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant. It is equal to the pressure of an ideal gas which has the same temperature and molar Gibbs free energy as the real gas. Typically, the fugacity is determined experimentally or estimated from various models, such as a Van der Waals gas that are closer to reality than an ideal gas. The ideal gas pressure and fugacity are related through the dimensionless fugacity coefficient φ.

For an ideal gas, fugacity and pressure are equal and so $\varphi = 1$. Taken at the same temperature and pressure, the difference between the molar Gibbs free energies of a real gas and the corresponding ideal gas is equal to RT ln φ.

The fugacity is closely related to the thermodynamic activity. For a gas, the activity is simply the fugacity divided by a reference pressure to give a dimensionless quantity. This reference pressure is called the standard state and normally chosen as 1 atmosphere or 1 bar.

Accurate calculations of chemical equilibrium for real gases should use the fugacity rather than the pressure. The thermodynamic condition for chemical equilibrium is that the total chemical potential of reactants is equal to that of products. If the chemical potential of each gas is expressed as a function of fugacity, the equilibrium condition may be transformed into the familiar reaction quotient form (or law of mass action) except that the pressures are replaced by fugacities.

For a condensed phase (liquid or solid) in equilibrium with its vapour phase, the chemical potential is equal to that of the vapour, and therefore the fugacity is equal to the fugacity of the vapour. This fugacity is approximately equal to the vapour pressure when the vapour pressure is not too high.

Fugacity is closely related to the chemical potential μ. In a pure substance, μ is equal to the Gibbs energy G_m for a mole of the substance, and

$$d\mu = dG_{\mathrm{m}} = -S_{\mathrm{m}}dT + V_{\mathrm{m}}dP$$

Here, T and P are referred as the temperature and pressure, V_m is the volume per mole and S_m is the entropy per mole.

Gas

An ideal gas has the equation of state,

$$V_{\mathrm{m}}^{\mathrm{ideal}} = \frac{RT}{P}$$

where R is the ideal gas constant. At constant temperature ($dT = 0$),

$$d\mu = RT d \ln P$$

This equation is very useful but is only accurate when gas molecules are small compared to the distances between them and rebound elastically off each other. Gases behave most like ideal gases at low pressures and high temperatures. At moderately high pressures, attractive interactions between molecules reduce the pressure compared to the ideal gas law; and at very high pressures, the sizes of the molecules are no longer negligible and repulsive forces between molecules increases the pressure. At low temperatures, molecules are more likely to stick together instead of rebounding elastically.

The ideal gas law can still be used to describe the behaviour of a real gas if the pressure is replaced by a fugacity ***f***, defined so that,

$$d\mu = RT d \ln f$$

and

$$\lim_{P \to 0} \frac{f}{P} = 1$$

That is, at low pressures f is the same as the pressure, so it has the same units as pressure. The ratio,

$$\varphi = \frac{f}{P}$$

This is called the fugacity coefficient. If a reference state is denoted by a zero superscript, then integrating the equation for the chemical potential gives,

$$\mu - \mu^0 = RT \ln a$$

where a, is a dimensionless quantity and is called the activity.

Condensed Phase

The fugacity of a condensed phase (liquid or solid) is defined the same way as for a gas:

$$d\mu_c = RT d \ln f_c$$

And

$$\lim_{P \to 0} \frac{f_c}{P} = 1$$

It is difficult to measure fugacity in a condensed phase directly; but if the condensed phase is saturated (in equilibrium with the vapour phase), the chemical potentials of the two phases are equal ($\mu_c = \mu_g$). Combined with the above definition, this implies that,

$$f_c = f_g$$

When calculating the fugacity of the compressed phase, one can generally assume the volume is constant. At constant temperature, the change in fugacity as the pressure goes from the saturation press P_{sat} to P is,

$$\ln \frac{f}{f_{\mathrm{sat}}} = \frac{V_{\mathrm{m}}}{RT} \int_{P_{\mathrm{sat}}}^{P} dp = \frac{V\,(P - P_{\mathrm{sat}})}{RT}.$$

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This fraction is known as the Poynting factor. Using $f_{\mathrm{sat}} = \varphi_{\mathrm{sat}} P_{\mathrm{sat}}$, where φ_{sat} is the fugacity coefficient,

$$f = \varphi_{\mathrm{sat}} P_{\mathrm{sat}} \exp\left(\frac{V\,(P - P_{\mathrm{sat}})}{RT} \right)$$

This equation allows the fugacity to be calculated using tabulated values for saturated vapour pressure. Often the pressure is low enough for the vapour phase to be considered an ideal gas, so the fugacity coefficient is approximately equal to 1.

Unless pressures are very high, the Poynting factor is usually small and the exponential term is near 1. Frequently, the fugacity of the pure liquid is used as a reference state when defining and using mixture activity coefficients.

2.4 DEBYE–HÜCKEL THEORY FOR ACTIVITY COEFFICIENTS

The Debye–Hückel theory was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes and plasmas. It is a linearized Poisson–Boltzmann model, which assumes an extremely simplified model of electrolyte solution but nevertheless gave accurate predictions of mean activity coefficients for ions in dilute solution. The Debye–Hückel equation provides a starting point for modern treatments of non-ideality of electrolyte solutions.

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have r^{-7} dependence, and for practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law, which has r^{-2} dependence. Consequently, the behaviour of an electrolyte solution deviates considerably from that an ideal solution. Indeed, this is why we utilize the activity of the individual components and not the concentration to calculate deviations from ideal behavior. In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, $\lambda\pm$, and could explain how the behaviour of ions in solution contribute to this constant.

The increase of equivalent conductance with dilution in case of weak electrolytes can be easily explained on the basis of Arrhenius theory which suggests that the conductance increases because the dissociation of the weak electrolyte increases with dilution. However, incase of strong electrolytes, as they are almost completely dissociated even at moderate concentration the increase in equivalent conductance with dilution must be due to some other factors.

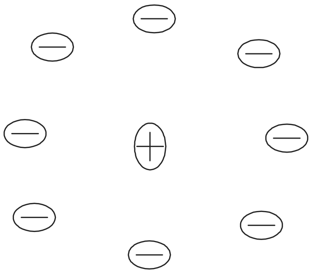
Debye - Huckel theory explains the increase in conductance of strong electrolytes on dilution based upon the following two effects:

Relaxation (or) Asymmetry Effect

In the solution, each ion is surrounded by an ionic atmosphere of opposite charge. So long as no electric field is applied, the ionic atmosphere remains symmetrical ,around the central ion. However, when a current is passed through the solution, the central ion moves oppositely charged electrode. As it is moving out of the ionic atmosphere, it has to rebuild an ionic atmosphere of opposite charge around around it and the old ionic atmosphere dies out. However, the destruction of the old ionic atmosphere and the formation of the new ionic atmosphere do not take place instantaneously. There is some time lag called time of relaxation between the destruction of the old and the formation of new ionic atmosphere. During this time, the old ionic atmosphere pulls the moving ion backward and hence retards the motion (Refer Figure 2.7) Hence, this effect is called relaxation effect.

Alternatively, it may be argued that as the central ion moves the symmetry ionic atmosphere is lost, more ions of the ionic atmosphere are left behind than are present on the front. The excess of ions of the ionic atmosphere present the moving ion drag the ion backward retard its motion.

Thus the effect arises because of the ionic atmosphere of the moving ion and hence is also called asymmetry effect.



Symmetric Ionic Atmosphere Around a +ve Ion

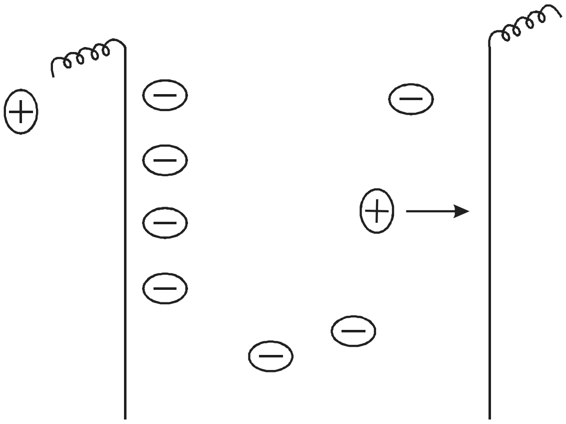


Fig. 2.7 *Ionic Atmosphere becoming Asymmetry when Central Ion Moves*

NOTES

Electrophoretic Effect

When EMF is applied, the central ion moves in one direction and the oppositely charged ionic atmosphere moves in the opposite direction. As this ionic atmosphere, moves the solvent molecules associated with also move. Thus the flow of ionic atmosphere moves in the opposite direction. As this ionic atmosphere moves the solvent molecules associated with it also move. Thus the flow of ionic atmosphere and that of the solvent molecules attached to its takes place in a direction opposite to that of the movement of the central ion. In other words, the central ion is moving against strem. Hence, motion of the ions is retarded. This effect is called electrophorectic effect. Based upon the above ideas, Debye Huckel derived a mathematical expression for the variation of eqivalent conductance with concentration. This equation further improved by on sagar and the now the equation is known as based on above theory.

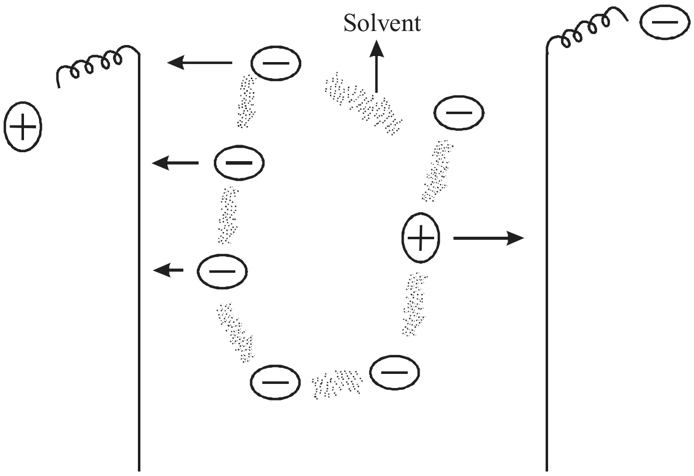


Fig. 2.8 *Movement of a Central Ion in a Direction Opposite to that of the Ionic Atmosphere and the Solvent Molecules*

For uni-valent electrolyte

$$\Lambda_C = \Lambda_0 = \left[\frac{[82.4}{(DT)\,{}^1\!/\!_2\,\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda_0 \right] \sqrt{C}$$

Λ_C = Equivalent conductance at concentration C.

Λ_0 = Equivalent conductance at infinite dilution

D = Dielectric constant of the medium

η = Viscosity of the medium

T = Temperature of the solution in degrees absolute

C = Concentration of the solution in moles/liter

As D and η are constants for a particular solvent therefore, constant temperature, the above equation can be written in the form

$\Lambda_C = \Lambda_0 - (A + B\ \Lambda\ 0)\sqrt{C}$

Where A and B are constants for a particular solvent at a particular temperature.

2.4.1 Activity and Activity Efficient

It may be pointed out that since the absolute value of free energy or chemical potential is not known, it is not possible to evaluate μ_i^* of a substance. This difficulty has been over come by referring all free energy or chemical potential measurements for any given substance to a standard reference point.

Let μ_i be the chemical potential of a substance *i* in pure state and let f_i be its fugacity Equation (21) may then be put

$$\mu_i = \mu_i^* + RT\ Inf_i \qquad ...(21)$$

$$\mu_i^0 = \mu_i^* + RT\ Inf_i^0 \qquad ...(22)$$

Let μ_i be the chemical potential of the same substance in some other state. Then

$$\mu_i = \mu_i^* + RT\ Inf_i$$

The difference between chemical potential of a substance in any state and that in the pure state is given by

$$\mu_i - \mu_i^0 = RT\ In\ (f_i/f_i^0)$$

Or

$$\mu_i - \mu_i^0 + RT\ In\ (f_i/f_i^0)$$

We may introduce here a new term, activity, *a* and define it as

$$a = f/f^0$$

Or, for a substance, *i* as

$$a = f_i/f_i^0$$

Activity of a substance in any given state is thus defined as the ratio of the fugaciy of the substance in that state to the fugacity of the same substant in the pure state.

Equation (22), therefore, reduces to

$$\mu_i = \mu_i^0 + RTln\ a$$

Let a system consisting of 1 mole of a substance change from a state in which its chemical potential (or free energy, both being identical since we are dealing with one mole of the substance) is μ_1, to another state in which its chemical potential is μ_2. The change in chemical potential, $\delta\mu$, is then given by

$$\delta\mu = \mu_2 - \mu_1 = (\mu^0 + RTln\ a_2) - (\mu^0 + RTln\ \mathrm{a}_1)$$

Or

$$\delta\mu = RTln\ (a_2/a_1) = \delta G$$

Comparing the above equation with that for an ideal gas, viz.

$$\delta G = \delta\mu = RTIn(P_2/P_1)$$

It is evident that in the case of real gases, activity replaces pressure. Thus, activity of a gas, like fugacity, serves as a thermodynamic counterpart of gas pressure.

As, we shall see later, in the case of solution it serves as a counterpart of concentration of the solute in the given solution.

Activities and concentrations can both be used to calculate equilibrium constants and reaction rates. However, most of the time we use concentration even though activity is also a measure of composition, similar to concentration. It is satisfactory to use concentration for diluted solutions, but when you are dealing with more concentrated solutions, the difference in the observed concentration and the calculated concentration in equilibrium increases.

An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances. In an ideal mixture, the microscopic interactions between each pair of chemical species are the same (or macroscopically equivalent, the enthalpy change of solution and volume variation in mixing is zero) and, as a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present, such as Raoult's law. Deviations from ideality are accommodated by modifying the concentration by an activity coefficient. Analogously, expressions involving gases can be adjusted for non-ideality by scaling partial pressures by a fugacity coefficient.

The concept of activity coefficient is closely linked to that of activity in chemistry. The chemical potential, μ_B, of a substance B in an ideal mixture of liquids or an ideal solution is given by,

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{\ominus} + RT \ln x_{\mathrm{B}}$$

Where $\mu_{\mathrm{B}}^{\ominus}$ is considered as the chemical potential of a pure substance B and x_B is the mole fraction of the substance in the mixture.

This is generalised to include non-ideal behaviour by writing,

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{\ominus} + RT \ln a_{\mathrm{B}}$$

when a_B is the activity of the substance in the mixture with,

$$a_{\mathrm{B}} = x_{\mathrm{B}} \gamma_{\mathrm{B}}$$

where γ_B is the **activity coefficient**, which may itself depend on x_B. As γ_B approaches 1, the substance behaves as if it were ideal. For instance, if γ_B H" 1, then Raoult's law is accurate. For $\gamma_B > 1$ and $\gamma_B < 1$, substance B shows positive and negative deviation from Raoult's law, respectively. A positive deviation implies that substance B is more volatile.

In many cases, as x_B goes to zero, the activity coefficient of substance B approaches a constant; this relationship is Henry's law for the solvent. These relationships are related to each other through the Gibbs–Duhem equation. In general activity, coefficients are dimensionless.

Ionic Solutions

For solution of substances which ionize in solution the activity coefficients of the cation and anion cannot be experimentally determined independently of each other because solution properties depend on both ions. Single **ion activity coefficients** must be linked to the activity coefficient of the dissolved electrolyte as if undissociated. In this case a mean stoichiometric activity coefficient of the dissolved electrolyte, γ±, is used. It is called stoichiometric because it expresses both the deviation from the ideality of the solution and the incomplete ionic dissociation of the ionic compound which occurs especially with the increase of its concentration.

For a 1:1 electrolyte, such as NaCl it is given by the following:

$$\gamma_\pm = \sqrt{\gamma_+\gamma_-}$$

where γ+ and γ” are the activity coefficients of the cation and anion, respectively. More generally, the mean activity coefficient of a compound of formula A_pB_q is given by,

$$\gamma_\pm = \sqrt[p+q]{\gamma_A^p\gamma_B^q}$$

Single-ion activity coefficients can be calculated theoretically, for example by using the Debye–Hückel equation. The theoretical equation can be tested by combining the calculated single-ion activity coefficients to give mean values which can be compared to experimental values.

Check Your Progress

1. State the first law of thermodynamic.
2. What do you understand the zeroth law of thermodynamic?
3. Define the entropy.
4. Give the unit of entropy.
5. Define free energy.
6. What do you understand by partial molar free energy?
7. Define the specific heat.
8. What is phase?
9. Define the fugacity.
10. What do you understand by Debye Hückel equation?
11. What is an activity of substance?
12. What do you understand by single-ion activity coefficients?

2.5 PHASE EQUILIBRIA

The phase rule is a generalization which seems to explain the equilibrium existing between the heterogeneous system and was theoretically deduced by Willard Gibbs in 1876. Mathematically, it may be stated as

$$F + P = C + 2$$

where F is the number of degrees of freedom, P is the number of phases and C is the number of components. This rule does not involve any assumptions as to the nature of matter and is valid provided the equilibrium between any number of phases is affected only by temperature, pressure and concentration and not by any other force, such as gravitational, electrical or magnetic. This rule, if properly applied, has no exceptions.

2.5.1 Definitions of Various Terms Involved in the Phase Rule

Phase. A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces.

Consider, for example, the system in which ice, liquid water and water vapour are existing together. Hence, each form constitutes a separate phase and is separated from other forms by definite bounding surfaces. However, each crystalline form of ice constitutes a separate phase since it is clearly marked off from the other forms. In general, every solid in a system is invariably regarded as an individual phase except in a solid solution (homogeneous) which will constitute a single phase no matter how many chemical compounds it may contain. Thus, Mohr's Salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ constitute a single phase although it consists of $FeSO_4$, $(NH_4)_2\ SO_4$ and H_2O. The same applies to a liquid solution. If two or any number of liquids are completely miscible with each other and form one liquid layer, it will constitute only one phase. If the two liquids are immiscible and there are two layers, as with benzene and water, there are two phases separated by a definite boundary. Similarly, if there are three immiscible liquids, there will be three phases. A gaseous system always constitutes a single phase, no matter it may consist of any number of gases because gases are always miscible and form homogeneous mixture.

Component. *The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in the form of a chemical equation.*

Consider the water system which can have three phases: ice, liquid water and water vapour in equilibrium. The composition of each of the three phases can be expressed in terms of the component H_2O. Hence, this is a one component system. It is true that molecular complexity of water is different in the three phases but the number of components is not affected. Similarly, sulphur system is also one component system although sulphur occurs in various different forms *viz*., rhombic sulphur, monoclinic sulphur, liquid and vapour sulphur (each form can be expressed in terms of only one component *i.e.,* Sulphur). The same applies to acetic acid which consists entirely of double molecules in the solid state, to a great extent in the liquid and partially in the vapour; the composition of each phase can however be expressed in terms of CH_3COOH and this is the only component.

Consider now the system represented by the equilibrium.

$$CaCO_3(s) = CaO(s) + CO_2(g)$$

In this system, there are three phases, *viz*., solid $CaCO_3$, solid CaO and gaseous CO_2 as two components. These two components may be chosen as any two of the substances involved in the equilibrium. If CaO and CO_2 are taken, then the compositions of various phases can be expressed as follows:

$$CaCO_3 : CaO + CO_2$$
$$CaO : CaO + 0CO_2$$
$$CO_2 : 0CaO + CO_2$$

NOTES

The composition of the three phases could be expressed equally by taking $CaCO_3$ and CaO or $CaCO_3$ and CO_2 as the components. Thus, we find that the smallest number of constituents by means of which the composition of each phase can be expressed is two and hence, this is a two-component system.

In the same way, it can be shown that the dissociation of any carbonate, oxide or similar compounds involves two components; the same is true for salt hydrate equilibria *e.g.,*

$$CuSO_45H_2O(s) \rightleftharpoons CuSO_4.3H_2O + 2H_2O$$

where the simplest components are evidently $CuSO_4$ and $H_2O(g)$.

Similarly for the equilibrium,

$$Fe(s) + H_2O(g) = FeO(s) + H_2(g)$$

it can be shown that it consists of three components.

Similarly, solution of sugar in water is a two component system because composition of both sugar and water must be specified to describe the system completely.

For chemically reactive systems, the number of components (C) is determined by using the reaction: C = S–R where *S* the number of chemical species present in the system and *R* is the number of independent chemical reactions which the various species can undergo. If ions are also present in the system, the condition of electroneutrality should also be considered and thus, for such, cases, the equation is modified as : C = S–(R + 1)

Consider the system KCl – NaCl – H_2O.

For this system, there are six species – KCl, NaCl, K^+, Cl^-, Na^+ and H_2O. Dissociation of water is neglected, the number of independent reactions are two:

$$NaCl \rightleftharpoons Na^+ + Cl^- \text{ and } KCl \rightleftharpoons K^+ + Cl^-$$

and the condition of electroneutrality is 1.

Thus $C = S - (R + 1) = 6 - (3) = 3$

Hence, the system KCl – NaCl – H_2O is a three component system.

The system NaCl – NaBr – KCl – H_2O is a four component system as shown below:

The number of species = 9 (KCl, KBr, NaBr, NaCl, Na^+, K^+, Cl^-, Br^-, H_2O) the number of independent reactions = 4

Thus $C = 9 - (4 + 1) = 4.$

In the same manner, Na_2SO_4 – H_2O system can be shown to be a two component systems. Thus, the summary of the above discussion is

For Nonreactive Systems

The number of components= Number of chemical species

For Reactive Systems

The number of components= (Number of chemical species – number of independent chemical reactions) – (restriction due to condition of electroneutrality)

Degree of freedom or variance: *The number of degrees of freedom or variance of a system is the number of variable factors such as temperature, pressure or concentration which must be specified in order to define the system completely.*

Consider any system having one phase only, say gaseous phase of water. In order to define completely the state of the system, it is necessary to specify both temperature and pressure. The system, therefore, has two degrees of freedom or it is said to be *bivariant*. When two phases are in equilibrium, say ice and water, only temperature or pressure need be arbitrarily fixed to define the system completely. This system has one degree of freedom or it is *univariant*. If a system has three phases in equilibrium, such as in the water system in which ice, water and water vapour are together present at triple point, then there are no degrees of freedom. The reason for this lies in the fact that three phases can co-exist in equilibrium only at a particular temperature and pressure which are thus automatically fixed. This type of system is said to be *invariant*.

2.5.2 Three-Component Systems

According to phase rule, the degree of freedom in a system of three components is given by:

$$F = C - P + 2$$

$$F = 3 - P + 2 = 5 - P$$

Since the minimum number of phases that can exist in any system is one, the maximum number of freedom is four. Hence, in order to completely define such a system, four variables are required namely, temperature, pressure and concentration of two of the three components. This will require a three-dimensional diagram for a complete graphical representation of these systems which is not possible. For this reason, it is customary to represent ternary systems at constant temperature and at constant pressure. By fixing the temperature and pressure, the number of degrees of freedom is reduced by two, so that $F = 3 - P$ and a system, has, at most, a variance of two. When temperature and pressure are constant, the remaining variables are concentration variables X_1, X_2 and X_3 of the three components. These concentration variables are related to each other by the equation $X_1 + X_2 + X_3 = 1$ and can be represented on a planner diagram. If we know any two of them, the value of third can be found.

Graphical representation of ternary system. Of the various method for plotting two dimensional equilibrium diagrams for ternary systems, the method of Stocks and Roozeboom is very popular and most generally employed. In this method, the variation is concentration of the three component mixtures at constant temperature and pressure are expressed by means of an equilateral triangle such as that shown in Fig. 2.9.

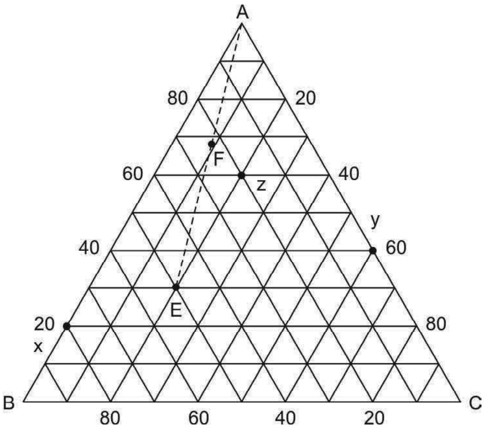


Fig. 2.9 Graphical Representation of Ternary Systems

Each apex of the triangle presents pure component *i.e.,* 100 per cent of the component with which it is designated. Each side is divided into 10 equal parts and the lines parallel to *BC*, *CA* and *AB* are drawn. Each of the lines parallel to *BC, CA* and *AB* are drawn. Each of the lines parallel to *BC, CA* and *AB* represent various percentages of *A, B* and *C* respectively. Any point on any side of the triangle refers to a binary system and two-component gives various proportions of constituents in a two-component system while any point within the triangle represents a ternary system and gives various proportions of any mixture composed of *A*, *B* and *C*. Thus, a point *X* on the line *AB* represents a two-component systems of 20 per cent *A* and 80 per cent *B*. Similarly, a point *Y* on the line *AC* represents a two-component system of 40 per cent *A* and 60 per cent *C.* Any point *Z* within the triangle represents a ternary system 20 per cent *C*, 20 per cent *B* and 60 per cent *A*. Another important property of this diagram is; 'Any point *F* on the line *AE* represents a mixture that will contain *A* and *F* in the length ratios *EF*: *AF* by weight, if weight percentage is plotted or by moles, if mole percentage is plotted.'

Three-component liquid systems showing partial miscibility. Systems composed of three liquids showing partial miscibility may belong to any one of the following three categories:

Type I :	Formation of one pair of partially miscible liquids.
Type II :	Formation of two pairs of partially miscible liquids.
Type III :	Formation of three pairs of partially miscible liquids.

Type I. Formation of One Pair of Partially Miscible Liquids

Consider the behaviour of a three-component liquid system *A-B-C* in which the pairs *A-B* and *A-C* air completely miscible while the pair *B-C* is partially miscible in each other at a given temperature and pressure. On mixing relative amounts of *B* and *C* and thoroughly shaking together, two layers will be obtained, one composed of a solution of *C* in *B*, the other of *B* in *C*. Let the compositions of the two layers be represented by the points *a* and *b* respectively and the overall composition of the system by *c*. When a small amount of *A* is added to the two-layer mixture, it will distribute itself between the two liquid layers and thereby increase the miscibility of *B* and *C*. The increase in miscibility brought about by adding *A* depends upon the amount of *A* added and on the amounts of *B* and *C* present. When enough *A* is added to the system, the composition of the two layers changes to a_1 and b_1 and the overall composition moves along the line *Ac* to the point c_1.

The straight line a_1b_1 through c_1 connects the compositions of the two layers in equilibrium, and is called a *tie-line*. In a similar manner continued addition of *A* moves the compositions to a_2b_2 and a_3b_3 and the overall composition moves to c_2 and c_3 along the dashed line. *C*-rich layer grows in size while *B* rich layer diminishes. Finally, at point b_4, only a trace of *B*-rich layer remains and thereafter, only a single solution is obtained.

Since the tie-lines are not parallel, the point at which the compositions of the two layers becomes identical and the two solutions coalesce into a single liquid phase does not lie at the top of the curve drawn through the series of miscibility points but off to one side at the point *D*. Point *D* is known either as *isothermal critical point* of the system of the *plait point* and can be obtained only by adding *A* to a single mixture of *B* and *C*, with overall composition *o*. See Fig. 2.10.

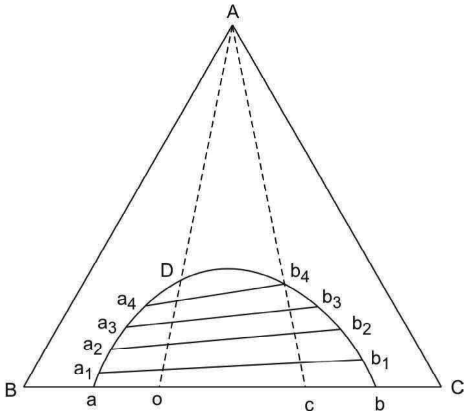


Fig. 2.10 *System with One Partially Miscible Pair*

It follows from the above discussion that any mixture of *A, B* and *C* of overall compositions falling within the dome-shaped area will yield two liquid layers of composition of the mixture. On the other hand, any mixture in the region outside the dome-shaped area will represent a homogeneous solution of the three liquid. The curve *aDb* is frequently called a *binodal curve.*

Examples. Systems such as acetic acid-chloroform-water and acetone-water-phenol belong to this category.

Type II. Formation of Two Pairs of Partially Miscible Liquids

Consider a system of three liquid *A-B-C* in which the pairs *A-B* and *A-C* are partially miscible, while the part *B-C* is completely miscible. Such a system will exhibit two binodal curves as shown in Fig. 2.11 (a).

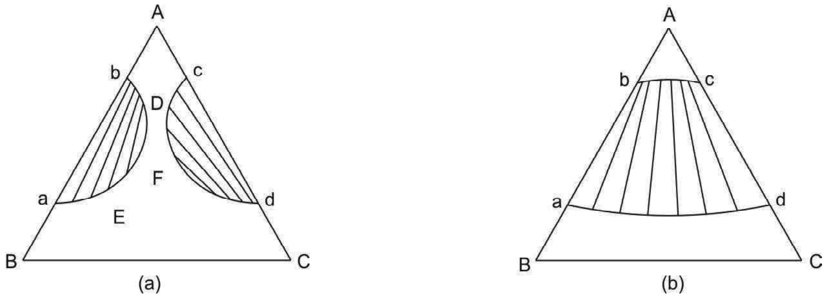


Fig. 2.11 *System with two partially miscible pairs*

The binodal curve *aDb* represents the range of compositions in which mixture of *A* and *B* contains *C* are partially miscible while the binodal curve *cFd* gives the range of compositions in which mixtures of *A* and *C* containing *B* are partially miscible. Any mixture of overall composition outside these curves will be completely miscible. The two point *D* and *F* are the respective plait points of the two heterogeneous systems. The tie-lines in the two curves show the compositions of the various layers in equilibrium.

In certain cases, it has been observed that the two binodal curves in Fig. 11.28 (a) may intersect each other on lowering the temperature. This will lead to the formation of the 'band' *abcd* across the two phase regions in the diagram as shown in Fig. 11.28(a). *ad* and *bc* give the compositions of the two layers respectively and the indicated tie-lines join various solutions in equilibrium.

Examples. System, such as succinic nitrile-water-ethyl alcohol between 18.5°C and 31°C belongs to type showing no band formation while systems, such as water-phenol-aniline and water-ethyl acetate-*n* butyl alcohol shows the formation of band.

Type III. Formation of Three Pairs of Partially Miscible Liquids

Consider a system in which all the three liquids are partially miscible. Such a system with exhibit three binodal curves as shown in Fig. 11.29(a).

Here again the dome-shaped area represent the regions of two-phase liquid while any point outside these areas represents the existence of only a single phase.

At a lower temperature, the three binodal curves intersect and the diagram takes on the appearance of Fig. 11.29 (b). In this diagram, a mixture having a composition in any area designated as I will represent a single phase region. On the other hand, area marked 2 and 3 represent two-phase region and three-phase region respectively.

According to phase rule, when the three phases are in equilibrium at constant temperature and pressure, the degree of freedom is zero. This means that the compositions of the three layers must be fixed and independent of the overall composition in the area marked 3. Points *X, Y* and *Z* represent constant compositions for the three liquid layers in equilibrium.

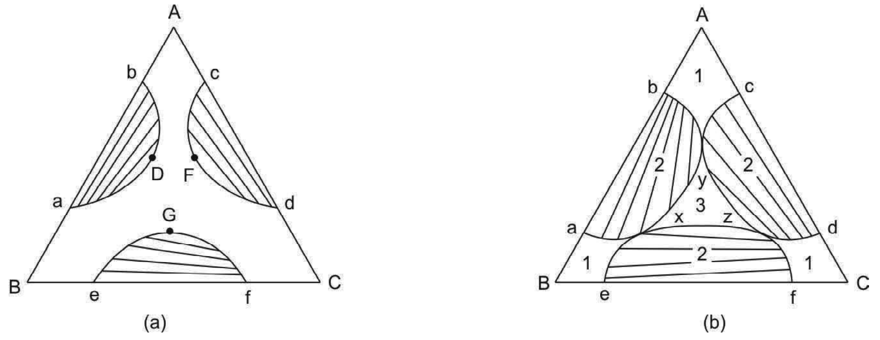


Fig. 2.12 *Liquid systems with three partially miscible pairs*

Examples. System, such as succinic nitrile-water-ether exhibits the behaviour corresponding to Fig. 2.12(a) at higher temperature while at lower temperature, exhibits the behaviour corresponding to Fig. 2.12(b).

Systems Composed of Two Solids and a Liquid

Systems composed of two solids and a liquid may belong to any one of the following five categories depending on the behaviour of the solid phases:

Type I. Crystallization of pure components only.

Type II. Formation of binary compounds.

Type III. Formation of ternary compounds.

Type IV. Formation of complete series of solid solutions.

Type V. Partial miscibility of solid phases.

In all these types, water will be taken as the liquid because water has by far been regarded the most important crystallization medium.

Type I. Crystallization of Pure Components Only. The isothermal equilibrium diagram for a system composed of water and two solid components *B* and *C* and where the crystallization of pure components occurs is shown in Fig. 11.30.

In this diagram, point *D* represents the saturated solution of *B* in water in the absence of *C*. Points between *B* and *D* represent various amounts of solid *B* in equilibrium with saturated solution of *D*. Points between *D* and H_2O represents the unsaturated solution of *B*.

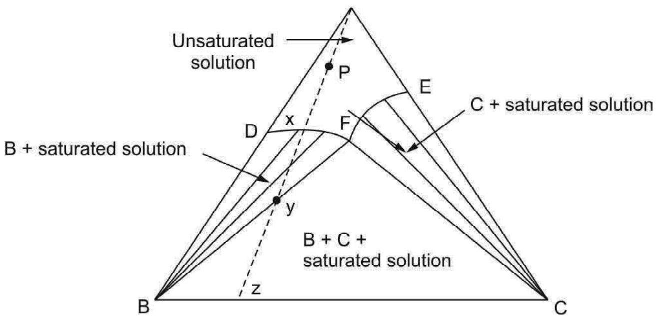


Fig. 2.13 *Two salts and water system in which the crystallization of pure components occur*

Similarly point *E* represents the saturated solution of *C* in water in the absence of *B*. Points between *C* and *E* represent various amounts of solid *C* in equilibrium with the saturated solution *E* and points between *E* and H_2O represent the unsaturated solution of *C*. When *C* is added to the solution saturated with *B*, the solubility of the latter changes along the line *DF*. Similarly, addition of *B* to the solution saturated with *C* changes the solubility curve of *C* in water containing *B*. At *F*, the point where the two solubility curves intersect, the solution becomes saturated with respect to both *B* and *C*. At this point, since three phases are in equilibrium, the degree of freedom is zero. Hence, *F* is called the *isothermal invariant point.* The tie-lines in the diagram connect the concentrations of the saturated solutions with the solid phase in equilibrium with them.

The manner in which such a diagram is used for crystallization is illustrated as follows:

On evaporating isothermally an unsaturated solution represented by *P*, the system moves along the line *PXYZ* which is drawn through apex H_2O and the point *P*. At *X, B* begins to crystallize and the composition of the solution changes along the line *XF*. At point *Y*, the composition of the solution is *F* and *C* also begins to crystallize. If the process of evaporation is continued, both *B* and *C* keep on depositing until the point *Z* is reached where the solution disappears completely.

This type of behaviour is exhibited by the systems containing two salts with a common ion and water such as $NH_4Cl—(NH_4)_2SO_4—H_2O$, $NH_2Cl—NH_4NO_3—H_2O$ and $NaCl—NaNO_3—H_3O$, etc.

The Method of Wet Residues

Experimental methods employed for the determination of equilibrium diagrams of three-component systems containing solid and liquid phases are simpler than those employed for two component systems. In the method under discussion, mixtures of various proportions of the solid components with water are prepared and agitated in a thermostat at a temperature slightly higher than that at which the system is to be studied. The solution is then allowed to attain equilibrium at the experimental temperature. The liquid phase is then separated from the wet crystals, and both are weighted and analyzed for two of the components. In this way, the compositions for saturated solution and the wet residue are obtained. The results for a number of solutions are then plotted on a triangular diagram in the usual manner.

Figure 2.14 shows a series of points obtained in this manner. In the diagram, S_1, S_2, etc. represent compositions of the saturated solutions while R_1R_1, etc., represent compositions of the corresponding wet residues. In order to ascertain the nature of the solid phases in equilibrium with the various solutions and present in the residue, we employ a graphical scheme known as the *Schreinemakers method of wet residues.* According to this scheme, various tie lines drawn through any corresponding pair of *R* and *S* points must intersect, on extension past *R*, at a common point which is the composition of the solid present. It follows from this reasoning that in this system, *B* is the solid phase for all solutions between *D* and *F* and *C* is the solid phase for those between *F* and *E*. Some tie lines drawn in such a manner cut the side *BC* at various points *H, I, J, K* and *L*. This means that the side saturated solution represented by F is in equilibrium with various proportions of B and C.

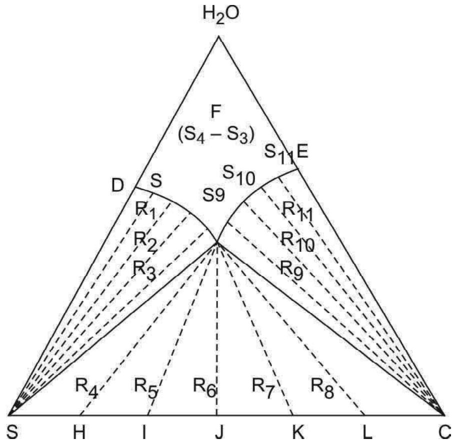


Fig. 2.14 The method of wet residue

Type II. Formation of Binary Compounds. When the two salts react to form a compound, a double salt of the general formula $BxCy$, the equilibrium diagram is:

In this diagram, point D represents the composition of the salt and line FG represents the compositions of solution saturated with this compound. At point F, the solution is saturated with B and D, while at point G, the solution is saturated with C and D. Points F and G are known as isothermal invariant points.

In order to determine the stability of the double salt in presence of water, we locate the position of the point D along BC. If point D lies in between I and J, the salt is said to be congruently saturating as it is possible to prepare saturated solution of salt by adding water to it. This is indicated by the line drawn through the apex H_2O and joining point D. On the other hand, if the point D lies either on the left of I or right J, the salt formed is said to be incongruently saturating as this case it will not be possible to prepare a saturated solution of the salt by adding water to it, see Fig. 2.15.

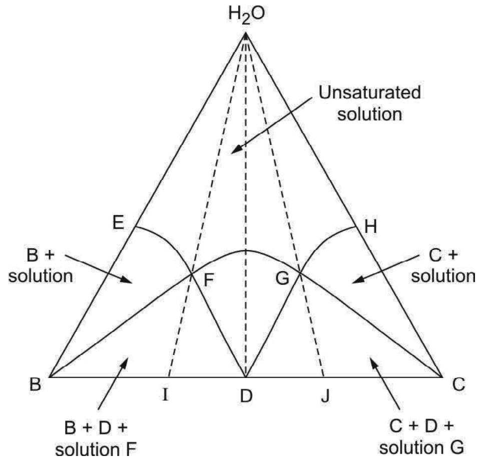


Fig. 2.15 Formation of double salt

The system NH_4NO_3—$AgNO_3$—H_2O shows the formation of the congruently saturating double salt $NH_4NH_3.AgNO_3$ at 30°C while the system KNO_3—$AgNO_3$—H_2O forms incongruently saturating double salt KNO_3. $AgNO_3$ at the same temperature.

If one of the salts, say *B*, forms a hydrate, then the system will have the appearance of phase diagram shown in Fig. 2.16.

In this diagram, point *D* represents the composition of the hydrate formed by *B* point *E* represents the solubility of hydrate in pure water at the given temperature, while line *EF* represents the solubility of the hydrate in solution containing *C*. Similarly, line *GF* represents the solubility of *C* in solutions containing hydrate. With in area *DEF*, the hydrate *D* exists in equilibrium with saturated solution given by the line *EF* while the area *CFG* contains *C* in equilibrium with saturated solutions along the line *GF*. At *F*, the isothermal invariant point, the solution becomes saturated with respect to both *D* and *C*. Within the area *DEC*, solids *D* and *C* coexist in equilibrium with saturated solution whereas the area *BDC* consists exclusively of the three solids *D, B* and *C*.

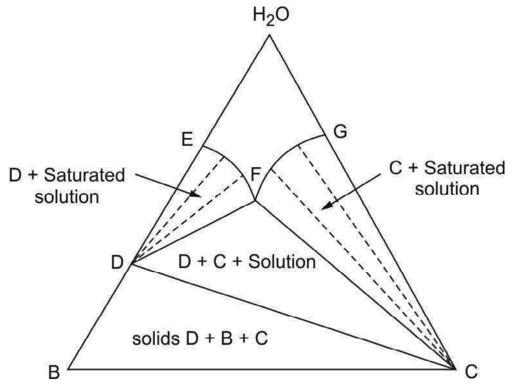


Fig. 2.16 *Formation of a hydrate*

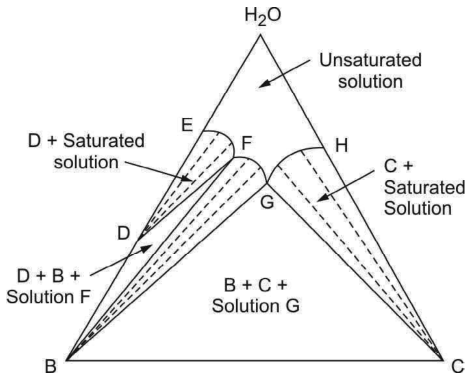


Fig. 2.17 *Formation of hydrate and pure components*

The system Na_2SO_4—NaCl—H_2O at 15°C gives the phase diagram shown above. The hydrate $Na_2SO_4.10H_2O$ is formed.

Under certain conditions, usually at higher temperature, the anhydrous salt may make its appearance along with the hydrate of the salt. The phase diagram, then, will have the appearance of Fig. 2.17.

In this diagram, *EF* is the saturation curve for the hydrate, *FG* of the anhydrous salt *B* and GH for *C*. *F* and *G* represent two invariant points. The various components present in any region are indicated in the diagram.

The system Na_2SO_4—NaCl—H_2O at 25°C exhibits this type of behaviour in which both Na_2SO_4. $10H_2O$ and Na_2SO_4 appear as saturating phases.

A system in which both solid components form a hydrate, will have the phase diagram showing in Fig. 2.18.

Here, points *D* and *E* represent the compositions of the hydrates formed by *B* and *C* respectively. *G* is this thermal invariant point. Within area *CDE*, solids *D*, *B* and *C* exist together. While in the area *BDC*, solids *D*, *B* and *C* exist together.

$MgCl_2$—$CaCl_2$—H_2O at 0°C is an example of such type of system in which the hydrates $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$ are formed.

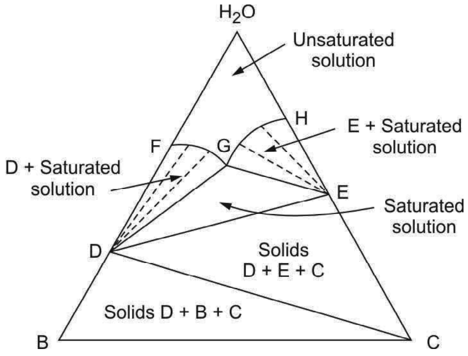


Fig. 2.18 *Formation of two hydrates*

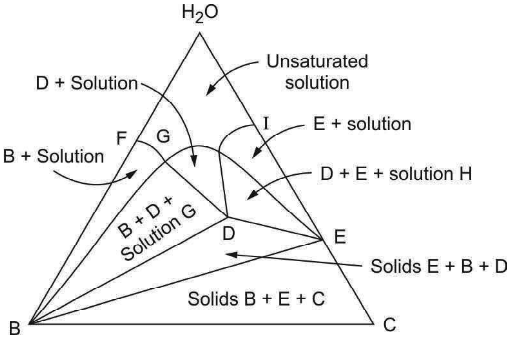


Fig. 2.19 *Formation of ternary compounds*

Type III. Formation of Ternary Compounds. In some cases, ternary compounds involving all the three components are formed. The equilibrium diagram for such a system is shown in Fig. 2.19.

In this diagram, point *E* represents the composition of binary compound (hydrate of *C*) and point *D* represents the composition of ternary compound formed by *B, E* and water. *G* and *H* are two isothermal invariant points. Various phases present in different regions are indicated in the diagrams.

In this type, the ternary compounds is of incongruently saturating type as it is decomposed when water is added. The system $CaCl_2$—$MgCl_2$—H_2O at 25°C is an example of this type which shows the formation of incongruently saturating ternary compounds $CaCl_2$. $MgCl_2$, $12H_2O$. On the other hand, alums, such as $X_2SO_4.Y_2(SO_4)_3.24H_2O$ where X = univalent metal and Y = trivalent metal belong to the class of congruently saturating type and are stable in presence of water.

Type IV. Formation of Solid Solutions: When two solid components *B* and *C* are completely soluble in each other in the solid phase, they will form a series of solid solutions ranging in composition from pure *B* to pure *C* in water. Such a system will exhibit no invariant point as there will be only two phases *viz*., solid solution and liquid saturated solution. The equilibrium diagram is shown in Fig. 2.20.

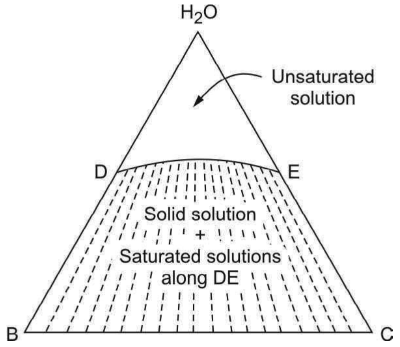


Fig. 2.20 *Formation of solid solutions*

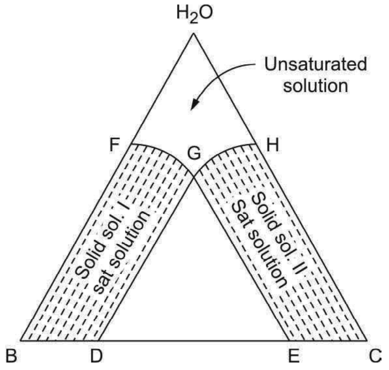


Fig. 2.21 *Partial miscibility of solid phases*

In this diagram, line *DE* represents the compositions of saturated solutions in equilibrium with solid solutions of *B* and *C* of compositions given by the tie lines. In the area above *DE* only unsaturated solutions can exist. Below *DE*, there are two phases—solid solutions in equilibrium with saturated solutions along *DE*.

Type V. Partial Miscibility of Solid Phases: The equilibrium diagram for such a system in which two solid phases are partially miscible is as shown in Fig. 2.21

In this type, two sets of solid solutions are formed—one of *C* in *B* lying between points *B* and *D* and another of *B* in *C* lying between points *E* and *C*. Line *FG* is the saturation solubility curve of solid solutions of *C* in *B* (solid solution *I*) while the line

GH is the saturation solubility curve of *B* in *C* (solid solution *II*). Between points *D* and *E*, mixture of *B* and *C* will give two solid phases one of which has the composition *D* and the other *E*. *G* is the isothermal non variant point. Any point lying within the area *GDE* will give composition of solution in equilibrium with two solid solutions *D* and *E*.

Salting Out

The phenomena in which the solubility of a non-electrolyte in water is decreased by the addition of an electrolyte is known as *salting-out*. This if some salt is added to a system comprising completely miscible pair of organic liquid and water, two layers are separated—one rich in the organic liquid, the other rich in water. Consider the ternary diagram for K_2CO_3—H_2O—CH_3OH which is typical of the system salt—water—alcohol. See Fig. 11.39.

In this diagram, region *Bab* represents K_2CO_3 in equilibrium with water-rich saturated solution; while region *Bed* represents K_2CO_3 in equilibrium with alcohol rich saturated solution, *bcd* represents region of two conjugate liquids (*b*—water rich and *d*—alcohol rich) joined by tie line and region *Bbd* represents K_2CO_3 in equilibrium with conjugate liquids *b* and *d*. Suppose that solid K_2CO_3 is added to a mixture of water and alcohol of composition *x*. Salt will be dissolved in the liquid and the system will move along the line *xyzB*. At *y*, two layers are separated; at *z*, further dissolution of K_2CO_3 stops so that solid K_2CO_3 and liquid *b* and *d* coexist. The liquid represented by point *d* is the alcohol rich layer and can separated from *b*, the water rich layer.

When water is added to an unsaturated solution of K_2CO_3 in alcohol of composition *x*′, the system will move along the line *x*′*y*′*z*′, K_2CO_3 will precipitate at *y*′ and redissolve at *z*′ with further addition of water.

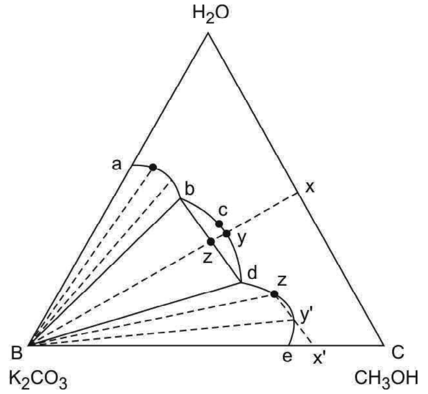


Fig. 2.22 *Salting out effect*

2.6 CONCEPT OF DISTRIBUTION IN STATISTICAL THERMODYNAMIC

The various methods of statistical mechanics are applied to discuss some average or most probable properties of large assemblies of electrons, atoms, molecules, etc. Before the advent of quantum mechanics, Maxwell, Boltzmann, Gibbs etc., applied statistical methods with the help of classical physics. These methods are collectively known as Classical Statistics or Maxwell-Boltzmann (MB) Statistics. These statistics were proved to be successful in explaining pressure, temperature, etc. of gaseous systems. But these could not explain some experimental results like the energy distribution in case of black-body radiation, specific heat at low temperature, etc. For explaining such phenomena Satyen Bose, Albert Einstein, Enrico Fermi, Paul A. Dirac had made use of some new statistic with the help of newly discovered quantum theories. The new statistics are known as Quantum Statistics and can be divided into following two categories:

(*i*) Bose-Einstein (BE) statistics

(*ii*) Fermi-Dirac (FD) statistics

We will discuss the various interesting features of these three (MB, BE, FD) statistics one by one in the following subsections.

2.6.1 Maxwell-Boltzmann (MB) Statistics

The basis postulates of MB statistics are:

(*i*) The associated particles are distinguishable.

(*ii*) Each energy state can contain any number of praticles.

(*iii*) Total number of particles in the entire system is constant.

(*iv*) Total energy of all the particles in the entire system is constant.

(*v*) Particles are spinless.

Examples: Gas molecules at high temperature and low pressure.

Maxwell-Boltzmann Distribution Law

Consider a system composed of N distinguishable, non-interacting particles. Let out of these N particles $N_1, N_2, ..., N_i$ particles are to be distributed in energy levels $E_1, E_2, ..., E_i$ respectively and these energy levels have $g_1, g_2, ..., g_i$, number of quantum states correspondingly. Since the total energy E and total number of particles N are constant for the system, we can write

$$\sum_i N_i E_i = E \qquad ...(23)$$

$$\sum_i N_i = N \qquad ...(24)$$

The number of ways in which the groups of particles $N_1, N_2, ..., N_i$ could be chosen from N particles is

$$W_1 = \frac{N!}{N_1!N_2!...N_i!} = \frac{N!}{\prod_i^n N_i!} \qquad ...(25)$$

where Π denotes the product.

Now, N_i particles can be distributed in g_i state in $(g_i)N_i$ ways. Considering all the values of i, total number of arrangement would be

$$W_2 = \prod_i^n (g_i)N_i \qquad ...(26)$$

Therefore, the total number of ways W by which all the N particles could be distributed among the quantum states is

NOTES

$$W = W_1 W_2 = \frac{N!}{\prod_i^n N_i!} \prod_i^n (g_i) N_i \qquad ...(27)$$

which is the Maxwell-Boltzmann distribution law for n distinguishable particles.

Now taking the natural logarithm on both sides of eqn. (27), we get,

$$\ln W = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i! \qquad ...(28)$$

Applying Stirling approximation (*i.e.*, $\ln x! = x \ln x - x$, where x is very large), we get from eqn. (28)

$$\ln W = N \ln N - N + \sum_i N_i \ln g_i - \left[\sum_i (N_i \ln N_i - N_i)\right]$$

$$= N \ln N - \sum_i N_i \ln \frac{N_i}{g_i} \text{ (using eqn. 28)} \qquad ...(29)$$

Now differentiating both sides, we get,

$$d(\ln W) = d(N \ln N) - \sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i N_i \, d\left(\ln \frac{N_i}{g_i}\right)$$

$$= -\sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i N_i \frac{dN_i}{N_i}$$

$$= -\sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i dN_i$$

$$= -\sum_i dN_i \ln \frac{N_i}{g_i} \qquad ...(30)$$

$$\left[\because \sum_i N_i = \text{constant}, \therefore \sum_i dN_i = 0\right]$$

For the most probable distribution, $d(\text{in } W)_{max} = 0$

$$\text{Therefore} \sum_i dN_i \ln \frac{N_i}{g_i} = 0 \qquad ...(31)$$

Since the system is in equilibrium, total number of particle and the total energy of the system are constant. So,

$$\sum_i dN_i = 0 \qquad ...(32)$$

$$\text{and} \sum_i E_i \, dN_i = 0 \qquad ...(33)$$

Multiplying eqn. (31) by α and eqn. (32) by β and then adding to eqn. (33), we get,

$$\sum_i \left[\ln\left(\frac{N_i}{g_i}\right) + \alpha + \beta E_i \right] dN_i = 0 \qquad ...(34)$$

Since dN_i's are independent of one another, the above equation hold only if,

NOTES

$$\ln\left(\frac{N_i}{g_i}\right) + \alpha + \beta E_i = 0 \text{ , or, } N_i = g_i e^{-(\alpha+\beta E_i)}$$

Now the Maxwell-Boltzmann distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)}} \qquad ...(35)$$

which physically gives the probability of a particle to occupy the energy state E_i.

2.6.2 Bose-Einstein (BE) Statistics

The basis postulates of BE statistics are:

(*i*) The associated particles are identical and *indistinguishable*.

(*ii*) Each energy state can contain any number of particles.

(*iii*) Total energy and total number of particles of the entire system are constant.

(*iv*) The particles have zero or integral spin, *i.e.,* $0\hbar$, $1\hbar$, $5\hbar$, $50\hbar$, etc., where $\hbar$ is the unit of spin.

(*v*) The wave function of the system is symmetric under the positional exchange of any two particles.

Examples: Photon, phonon, all mesons (π, κ, η) etc., these are known as *Bosons*.

[**Note: Symmetric and Anti-symmetric wave function**

Suppose the allowed wave function for *n*-particles system is $\psi(1, 2, 3, ..., r, s, ... n)$, where the integers within the argument of ψ represent the coordinates of the *n*-particles relative to some fixed orgion. Now, if we interchange the position of any two particles, say, *r* and *s*, the resulting wave function becomes $\psi(1, 2, 3, ..., s, r, ...n)$. The wave function ψ is said to be symmetric when

$\psi(1, 2, 3, ..., r, s, ...n) = \psi(1, 2, 3, ..., s, r, ...n)$,

and anti-symmetric when

$\psi(1, 2, 3, ..., r, s, ...n), = -\psi(1, 2, 3, ..., s, r, ...n)$]

Bose-Einstein Distribution Law

Let N_i number of identical, indistinguishable, non-interacting particles are to be distributed among g_i quantum states each having energy E_i. So, in the *i*th energy level, there are $(N_i + g_i)$ total objects. Keeping the first quantum state fixed, the remaining $(N_i + g_i - 1)$ objects can permuted in $(N_i + g_i - 1)!$ possible ways. But since the particles and the quantum states are indistinguishable, we have to deduct $N_i!$ ways and $(g_i - 1)!$ ways from the all possible ways to get effective number of arrangements. Thus, total number of possible ways of arrangement for the *i*th state is

$$W_i = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \qquad ...(36)$$

Hence the total number of ways of the entire distribution of N particles in n number of energy levels of the system is

NOTES

$$W = \prod_i^n \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \qquad ...(37)$$

where Π denotes the product symbol.

If we assume that N_i and g_i are very large, eqn. (37) reduces to

$$W = \prod_i^n \frac{(N_i + g_i)!}{N_i!\, g_i!} \qquad ...(38)$$

Taking natural logarithm of both the sides of eqn. (38) we get,

$$\ln W = \sum_i \left[\ln (N_i + g_i)! - \ln N_i! - \ln g_i!\right]$$

$$= \sum_i \left[(N_i + g_i)\ln (N_i + g_i) - N_i \ln N_i - g_i \ln g_i\right] \qquad ...(39)$$

(using Stirling approximation)

Now, differentiating equation (40) to obtain the probable distribution, we get,

$$d(\ln W)_{\max} = \sum_i [\ln (N_i + g_i) - \ln N_i]\, dN_i = 0 \qquad ...(40)$$

Also we have other two conditions given by

$\sum_i d N_i = 0$ (conservation of total no. of particles) ...(41)

$\sum_i E_i\, d N_i = 0$ (conservation of total energy) ...(42)

Multiplying eqn. (41) by ($-\alpha$) and eqn. (42) by ($-\beta$) and then adding with eqn. (40) we get,

$$\sum_i [\ln (N_i + g_i) - \ln N_i - \alpha - \beta E_i]\, dN_i = 0 \qquad ...(43)$$

Since dN_i's are independent of one another, the above equation holds only if,

$$\sum_i [\ln (N_i + g_i) - \ln N_i - \alpha - \beta E_i] = 0$$

or, $$N_i = \frac{g_i}{e^{(\alpha + \beta E_i)} - 1} \qquad ...(44)$$

Now the Bose-Einstein distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} - 1} \qquad ...(45)$$

which represents the probability of finding a boson with energy E_i.

2.6.3 Fremi-Dirac (FD) Statistics

The basis postulates of FD statistics are:

(*i*) Particles are identical and indistinguishable.

(*ii*) Total energy and total number of particles of the entire system is constant.

(*iii*) Particles have half-integral spin, *i.e.,* $\frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{37}{2}\hbar$, etc.

(*iv*) Particles obey Pauli's exclusion principle, *i.e.,* no two particles in a single system can have the same value for each of the four quantum numbers. In other words, a single energy state can contain at best a single particle with appropriate spin.

(*v*) The wave function of the system is anti-symmetric under the positional exchange of any two particles.

Example: Electron, proton, neutron, all hyperons (Λ, Σ, Ξ, Ω) etc., these are known as *Fremions*.

Fermi-Dirac Distribution Law

Consider a system of N indistinguishable, non-interacting particles obeying Pauli's exclusion principle. Let $N_1, N_2, N_3, ..., N_i, ..., N_n$ particles in the system have energies $E_1, E_2, E_3, ..., E_i, ..., E_n$, respectively and let g_i is the number of degenerate quantum state in the energy level E_i. According to Pauli's exclusion principle, a single quantum state can be occupied by at best one particle. Since N_i particles are to be distributed among g_i degenerate states ($g_i \geq N_i$) having the same energy E_i, N_i states will be filled up and $(g_i - N_i)$ states will remain vacant. Now g_i states can be arranged in $g_i!$ possible ways. But since the particles and the quantum states are indistinguishable, we have to deduct $N_i!$ ways and $(g_i - N_i)!$ ways from the all possible ways to get effective number of arrangements. Thus, total number of possible ways of arrangement for the *i*th state is

$$W_i = \frac{(g_i)!}{N_i!(g_i - N_i)!} \quad ...(46)$$

Hence the total number of ways for the entire distribution of N particles in n number of energy levels of the system is

$$W = \prod_i^n \frac{(g_i)!}{N_i!(g_i - N_i)!} \quad ...(47)$$

where Π denotes the product symbol.

Now taking natural logarithm on both sides of eqn. (47) and applying Stirling approximation, we get,

$$\ln W = \sum_i [\ln g_i - \ln N_i - \ln (g_i - N_i)]$$

$$= \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)] \quad ...(48)$$

Now, differentiating eqn. (48) to obtain the most probable distribution, we get,

$$d(\ln W)_{\max} = \sum_i [-\ln N_i + \ln(g_i - N_i)] d N_i = 0 \qquad ...(49)$$

Considering the conservation of total energy and total number of particles, we can write

NOTES

$$\sum_i dN_i = 0 \text{ (conservation of total no. of particles)} \qquad ...(50)$$

$$\sum_i E_i \, dN_i = 0 \text{ (conservation of total energy)} \qquad ...(51)$$

Multiplying eqn. (49) by α and eqn. (50) by β and then adding to eqn. (51) we get,

$$\sum_i [-\ln N_i + \ln(g_i - N_i) - \alpha - \beta E_i] dN_i = 0 \qquad ...(52)$$

Since dN_i's are independent of one another, the expression in the bracket in the eqn. (52) is zero for each N_i. Thus

$$N_i = \frac{g_i}{e^{(\alpha + \beta E_i)} + 1} \qquad ...(53)$$

Hence the Fermi-Dirac distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + 1} \qquad ...(54)$$

which represents the probability of finding a fermion with energy E_i.

Application of Fermi-Dirac statistics

Fermi Distribution at Zero and Non-zero Temperatures

The Fremi-Dirac distribution function is

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + 1}$$

Now for the fermions in statistical equilibrium at absolute temperature T, it is found that $\alpha = \frac{-E_F}{kT}$ and $\beta = \frac{1}{kT}$

where, E_F is the *Fremi energy* of the system (*i.e.,* the maximum energy at absolute zero) k is the Boltzmann constant = 1.38×10^{-23} Joule/Kelvin.

Here $\frac{N_i}{g_i}$ is known as the *occupation index*.

Thus, the *F-D* distribution function reduces to

$$(E_i) = \frac{1}{e^{(E_i - E_F)/kT} + 1} \qquad ...(55)$$

Now, let us discuss two distinct cases.

Case – 1 ($T = 0$ K)

$$f(E_i) = 1, \text{ when } E_i < E_F$$
$$= 0, \text{ when } E_i > E_F$$

Thus at $T = 0$ K, $f(E_i)$ is a step function (see Fig. 2.23) which implies all the energy states up to $E_i = E_F$ are filled up and the states above E_F are empty.

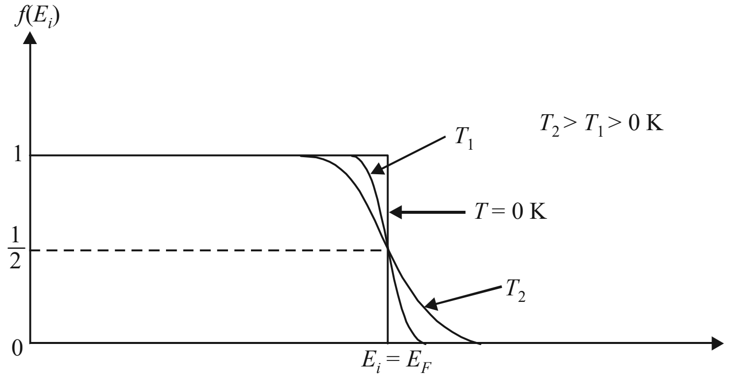


Fig. 2.23 *Plot of Fermi-Dirac distribution function as a function of* E_i

Case – 2 ($T > 0$ K)

As the temperature increases beyond $T = 0$ K, some of the electrons in the level just below the Fermi level go to levels just above E_F resulting a gradual change in the occupation index $f(E_i)$. If $E_i = E_F$, $(E_i) = \dfrac{1}{e^0 + 1} = \dfrac{1}{2}$, *i.e.*, at a finite temperatur Fermi energy of a system is that energy for which 50% energy states are filled and 50% states are vacant.

Fermi Energy for Electron Gas in Metals

Metals are characterised by the presence of a good number of free electrons. These electrons move about at random within the metals. While moving the free electrons collide among themselves also encounter with the fixed ion cores. Such behaviour of the free electrons is similar to that of molecules of a gas. Thus metals can be treated as electron gas. Since the electrons have half-integral spin angular momenta and they obey Pauli's exclusion principle, they follow F-D statistics.

Let us consider an electron gas consisting of N electrons occupying volume V. If N is very large, the spacing between two successive energy levels becomes very small making the energy levels almost continuous. Then if the energy of the electrons ranges between E to $E + dE$, the number of degenerate states g_i should be replaced by $g(E)\,dE$ and the total number of electrons N_i in these states should be replaced by $N(E)\,dE$ in the distribution function given by equation (53). Thus the total number of electrons in the electron gas having energy between E to $E + dE$ can be written eqn.(54) and eqn. (55) as

$$N(E)dE = \frac{g(E)\,dE}{\exp\left(\dfrac{E_i - E_F}{kT}\right) + 1} \qquad ...(56)$$

Since the electrons have *two* allowed values of spin quantum number $\left(m_s = \pm\frac{1}{2}\right)$, the total number of their allowed states between energy for the energy range E to $E + dE$ can be written following eqn. as

$$g(E)dE = 2 \times \frac{1}{h^3}(4\pi V\sqrt{2E}m^{3/2})\,dE \qquad ...(57)$$

Hence the density of states $g(E)$ for a Fermionic gas is given by

$$g(E) = \frac{1}{h^3}(8\pi V\sqrt{2mE}m) \qquad ...(58)$$

which shows that $g(E)$ depends only on E for a single type of fermionic gas kept in a fixed volume V.

From Fig. (2.9) it is obvious that at $T = 0$ K, all the single-particle state up to energy E_F are filled up. Thus at $T = 0$ K,

$$N(E)dE = \frac{g(E)\,dE}{e^{-\infty}+1} = g(E)dE \quad [\text{Œ}\; e^{-\infty} = 0] \qquad ...(59)$$

i.e., total number of electrons is equal to the total number of single-particle energy states, hence

$$N = \int_0^{E_F} N(E)\,dE$$

$$= \int_0^{E_F} g(E)\,dE \qquad \text{[using eqn. (59)]}$$

$$= \frac{1}{h^3}(8\sqrt{2}\pi Vm^{3/2})\int_0^{E_F} E^{1/2}dE \qquad \text{[using eqn. (58)]}$$

or, $$N = \frac{16\sqrt{2}\pi Vm^{3/2}}{3h^3}E_F^{3/2} \qquad ...(6.)$$

which is the expression for the *total number of electrons* in the metal at $T = 0$ K.

Therefore,

$$E_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad ...(61)$$

which is the expression for *Fermi energy* of the electrons in the metal.

If $n = N/V$ denotes the concentration of the electrons in the metal, the Fermi energy of the electrons in the metal is

$$E_F = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} \qquad ...(62)$$

which showns that Fermi energy of the electrons depends solely on their *concentration*.

Total Energy at Absolute Zero Temperature

The total energy of electrons at absolute zero ($T = 0$ K) is given by

$$(E_0)_{\text{tot}} = \int_0^{E_F} E.N(E)\,dE$$

$$= \int_0^{E_F} E.g(E)\,dE \qquad \text{[using eqn. (7.42)]}$$

$$= \frac{1}{h^3}(8\sqrt{2}\pi V m^{3/2}) \int_0^{E_F} E^{3/2} dE \qquad \text{[using eqn. (7.41)]}$$

$$= \frac{16\sqrt{2}\pi V m^{3/2}}{5h^3} E_F^{5/2}$$

$$= \frac{3}{5} N E_F \qquad \text{[using eqn. (7.43)]} \qquad \ldots(7.46)$$

which shows *quantum effect because, classically the total energy of a system at absolute zero is nothing but zero.*

The average energy per electron at $T = 0$ K can be written as

$$<E_0> = \frac{(E_0)_{\text{tot}}}{N} = \frac{3}{5} E_F \qquad \ldots(7.47)$$

which shows that at absolute zero temperature, the average energy per electron is equal to $\frac{3}{5}$ times the Fermi energy.

The ground-state pressure of the system is defined by

$$P_0 = \frac{2E_0}{3V} = \frac{2}{5} n E_F \qquad \text{[using eqn. (7.46)]}$$

Substituting for E_F, the foregoing expression takes the form

$$P_0 = \frac{2}{5} \frac{h^2}{8m} \left(\frac{3}{\pi}\right)^{2/3} n^{5/3} \propto n^{5/3}$$

Thus the ground-state pressure of an electron gas at absolute zero solely depends on its concentration.

Fermi Temperature (T_F)

Fermi temperature (T_F) is the temperature equivalent of Fermi energy (F_F) and it is defined as $T_F = \frac{E_F}{k}$, where k (= 1.38×10^{-23} Joule/Kelvin) is the Boltzmann constant.

2.6.4 Ensemble Averaging

In ***statistical mechanics***, the ensemble average is defined as the mean of a quantity that is a function of the microstate of a system, according to the distribution of the system on its micro-states in this ensemble.

Since the ensemble average is dependent on the ensemble chosen, its mathematical expression varies from ensemble to ensemble. Though, the mean obtained for a given physical quantity does not depend on the ensemble chosen at the thermodynamic limit. The grand canonical ensemble is an example of an ***open system***.

Canonical Ensemble Average

For a classical system in thermal equilibrium with its environment, the ensemble average takes the form of an integral over the phase space of the system as below:

$$\bar{A} = \frac{\int A e^{-\beta H(q_1, q_2, \dots q_M, p_1, p_2, \dots p_N)} d\tau}{\int e^{-\beta H(q_1, q_2, \dots q_M, p_1, p_2, \dots p_N)} d\tau}$$

Where:

$\bar{A}$ is the ensemble average of the system property A,

β is $\frac{1}{kT}$, known as thermodynamic beta,

H is the Hamiltonian of the classical system in terms of the set of coordinates q_i and their conjugate generalized momenta p_i, and

$d\tau$ is the volume element of the classical phase space of interest.

The denominator in this expression is known as the partition function, and is denoted by the letter Z.

Microcanonical Ensemble

The ***microcanonical ensemble*** represents an isolated system in which energy (E), volume (V) and the number of particles (N) are all constant.

In ***statistical mechanics***, the microcanonical ensemble is a statistical ensemble that represents the possible states of a mechanical system whose total energy is exactly specified. The system is assumed to be isolated in the sense that it cannot exchange energy or particles with its environment, so that (by the law of conservation of energy) the energy of the system does not change with time.

The primary macroscopic variables of the microcanonical ensemble are the total number of particles in the system (symbol: N), the system's volume (symbol: V), as well as the total energy in the system (symbol: E). each of these is assumed to be constant in the ensemble. For this reason, the microcanonical ensemble is sometimes called the NVE ensemble.

In simple terms, the microcanonical ensemble is defined by assigning an equal probability to every microstate whose energy falls within a range centered at E. All other microstates are given a probability of zero. Since the probabilities must add up to 1, the probability P is the inverse of the number of microstates W within the range of energy,

$$P=1/W,$$

The range of energy is then reduced in width until it is infinitesimally narrow, still centered at E. In the limit of this process, the microcanonical ensemble is obtained.

Canonical Ensemble

NOTES

In statistical mechanics, a ***canonical ensemble*** is the statistical ensemble that represents the possible states of a mechanical system in thermal equilibrium with a heat bath at a fixed temperature. The system can exchange energy with the heat bath, so that the states of the system will differ in total energy.

The principal thermodynamic variable of the canonical ensemble, determining the probability distribution of states, is the absolute temperature (symbol: T). The ensemble typically also depends on mechanical variables, such as the number of particles in the system (symbol: N) and the system's volume (symbol: V), each of which influence the nature of the system's internal states. An ensemble with these three parameters is sometimes called the NVT ensemble.

The canonical ensemble assigns a probability P to each distinct microstate given by the following exponential:

$$P=e^{(F-E)/(kT)}$$

Where E is the total energy of the microstate, and k is Boltzmann's constant.

Grand Canonical Ensemble

In statistical mechanics, a ***grand canonical ensemble*** (also known as the macrocanonical ensemble) is the statistical ensemble that is used to represent the possible states of a mechanical system of particles that are in thermodynamic equilibrium (thermal and chemical) with a reservoir.The system is said to be open in the sense that the system can exchange energy and particles with a reservoir, so that various possible states of the system can differ in both their total energy and total number of particles. The system's volume, shape, and other external coordinates are kept the same in all possible states of the system.

The thermodynamic variables of the grand canonical ensemble are chemical potential (symbol: **μ**) and absolute temperature (symbol: **T**). The ensemble is also dependent on mechanical variables such as volume (symbol: **V**) which influence the nature of the system's internal states. This ensemble is therefore sometimes called the **μVT** ensemble, as each of these three quantities are constants of the ensemble.

Ensemble averaging is a data acquisition method that enhances the signal-to-noise of an analytical signal through repetitive scanning. Ensemble averaging can be done in real time, which is extremely useful for analytical methods such as:

- Nuclear Magnetic Resonance Spectroscopy (NMR)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Near-Infrared (NIR) Spectrophotometry
- UV-Visible Spectrophotometry

Ensemble averaging also works well with multiple datasets once data acquisition is complete. In either case, this method of S/N enhancement requires that:

- The analyte signal must be stable
- The source of noise is random

2.7 PARTITION FUNCTION

NOTES

In physics, a ***partition function*** describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the combined thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, we can be expressed this terms of the partition function or its derivatives. The partition function is ***dimensionless***, it is a pure number.

Each ***partition function*** is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy). The most common statistical ensembles have named partition functions. The canonical partition function applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The ***grand canonical partition function*** applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. Other types of partition functions can be defined for different circumstances; see partition function (mathematics) for generalizations. The partition function has many physical meanings, as discussed in Meaning and significance.

Calculating the Thermodynamic Total Energy

In order to determine the usefulness of the partition function, let us calculate the thermodynamic value of the total energy. This is simply the expected value, or ensemble average for the energy, which is the sum of the microstate energies weighted by their probabilities:

$$\langle E\rangle = \sum_s E_s P_s = \frac{1}{Z}\sum_s E_s e^{-\beta E_s} = -\frac{1}{Z}\frac{\partial}{\partial\beta}Z(\beta, E_1, E_2, \cdots) = -\frac{\partial \ln Z}{\partial\beta}$$

Or equivalently,

$$\langle E\rangle = k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

Incidentally, one should note that if the microstate energies depend on a parameter **λ** in the manner

$$E_s = E_s^{(0)} + \lambda A_s \qquad \text{for all } s$$

Then the expected value of ***A*** is,

$$\langle A\rangle = \sum_s A_s P_s = -\frac{1}{\beta}\frac{\partial}{\partial\lambda}\ln Z(\beta, \lambda).$$

This provides us with a method for calculating the expected values of many microscopic quantities. We add the quantity artificially to the microstate energies (according to quantum mechanics, to the Hamiltonian), calculate the new partition function and expected value, and then set **λ** to zero in the final expression. This is analogous to the source field method used in the path integral formulation of quantum field theory.

Relation to Thermodynamic Variables

In this section, we will state the relationships between the ***partition function*** and the ***various thermodynamic*** parameters of the system. These results can be derived using the method of the previous section and the various thermodynamic relations.

As we have already seen, the thermodynamic energy is,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}.$$

The variance in the energy (or 'Energy Fluctuation') is,

$$\langle (\Delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}.$$

The ***heat capacity*** is,

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \langle (\Delta E)^2 \rangle.$$

In general, consider the extensive variable ***X*** and intensive variable ***Y*** where ***X*** and ***Y*** form a pair of conjugate variables. In ensembles where ***Y*** is fixed (and ***X*** is allowed to fluctuate), then the average value of ***X*** will be:

$$\langle X \rangle = \pm \frac{\partial \ln Z}{\partial \beta Y}.$$

The sign will depend on the specific definitions of the variables **X** and **Y**. An example would be **X** = volume and **Y** = pressure. Additionally, the variance in **X** will be:

$$\langle (\Delta X)^2 \rangle \equiv \langle (X - \langle X \rangle)^2 \rangle = \frac{\partial \langle X \rangle}{\partial \beta Y} = \frac{\partial^2 \ln Z}{\partial (\beta Y)^2}.$$

In the special case of entropy, entropy is given by,

$$S \equiv -k_B \sum_s P_s \ln P_s = k_B(\ln Z + \beta \langle E \rangle) = \frac{\partial}{\partial T}(k_B T \ln Z) = -\frac{\partial A}{\partial T}$$

Where ***A*** is the Helmholtz free energy defined as ***A* = *U* “ *TS***, where ***U* = *è'Eé'*** is the total energy and ***S*** is the entropy so that,

$$A = \langle E \rangle - TS = -k_B T \ln Z.$$

Furthermore, the heat capacity can be expressed as,

$$C_v = T\frac{\partial S}{\partial T} = -T\frac{\partial^2 A}{\partial T^2}.$$

Translational Partition Function

In statistical mechanics, the ***translational partition function***, q_T is that part of the partition function resulting from the movement (translation) of the centre of mass. For a single atom or molecule in a low pressure gas, neglecting the interactions of molecules, the canonical ensemble q_T can be approximated by:

$$q_T = \frac{V}{\Lambda^3} \text{ where } \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Here, ***V*** is the volume of the container holding the molecule (volume per single molecule so, for example suppose 1 mole of gas the container volume should be divided by the ***Avogadro number***), **Λ** is the Thermal **de Broglie wavelength**, **h** is the Planck constant, **m** is the mass of a molecule, **kB** is the ***Boltzmann constant*** and **T** is the absolute temperature. This approximation is valid as long as **Λ** is much less than any dimension of the volume the atom or molecule is in. Since typical values of **Λ** are on the order of **10-100** pm, this is almost always an excellent approximation.

When considering a set of **N** non-interacting but identical atoms or molecules, when **QT k” N** , or equivalently when **ρ Λ j” 1** where **ρ** is the density of particles, the total translational partition function can be written

$$Q_T(T, N) = \frac{q_T(T)^N}{N!}$$

The factor of **N!** arises from the restriction of allowed **N** particle states due to Quantum exchange symmetry. Most substances form liquids or solids at temperatures much higher than when this approximation breaks down significantly.

Rotational Partition Function

The rotational partition function relates the rotational ***degrees of freedom*** to the rotational part of the energy.

Definition

The total canonical partition function Z of a system of *N* identical, indistinguishable, non-interacting atoms or molecules can be divided into the atomic or molecular partition functions **ζ**:

$$Z = \frac{\zeta^N}{N!}$$

with :

$$\zeta = \sum_j g_j e^{-E_j/k_B T} .$$

Where g_j is the degeneracy of the ***jth*** quantum level of an individual particle, k_B is the Boltzmann constant, and **T** is the absolute temperature of system. For molecules, under the assumption that total energy levels E_j can be partitioned into its contributions from different degrees of freedom (weakly coupled degrees of freedom)

$$E_j = \sum_i E_j^i = E_j^{trans} + E_j^{ns} + E_j^{rot} + E_j^{vib} + E_j^e$$

And the number of degenerate states are given as products of the single contributions

$$g_j = \prod_i g_j^i = g_j^{trans} g_j^{ns} g_j^{rot} g_j^{vib} g_j^e,$$

Where '**Trans**', '**ns**', '**rot**', '**vib**' and '**e**' denotes translational, nuclear spin, rotational and vibrational contributions as well as electron excitation, the molecular partition functions

$$\zeta = \sum_i g_j e^{-E_j/k_B T}$$

Can be written as a product itself

$$\zeta = \prod_i \zeta^i = \zeta^{trans} \zeta^{ns} \zeta^{rot} \zeta^{vib} \zeta^e.$$

Electronic Partition Function

Our ***quantum-mechanical*** model for a diatomic molecule takes the zero of energy to be the infinitely separated atoms at rest, i.e., with no ***kinetic energy***. This is the energy of the lowest electronic state of the molecule. The lowest electronic state is called the ***ground state***.

The ***electrical interactions*** among the nuclei and electrons are such that, as the atoms approach one another, a bond forms and the energy of the two-atom system decreases. At some ***inter-nuclear distance***, the energy reaches a minimum; at ***shorter inter-nuclear distances***, the repulsive interactions between nuclei begin to dominate, and the energy increases. We can use quantum mechanics to find the wave function and energy of the molecule when the nuclei are separated to any fixed distance. By repeating the calculation at a series of inter-nuclear distances, we can find the distance at which the molecular energy is a minimum. We take this minimum energy as the electronic energy of the molecule, and the corresponding inter-nuclear distance as the bond length.

Excited electronic states exist, and their energies can be estimated from spectroscopic measurements or by quantum mechanical calculation. For most molecules, these excited electronic states are at much higher energy than the ground state. When we compare the terms in the electronic partition function, as per following equation,

$$\exp\left(-\epsilon_{e,1}/kT\right) \gg \exp\left(-\epsilon_{e,2}/kT\right)$$

The term for any higher energy level is insignificant compared to the term for the ground state. The electronic partition function becomes just

$$z_e = g_1 \exp\left(-\epsilon_{e,1}/kT\right)$$

The ground-state degeneracy, g_1, is one for most molecules. For unusual molecules the ground-state degeneracy can be greater; for molecules with one unpaired electron, it is two.

NOTES

Applications of Partition Function

- In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium.
- The partition function is dimensionless, it is a pure number. Each partition function is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy).
- The partition function at temperatures up to 300 K, but these are too low as it would appear that only the rotational contribution to the partition function is represented.
- A partition function is the bridge between thermodynamics, spectroscopy, and quantum mechanics. Once it is known, a partition function can be used to calculate thermodynamic functions, heat capacities, entropies, and equilibrium constants. It also sheds light on the significance of these properties.
- A partition describes how n particles are distributed among ***k*** energy levels.
- Probably the 'Partition Function' is named so (indeed a bit uninspired), because it is a function associated to the way particles are partitioned among energy levels.
- The partition function or configuration integral, as used in probability theory, information theory and dynamical systems, is a generalization of the definition of a partition function in statistical mechanics. It is a special case of a normalizing constant in probability theory, for the ***Boltzmann distribution.***

2.8 HEAT CAPACITY OF SOLIDS

The molecules (or ions) in a solid cannot move about normally, cannot rotate: they can, however, vibrate about their mean position. The kinetic energy in solid is therefore entirely vibrational energy. It was discovered in 1819 by Dulong and Petit that the heat capacities of solid elements, measured at ordinary temperatures, has an almost constant value of 6.3 cal/(deg) (g atom).

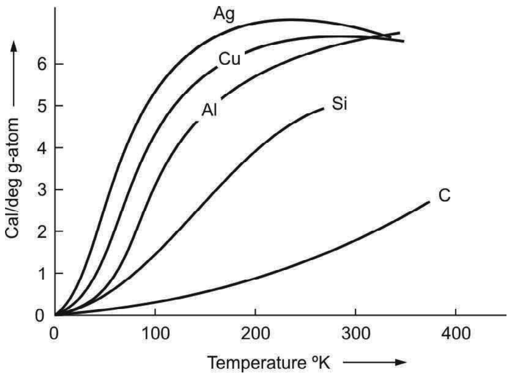


Fig. 2.24 The heat capacities of simple crystalline solids at low temperature

There are, however, exceptions to the rule. Certain elements like carbon, beryllium, boron have heat capacities less than 6.3 cal/(deg) (g atom). The essential conclusion which can be drawn from the Debye statement is that the heat capacity of an element may reach maximum value of about 6.3 cal/(deg) (g atom) at a certain temperature called the characteristic temperature of that element. It so happens that the characteristic temperature of most elements is below room temperature, but in the case of carbon and a few other elements it is much higher.

According to the classical approach, each vibrational degree of freedom would be expected to have an average kinetic energy $\frac{1}{2}kT$ and average kinetic energy for the three perpendicular vibration modes of the atom would then be $\frac{3}{2}kT.$ For a vibrating particle, as in the case of a swimming pendulum, there is constant interchange of kinetic and potential energy.

$\therefore$ For one atom

$$E = E_{\text{kinetic}} + E_{\text{potential}}$$

$$= \frac{3}{2}kT + \frac{3}{2}kT = 3kT$$

and for one gram atom

$$E = 3NkT$$

Since, the Boltzman constant

$$k = \frac{R}{N}$$

$$E = 3N \times \frac{R}{N}T = 3RT$$

and $$C_p \approx Cv = \frac{dE}{dT} = 3R = 6 \text{ cal/(deg) (g atom)}$$

Einstein has calculated the heat capacities of solids from the quantum theory. The heat capacity of a crystalline solid, containing an Avogadro's's number of single particle, C_v is given by

$$C_v = 3R\left(\frac{hv}{kT}\right)^2 \cdot \frac{e^{hv/kt}}{(e^{hv/kT} - 1)^2}$$

where v is the vibrational frequency.

Debye recognized that all the particles of a crystal do not vibrate with the samefrequency. For small values of temperature, the Debye equation for the atomic heat capacity reduces to the form

$$C_v = 464.5\left(\frac{T}{\theta}\right)^3 \text{ cal deg}^{-1} \text{ g. atom}^{-1}$$

This equation has been found to hold at temperature below about 25 K within experimental error. The experimental values can be extrapolated to zero degrees K. It has been found that as the temperature approaches absolute zero, the heat capacity should tend toward zero. These are in agreement with the experimental observations.

2.8.1 Chemical Equilibria

This will depend upon the type of reaction. In reactions of type I ($\Delta n = 0$), addition of an inert gas will simply increase the total pressure of the system without changing the partial pressures of various reacting species. But, as we have seen earlier, reactions of type I remain unaffected by change of pressure. Hence the addition of inert gas to such type of reactions will not affect the extent of reaction at equilibrium.

In reactions of type II ($\Delta n \neq 0$), the addition of an inert gas does effect the extent of reaction at equilibrium because it decreases the partial pressures of the reactants and products of a given total equilibrium pressure. Consider, for example, the dissociation of phosphorus pentachloride:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The equilibrium constant expressions in terms of pressure and concentration for this reaction are

$$K_p = \frac{\alpha^2 P}{1-\alpha^2};\ K_c = \frac{n\alpha^2}{(1-\alpha)V}$$

Let us now consider two cases:

1. If an inert gas is added at constant volume, the various equilibrium concentration terms involved are not changed. Since, the concentration of an inert gas is not involved in the equilibrium constant expression, therefore, the equilibrium remains unchanged.

2. If an inert gas is added at constant pressure, the volume V of the system will increase, this will cause dilution of the reactants and products thereby decreasing the concentration and partial pressures of the species involved. From the expression for K_c, if V increases, α must increase to keep K_c constant, this means that more of phosphorus pentachloride will dissociate, or in the other words, the formation of the product is favoured.

In general we can say that for those reactions in which the number of molecules of products are more than those of reactants, addition of an inert gas at constant pressure will favour the product formation. However, for reactions in which Δn is negative, pressure will favour the formation of reactants.

Types of Chemical Equilibria

There are two types of equilibria:

1. **Homogeneous equilibria** in which only one phase occurs. For example, a system containing only gases or a single liquid or solid phase.
2. **Heterogeneous equilibria** in which more than a single phase appears.

For example, equilibrium between solid and gas, liquid and gas, solid and liquid, solid and solid, immiscible liquids, etc.

Application of Law of Mass Action to Homogeneous Gaseous Equilibria

Type I. Reactions in which there is no change in the number of molecules.

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It this type, the number of molecules of reactants is the same as the number of molecules of products.

Some examples are

$$H_2 + I_2 \rightleftharpoons 2HI$$
$$N_2 + O_2 \rightleftharpoons 2NO$$
$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

In all such reactions, $\Delta n = 0$. Hence from equation (10.22), the equilibrium constants K_p and K_c will be equal for reversible reactions of this type.

Hydrogen iodide-equilibrium. Let us start with a moles of hydrogen and b moles of iodine and let x is the amount of hydrogen iodide formed at equilibrium. If V is the volume of the system, then the various concentration terms at equilibrium are given by

$$C_{H_2} = \frac{a-x}{V},$$

$$C_{I_2} = \frac{b-x}{V}$$

and $$C_{HI} = \frac{2x}{V}$$

The equilibrium may be represented as follows.

$$\begin{array}{lccccc} \text{Initial molar concentrations} & a/V & & b/V & & 0 \\ & H_2 & + & I_2 & \rightleftharpoons & 2HI \\ \text{Equilibrium molar concentrations} & \frac{a-x}{V} & & \frac{b-x}{V} & & \frac{2x}{V} \end{array}$$

The equilibrium constant for this reaction is, thus, given by

$$K_c = \frac{C_{HI}^2}{C_{H_2} \cdot C_{I_2}} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)\,(b-x)} \qquad \text{...(64)}$$

It should be noted that the volume V has disappeared from equation (64). This is characteristic of all reactions in which the total number of moles of reactants are equal to the total number of moles of products. Hence, *the equilibrium constant remains unchanged by change of volume and pressure.*

The equilibrium constant in terms of pressure, K_p can be determined as given below:

NOTES

$$\begin{array}{lcccccc} \text{Initial number of moles} & a & & b & & 0 \\ & H_2 & + & I_2 & \rightleftharpoons & 2HI \\ \text{Number of moles at equilibrium} & a-x & & b-x & & 2x \end{array}$$

Total number of gaseous moles present at equilibrium is

$$n_i = a - x + b - x + 2x = a + b$$

If the total equilibrium pressure is P, then by means of Dalton's law of partial pressure, the various partial pressures are given by:

$$P_{H_2} = \frac{(a-x)}{(a+b)}P$$

$$P_{I_2} = \frac{(b-x)}{a+b}P$$

and
$$P_{HI} = \frac{(2x)}{(a+b)}P$$

Therefore,

$$K_p = \frac{P_{HI}^2}{P_{H_2} . P_{I_2}}$$

$$K_p = \frac{\left(\frac{2x}{a+b}\right)^2 . P^2}{\frac{(a-x)}{(a+b)}P . \frac{(b-x)}{(a+b)}P}$$

$$K_p = \frac{\frac{4x^2}{(a+b)^2}P^2}{\frac{(a-x)(b-x)}{(a+b)^2} . P^2}$$

$$K_p = \frac{4x^2}{(a-x)(b-x)} \quad ...(65)$$

Hence, as can be seen from equations (64) and (65),

$$K_p = K_c.$$

Experimental verification of the law of mass action. This was done by Bodenstein in 1897 when he studied hydrogen iodide equilibria. He heated a known amount of hydrogen and iodine together in various proportions in sealed glass tubes to a temperature of about 450ºC by keeping the bulbs in a boiling sulphur bath. After sometimes, sufficient for the attainment of equilibrium, the tubes were suddenly cooled to fix the equilibrium. The unrelated contents were then analysed by opening the bulbs in KOH solution; which absorbed unreacted iodine and hydrogen iodide formed in the reaction. The amount of hydrogen left was then determined by measuring the volume.

The value of K_c for various initial concentrations of H_2 and I_2 was then determined from equation (10.21). It was always found to be constant.

Bodenstein further confirmed the results by approaching the equilibrium from the opposite direction. He heated hydrogen iodide alone to the same temperature and determined the amounts of hydrogen and iodine formed. Let n be the initial number of moles of hydrogen iodide and α is its degree of dissociation at equilibrium. If V is the total volume, the equilibrium is represented as

$$\begin{array}{lcccccc} \text{Initial molar concentration} & n/V & & 0 & & 0 \\ & 2HI & \rightleftharpoons & H_2 & + & I_2 \\ \text{Molar concentration at equilibrium} & \dfrac{n(1-\alpha)}{V} & & \dfrac{n\alpha}{2V} & & \dfrac{n\alpha}{2V} \end{array}$$

The equilibrium constant, K'_c for this is given by

$$K'_c = \frac{C_{H_2} \,.\, C_{I_2}}{C^2_{HI}}$$

$$K'_c = \frac{\dfrac{\eta\alpha}{2V} \cdot \dfrac{\eta a}{2V}}{\left[\dfrac{n(1-\alpha)}{V}\right]^2}$$

$$K'_c = \frac{\alpha^2}{4(1-\alpha)^2}$$

The equilibrium constants for direct and reverse reactions at the same temperature are related to each other by this expression, $K_c = \frac{1}{K'_c}$.

The results of hydrogen iodide equilibrium at 457.6ºC are shown in table

The $H_2 + I_2 \rightleftharpoons 2HI$ *equilibrium at* 457.6^o *C*

$C_{H_2} \times 10^2$ moles/litre	$C_{l_2} \times 10^3$ moles/litres	$C_{HI} \times 10^3$ moles/litres	K_c
5.617	0.5936	12.70	48.4*
4.580	0.9733	14.86	49.5*
3.841	1.524	16.87	48.6*
1.433	1.433	10.00	48.7**
1.696	1.696	11.81	48.5**
4.213	4.217	29.43	48.8**

* Equilibrium approached from hydrogen and iodine.

** Equilibrium approached from hydrogen iodide.

It can be seen from this table that the value of K_c are considerably constant although equilibrium was approached from different amounts of both the reactants and products.

This verifies law of mass action.

Problem

15 gram molecules of H_2, on interaction with 5.2 gram molecules of iodine vapours at 444°C, produced 10 gram molecules of HI. Determine the equilibrium constant of the reaction

Solution.

$$\begin{array}{ccccc} a & & b & & 0 \\ H_2 & + & I_2 & \rightleftharpoons & 2HI \\ (a-x) & & (b-x) & & 2x \end{array}$$

In the present case, $(a-x)$ $(b-x)$ $2x$

$$a = 15, \quad b = 5.2$$

and $$2x = 10 \quad \text{or} \quad x = 5$$

Therefore, $$a - x = 15 - 5 = 10$$

$$b - x = 5.2 - 5 = 0.2$$

Applying the law of mass action,

$$K_c = \frac{C_{HI}^2}{C_{H_2} . C_{I_2}}$$

$$K_c = \frac{(10)^2}{(10)\,(0.2)} = 50$$

Problem

The degree of dissociation of 2.40 moles of hydrogen iodide at 448°C was found to be 22 per cent. Calculate the number of moles of hydrogen iodide, hydrogen and iodine formed at equilibrium. Also calculate the equilibrium constant for the dissociation reaction.

Solution. The reaction is

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2 \\ n(1-\alpha) & & \frac{n(\alpha)}{2} & & \frac{n(\alpha)}{2} \end{array}$$

Here $$n = 2.40 \text{ moles}$$

and $$\alpha = 0.22$$

At equilibrium,

Number of moles of hydrogen iodide

$$= n(1 - \alpha) = 2.40\ (1 - 0.22)$$

$$= 1.872$$

Number of moles of hydrogen $= 2.40 \times \frac{(0.22)}{2} = 0.264$

Number of moles of iodine $= 2.40 \times \frac{(0.22)}{2} = 0.264$

Again, to calculate the equilibrium constant for the reaction, let V litres be the volume of the reaction vessel,

NOTES

$$K_c = \frac{\frac{n\alpha}{V} \cdot \frac{n\alpha}{V}}{\frac{[2n(1-\alpha)]^2}{V^2}} = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$K_c = \frac{(0.22)^2}{4(1-0.22)^2} = 0.0199.$$

Problem

A mixture containing 25 moles of hydrogen and 18 moles of iodine was heated in a sealed tube at 256ºC till equilibrium, when 30.8 moles of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 456ºC.

Solution. Formation of hydrogen iodide is represented as below

$$\begin{array}{ccccc} a & & b & & 0 \\ H_2 & + & I_2 & \rightleftharpoons & 2HI \\ (a-x) & & (b-x) & & 2x \end{array}$$

and in the present case, $2x = 30.8$ or $x = 15.4$, $a = 25$, $b = 18$

∴ Equilibrium constant,

$$K_c = \frac{(2x)^2}{(a-x)\,(b-x)}$$

$$K_c = \frac{(30.8)^2}{(25-15.4)\,(18-15.4)} = 38$$

Dissociation of hydrogen iodide is represented as below

$$2HI \rightleftharpoons H_2 + I_2$$

If we start with 1 mole of hydrogen iodide and assume that α is its degree of dissociation, the equilibrium constant is given by

$$\frac{\alpha^2}{4(1-\alpha)^2} = \frac{1}{K_c} = \frac{1}{38}$$

or $\alpha = 0.245$

Formation of Nitric Oxide

Nitric oxide is obtained from nitrogen and oxygen according to the equation

$$N_2 + O_2 \rightleftharpoons 2NO$$

This is a reversible process and hence, the law of mass action can be applied to it.

The expressions of K_c and K_p for this reaction can be obtained exactly in the same way as were obtained in the case of hydrogen iodide equilibrium.

The Water Gas Equilibrium

This is again a reversible gaseous reaction and is represented by the equation

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

NOTES

Let us start with a moles of carbon dioxide and b moles of hydrogen and let x is the amount of each of carbon monoxide and water formed at equilibrium. If V is the volume of the system then the various concentration terms at equilibrium are given by

$$C_{CO_2} = \frac{a-x}{V}; \qquad C_{H_2} = \frac{b-x}{V};$$

$$C_{CO} = \frac{x}{V}$$

and

$$C_{H_2O} = \frac{x}{V}$$

The equilibrium constant in terms of concentration for the water gas reaction is then given by

$$K_c = \frac{C_{CO} \cdot C_{H_2O}}{C_{CO_2} . C_{H_2}}$$

$$K_c = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\left(\frac{a-x}{1}\right)\left(\frac{b-x}{V}\right)}$$

$$K_c = \frac{x^2}{(a-x)\,(b-x)}$$

The equilibrium constant in terms of pressure can also be obtained as given below:

Initial number of moles	a	b		0	0
	CO_2 +	H_2	$\rightleftharpoons$	CO +	H_2O
Number of moles at equilibrium	$a-x$	$b-x$		x	x

Therefore, total number of moles at equilibrium,

$$n_1 = a - x + b - x + x + x = a + b$$

If the total equilibrium pressure is P, then by means of Dalton's law of partial pressure, the various partial pressures are given by

$$P_{CO_2} = \frac{(a-x)}{(a+b)} P$$

$$P_{H_2} = \frac{(b-x)}{(a+b)} P$$

$$P_{\text{CO}} = \frac{(x)}{(a+b)}P$$

and $$P_{\text{H}_2\text{O}} = \frac{(x)}{(a+b)}P$$

Now since, $$K_p = \frac{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}}{P_{\text{CO}} \cdot P_{\text{H}_2}}$$

$$K_p = \frac{\dfrac{(x)}{(a+b)}P \cdot \dfrac{(x)}{(a+b)}P}{\dfrac{(a-b)}{(a+b)}P \; \dfrac{(b-x)}{(a+b)}P}$$

$$K_p = \frac{x^2}{(a-x)\,(b-x)}$$

As can be seen from equations (10.25) and (10.26), $K_p = K_c$. It should be noted that in Type 1 reactions, the equilibrium constant expressions do not involve any volume terms and hence, are independent of any pressure or volume change.

Problem

Starting with equimolar amounts of carbon monoxide and steam, calculate the molar percentage composition of the water gas system at equilibrium at 1000 K; the equilibrium constant at this temperature is 0.719.

Solution: Since the number of moles of CO and H_2O are equal at the commencement, they must obviously remain equal throughout the reaction; let these values be n_1 at equilibrium. Similarly, the number of moles of CO_2 and H_2 must be equal; let these be n_2 at equilibrium. It follows, then, from expression for the equilibrium constant.

$$K = \frac{n_{\text{CO}} \cdot n_{\text{H}_2\text{O}}}{n_{\text{CO}_2} \cdot n_{\text{H}_2}}$$

Substituting the various values, we get

$$0.719 = \frac{n_1^2}{n_2^2} \text{ or } \frac{n_1}{n_2} = \sqrt{0.719} = 0.848$$

The amounts of CO, H_2O, CO_2 and H_2 at equilibrium are, therefore, present in the molar ratio of 0.848 : 0.848 : 1.00 : 1.00,

∴ The molar percentage composition of CO and H_2O are same and is

$$= \frac{0.848}{(2 \times 0.848) + (2 \times 1.00)} \times 100 = 22.9\%$$

The molar percentages of CO_2 and H_2 are then each 27.1 per cent. The composition of the water gas at equilibrium at 1000 K is thus, CO, 22.9; H_2O, 22.9; CO_2, 27.1 and H_2; 27.1 moles per cent.

Type II. Reactions in which there is a change in the number of molecules. In this type, the number of molecules of reactants is not equal to the number of molecules of products. Some examples of this type are

NOTES

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$N_2O_4 \rightleftharpoons 2NO_2$$
$$COCl_2 \rightleftharpoons CO + Cl_2 \text{ (dissociation of phosgene)}$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$
$$2H_2S \rightleftharpoons 2H_2 + 2S$$

In all these reactions, there is a change in the number of molecules. Hence, $K_p \neq K_c$.

We shall study some of the reactions in detail.

Dissociation of Phosphorus Pentachloride

Let us start with n moles of PCl_5 and let α is the degree of dissociation of PCl_3. If V is the volume of the system, then the equilibrium is represented by

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial molar concentrations	$\frac{n}{V}$		0		0
Equilibrium molar concentrations	$\frac{n(1-\alpha)}{V}$		$\frac{n\alpha}{V}$		$\frac{n\alpha}{V}$

The equilibrium constant in terms of concentration is given by

$$K_c = \frac{C_{PCl_3}\, C_{Cl_2}}{C_{PCl_5}}$$

$$K_c = \frac{\frac{n\alpha}{V} \cdot \frac{n\alpha}{V}}{\frac{n(1-\alpha)}{V}} = \frac{n\alpha^2}{(1-\alpha)V}$$

It should be noted that V occurs in the denominator. Hence, as V increases,

$$\frac{\alpha^2}{(1-\alpha)}$$

must also increase to maintain constancy of K_c.

This means that an increase in volume (or decrease in pressure) will increase the degree of dissociation. This is also confirmed when equilibrium constant in terms of pressure is calculated.

This is shown below:

	PCl_5	$\rightleftharpoons$	PCl_3	$+ Cl_2$
Initial number of moles	n		0	0
Number of moles at equilibrium	$n(1-\alpha)$		$n\alpha$	$n\alpha$

Total number of moles at equilibrium,

$$n_t = n - n\alpha + n\alpha + n\alpha$$
$$= n(1+\alpha)$$

Let the equilibrium pressure is P.

Therefore, the various partial pressures are given by

$$P_{PCl_5} = \left[\frac{n(1-\alpha)}{n(1+\alpha)}\right]P = \left(\frac{1-\alpha}{1+\alpha}\right)P$$

$$P_{PCl_3} = \left[\frac{n(\alpha)}{n(1+\alpha)}\right]P = \left(\frac{\alpha}{1+\alpha}\right)P$$

and
$$P_{PCl_2} = \left[\frac{n\alpha}{n(1+\alpha)}\right]P = \left(\frac{\alpha}{1+\alpha}\right)P$$

$$K_p = \frac{P_{PCl_3} \, . \, P_{Cl_2}}{P_{PCl_5}}$$

$$K_p = \frac{\left(\frac{\alpha}{1+\alpha}\right)P . \left(\frac{\alpha}{1+\alpha}\right)P}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

or
$$K_p = \frac{\alpha^2}{1-\alpha^2} \; . \; P$$

From this equation, it can easily be shown that a decrease in P will increase α. This is also in agreement with Le-Chatelier Braun principle.

Dissociation of Nitrogen Tetraoxide

Let n is the initial number of moles of nitrogen tetraoxide and let α be the degree of dissociation at equilibrium. The total volume of the system is V. The equilibrium is represented as,

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial number of moles	n		0
Number of moles at equilibrium	$n(1-\alpha)$		$2n\alpha$

$$\therefore \qquad K_c = \frac{C^2_{NO_2}}{C_{N_2O_4}} = \frac{\left(\frac{2n\alpha}{V}\right)^2}{\frac{n(1-\alpha)}{V}}$$

$$K_c = \frac{4n\alpha^2}{(1-\alpha)V}$$

NOTES

Again, $$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

Total number of moles at equilibrium

$$n_t = n(1-\alpha) + 2n\alpha = n(1+\alpha)$$

If the total equilibrium pressure is P, the partial pressures of the various gases are given by

$$P_{NO_2} = \left[\frac{2n\alpha}{n(1+\alpha)}\right]P = \left(\frac{2\alpha}{1+\alpha}\right)P$$

and $$P_{N_2O_4} = \left[\frac{n(1-\alpha)}{n(1+\alpha)}\right]P = \left(\frac{1-\alpha}{1+\alpha}\right)P$$

$\therefore$ $$K_p = \frac{\left[\left(\frac{2\alpha}{1+\alpha}\right)P\right]^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P} = \frac{4\alpha^2 P}{1-\alpha^2}$$

The effect of pressure change is similar as in the case of dissociation of PCl_5. From equation (66), it is evident that from a knowledge of K_p, degree of dissociation at any pressure can be calculated.

The Ammonia Equilibria: Ammonia is obtained by combining one part of nitrogen with three parts of hydrogen. The reaction is reversible as shown below:

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

Let us start with 1 mole of nitrogen and 3 moles of hydrogen in a closed vessel of volume V and let x moles be the amount of ammonia at equilibrium.

The various concentration terms at equilibrium are given by

$$C_{N_2} = \frac{1-x}{V};\ C_{H_2} = \frac{3-3x}{V}$$

and $$C_{NH_3} = \frac{2x}{V}$$

Therefore, equilibrium constant in terms of concentration is given by

$$K_c = \frac{C^2_{NH_3}}{C_{N_2}\,.\,C^3_{H_2}}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}$$

$$K_c = \frac{4x^2V^2}{27(1-x)^4} \qquad \text{...(67)}$$

To calculate the equilibrium constant in terms of pressure, i.e., K_p we proceed as follows:

At equilibrium:

Number of moles of $N_2 = 1 - x$

Number of moles of $H_2 = 3 - 3x = 3\ (1 - x)$

Number of moles of $NH_3 = 2x$

Therefore, the total number of moles

$$= 1 - x + 3 - 3x + 2x = 4 - 2x$$

If P is the total equilibrium pressure, the partial pressures of the various gases are given by

$$P_{N_2} = \frac{(1-x)}{(4-2x)} P$$

$$P_{H_2} = \frac{3(1-x)}{4-2x} P$$

$$P_{NH_3} = \frac{2x}{4-2x} P$$

and

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \,.\, P^3_{H_2}}$$

$$K_p = \frac{\left(\frac{2x}{4-2x}\right)^2 P^2}{\frac{(1-x)}{(4-2x)} P \,.\, \left[\frac{3(1-x)}{4-2x}\right]^3 P^3}$$

$$K_p = \frac{4x^2(4-2x)^2}{27(1-x)^4 P^2} \qquad \text{...(68)}$$

If x is negligibly small as compared to unity, then equation (68) becomes

$$K_p = \frac{64x^2}{27P^2} \quad \text{or} \quad x^2 = \frac{27}{64} K_p P^2$$

From this, it is clear that $x \propto P$ (K_p is constant at constant temperature).

In other words the formation of ammonia increases with increase of pressure. This is also evident from Le-Chatelier Braun principle according to which the formation of ammonia is favoured by an increase of pressure (since formation of ammonia is attended by a decrease in volume from 4 molar volumes to two molar volumes). Hence, in the synthesis of ammonia, a pressure of 200 atmosphere or more, is used in practice.

Problem

NOTES

In a mixture of 1 part of N_2 to 3 parts of H_2, the mole per cent of NH_3 at equilibrium was found to be 1.20 at 500°C at a total pressure of 10 atm. Calculate the value of K_p and the pressure at which the equilibrium mixture at this temperature contains 10.4 mole per cent of NH_3.

Solution. Let x be the mole fraction of NH_3 at equilibrium, so that $100\,x$ is the mole per cent. The sum of the mole fractions of N_2 and H_2 must then be $1-x$, and since these gases are in the ratio of 1 to 3, it follows that

$$X_{N_2} = \frac{1}{4}(1-x) \text{ and } \qquad X_{H_2} = \frac{3}{4}(1-x)$$

and so, if P is the total pressure,

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}}$$

$$K_p = \frac{(xP)^2}{\frac{1}{4}(1-x)P \times \left(\frac{3}{4}(1-x)P\right)^3}$$

In the present example, P is 10 atm;

100 x is 1.20 so that $\quad x = 0.0120$

and $\quad 1 - x = 0.988.$

Consequently
$$K_p = \frac{(0.0120 \times 10)^2}{\left(\frac{1}{4} \times 0.988 \times 10\right)\left(\frac{3}{4} \times 0.988 \times 10\right)^3}$$

$$= 1.43 \times 10^{-5}$$

with the pressure in atm.

It is now required to calculate P corresponding to $100\,x = 10.4$

i.e., $\quad x = 0.104$ and $1 - x = 0.896$; thus

$$K_p = 1.43 \times 10^{-5}$$

$$K_p = \frac{(0.104 \times P)^2}{\left(\frac{1}{4} \times 0.896 \times P\right) \times \left(\frac{3}{4} \times 0.896 \times P\right)^3}$$

2.8.2 Entropy Balance Equation for Different Irreversible Process

When heat flows from high to low temperature or a gas expands in vacuum, it is observed that these processes occur spontaneously and are thermodynamically irreversible. All natural processes are more or less irreversible. The driving force that causes reactions to proceed spontaneously is the lack of balance in these processes. We can define irreversible processes as those which have a natural tendency to occur. These processes are spontaneous.

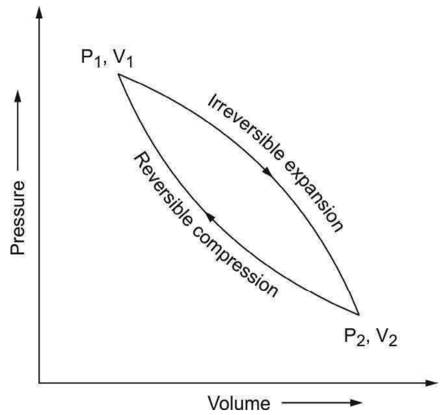

Fig. 2.25 Entropy change for a cycle containing an irreversible step

In order to calculate entropy change for any irreversible process, advantage is taken of the fact that the entropy change of the system depends only on the initial and final states and not on the path of the reaction.

Consider an isothermal and irreversible expansion of the substance from volume V_1 to V_2. During this process, let q be the amount of heat absorbed by the substance. The work done by the substance (W) during its irreversible expansion is less than that done in a reversible compression (W_{rev}). The heat absorbed q will also be less than heat absorbed (q_r) for a reversible expansion. Since the heat change in a process depends on the path adopted, the heat taken up irreversibly can have any value between $q = 0$ and $q = q_r$, i.e., the maximum value is that for a reversible process. But ΔS, being a function of state, will have only one value for a change between the same initial and final states irrespective of how the process is carried out. Thus, we have

$$\Delta S_{\text{irr}, V_1 \to V_2(\text{system})} = \Delta S_{rev, V_1 \to V_2(\text{system})} = \frac{q_r}{T}$$

However, the loss of heat q_r from the surroundings is considered to have taken place reversibly and so the entropy change of the surroundings is

$$\Delta S_{\text{surroundings}} = \frac{-q}{T}$$

Therefore, the total entropy change for the isothermal irreversible expansion of the substance is

$$\Delta S_{(\text{expansion})} = \Delta S_{(\text{system})} + \Delta S_{(\text{surroundings})}$$

$$= \frac{q_r}{T} - \frac{q}{T} > 0 \text{ (since } q_r > q)$$

...(74*a*)

Hence, an irreversible process occurring isothermally in an isolated system leads to an increase in the total entropy of the system.

In order to complete the cycle, the substance is returned to its original state by compressing it reversibly and isothermally from V_2 to V_1. In order to accomplish this, work is done on the substance and the amount of heat, q_r, produced is returned to the surroundings. The net result is that the change in entropy of the working substance will be equal to $\frac{-q_r}{T}$ and the entropy change of the surroundings will be $\frac{q_r}{T}$. Therefore, total change of entropy during reversible, isothermal compression is given by equation (8.20b).

$$\Delta S_{(\text{compression})} = -\frac{q_r}{T} + \frac{q_r}{T} = 0 \qquad ...(74b)$$

which is the usual result for a reversible process in an isolated system.

The total entropy change for the irreversible cycle will be the sum of equations (74*a*) and (74*b*), i.e.,

$$\Delta S_{\text{total}} = \frac{q_r}{T} - \frac{q}{T} > 0 \qquad ...(75)$$

Thus, *in any irreversible cyclic process, there is an increase in the entropy.*

The increase in entropy for any irreversible cyclic process is due to conversion of work into heat. At the end of the cycle, since the working substance has returned to its original state, it suffers no change of any kind. However, the surroundings lost heat equal to q, in the irreversible expansion but gained heat equal to q_r in the reversible compression. The net heat gained by the reservoir is thus $(q_r - q)$ and hence, its entropy gain is $\left(\frac{q_r}{T} - \frac{q}{T}\right)$ a quantity greater than zero. At the same time, the work performed by the working substance in the irreversible expansion is W while that performed on the working substance in W_m. Thus, the net work in cycle is $(W - W_m)$ which is less than zero since $W_m > W$. A negative value of the net work indicates that this work was done by the working substance and this resulted in the liberation of heat which was taken up by the surroundings; thus causing an entropy increase in the surroundings.

The statements of equations (8.20) and (8.21) are also valid for non - isothermal processes.

2.8.3 Fluxes and Forces

Transformation of the Generalized Fluxes and Forces

The external fields modify the internal energy of the semiconductor, which defines the variables representing the thermodynamic system. The fluxes are the response to the forces that interact with the thermodynamic model of the system. They are the whole current, the electron current, and the total energy. The forces, also called affinities, are the gradients of the quasi Fermi levels and the temperature.

The fundamental relation of classical equilibrium thermodynamics,

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum_{i=1}^{s} \frac{\mu_i}{T} dN_i$$

NOTES

expresses the change in entropy dS of a system as a function of the intensive quantities temperature T, pressure p and *i* chemical potential μ_i and of the differentials of the extensive quantities energy U, volume V and *i* particle number N_i.

2.8.4 Phenomenological Equations

phenomenology is the application of theoretical physics to experimental data by making quantitative predictions based upon known theories. It is related to the philosophical notion of the same name in that these predictions describe anticipated behaviours for the phenomena in reality. Phenomenology stands in contrast with experimentation in the scientific method, in which the goal of the experiment is to test a scientific hypothesis instead of making predictions.

Phenomenology is commonly applied to the field of particle physics, where it forms a bridge between the mathematical models of theoretical physics, such as quantum field theories and theories of the structure of space-time and the results of the high-energy particle experiments.

In the absence of matter flows, Fourier's law is usually written:

$$\mathbf{J}_u = -k\nabla T$$

where *k* is the thermal conductivity. However, this law is just a linear approximation, and holds only for the case where {\displaystyle \nabla T\ll T} $\nabla T \ll T$, with the thermal conductivity possibly being a function of the thermodynamic state variables, but not their gradients or time rate of change. Assuming that this is the case, Fourier's law may just as well be written:

$$\mathbf{J}_u = kT^2\nabla(1/T)$$

In the absence of heat flows, Fick's law of diffusion is usually written:

$$\mathbf{J}_\rho = -D\nabla\rho$$

where *D* is the coefficient of diffusion. Since this is also a linear approximation and since the chemical potential is monotonically increasing with density at a fixed temperature, Fick's law may just as well be written:

$$\mathbf{J}_\rho = D'\nabla(-\mu/T)$$

where, again, D' is a function of thermodynamic state parameters, but not their gradients or time rate of change. For the general case in which there are both mass and energy fluxes, the phenomenological equations may be written as:

$$\mathbf{J}_u = L_{uu}\nabla(1/T) + L_{u\rho}\nabla(-\mu/T)$$
$$\mathbf{J}_\rho = L_{\rho u}\nabla(1/T) + L_{\rho\rho}\nabla(-\mu/T)$$

or, more concisely,

$$\mathbf{J}_\alpha = \sum_\beta L_{\alpha\beta} \nabla f_\beta$$

where the entropic 'Thermodynamic Forces' conjugate to the 'Displacements'

ρ are $\nabla f_u = \nabla(1/T)$ and $\nabla f_\rho = \nabla(-\mu/T)$ and $L_{\alpha\beta}$ is the Onsager matrix of transport coefficients.

2.8.5 Electrokinetic Phenomenon

Maceration is the winemaking process where the phenolic materials of the grape—tannins, coloring agents (anthocyanins) and flavor compounds—are leached from the grape skins, seeds and stems into the must. To macerate is to soften by soaking, and maceration is the process by which the red wine receives its red color, since raw grape juice (with the exceptions of teinturiers) is clear-grayish in color. In the production of white wines, maceration is either avoided or allowed only in very limited manner in the form of a short amount of skin contact with the juice prior to pressing. This is more common in the production of varietals with less natural flavor and body structure like Sauvignon blanc and Sémillon. For Rosé, red wine grapes are allowed some maceration between the skins and must, but not to the extent of red wine production.

The process of maceration begins, to varying extent, as soon as the grapes' skins are broken and exposed to some degree of heat. Temperature is the guiding force, with higher temperatures encouraging more breakdown and extraction of phenols from the skins and other grape materials. Maceration continues during the fermentation period, and can last well past the point when the yeast has converted all sugars into alcohol. The process itself is a slow one with compounds such as the anthocyanins needing to pass through the cell membrane of the skins to come into contact with the wine. During fermentation, higher temperatures and higher alcohol levels can encourage this process with the alcohol acting as a solvent to assist in the breakdown of the organic compounds within the grape materials. This process seems to slow once the wine reaches an alcohol level of 10%.

PAGE

PolyAcrylamide Gel Electrophoresis (PAGE) is a technique widely used in biochemistry, forensic chemistry, genetics, molecular biology and biotechnology to separate biological macromolecules, usually proteins or nucleic acids, according to their electrophoretic mobility. Electrophoretic mobility is a function of the length, conformation and charge of the molecule. Polyacrylamide gel electrophoresis is a powerful tool used to analyze RNA samples. When polyacrylamide gel is denatured after electrophoresis, it provides information on the sample composition of the RNA species.

Hydration of acrylonitrile results in formation of acrylamide molecules (C_3H_5NO) by nitrile hydratase. Acrylamide monomer is in a powder state before addition of water. Acrylamide is toxic to the human nervous system, therefore all safety measures must be followed when working with it. Acrylamide is soluble in water and upon addition of water it polymerizes resulting in formation of polyacrylamide. It is useful to make polyacrylamide gel via acrylmide hydration because pore size can be regulated. Increased concentrations of acrylamide result in decreased pore size after polymerization. Polyacrylamide gel with small pores helps to examine smaller molecules better since the small molecules can enter the pores and travel through the gel while large molecules get trapped at the pole openings.

As with all forms of gel electrophoresis, molecules may be run in their native state, preserving the molecules' higher-order structure. This method is called native-PAGE. Alternatively, a chemical denaturant may be added to remove this structure and turn the molecule into an unstructured molecule whose mobility depends only on its length (because the protein-SDS (Sodium Dodecyl Sulphate) complexes all have a similar mass-to-charge ratio). This procedure is called SDS-PAGE. Sodium Dodecyl Sulfate PolyAcrylamide Gel Electrophoresis (SDS-PAGE) is a method of separating molecules based on the difference of their molecular weight. At the pH at which gel electrophoresis is carried out the SDS molecules are negatively charged and bind to proteins in a set ratio, approximately one molecule of SDS for every 2 amino acids. In this way, the detergent provides all proteins with a uniform charge-to-mass ratio. By binding to the proteins the detergent destroys their secondary, tertiary and/or quaternary structure denaturing them and turning them into negatively charged linear polypeptide chains. When subjected to an electric field in PAGE, the negatively charged polypeptide chains travel toward the anode with different mobility. Their mobility, or the distance travelled by molecules, is inversely proportional to the logarithm of their molecular weight. By comparing the relative ratio of the distance travelled by each protein to the length of the gel (RF) one can make conclusions about the relative molecular weight of the proteins, where the length of the gel is determined by the distance traveled by a small molecule like a tracking dye.

For nucleic acids, urea is the most commonly used denaturant. For proteins, Sodium Dodecyl Sulfate (SDS) is an anionic detergent applied to protein samples to coat proteins in order to impart two negative charges (from every SDS molecule) to every two amino acids of the denatured protein. 2-Mercaptoethanol may also be used to disrupt the disulfide bonds found between the protein complexes, which helps further denature the protein. In most proteins, the binding of SDS to the polypeptide chains impart an even distribution of charge per unit mass, thereby resulting in a fractionation by approximate size during electrophoresis. Proteins that have a greater hydrophobic content — for instance, many membrane proteins, and those that interact with surfactants in their native environment — are intrinsically harder to treat accurately using this method, due to the greater variability in the ratio of bound SDS. Procedurally, using both Native and SDS-PAGE together can be used to purify and to separate the various sub units of the protein. Native-PAGE keeps the oligomeric form intact and will show a band on the gel that is representative of the level of activity. SDS-PAGE will denature and separate the oligomeric form into its monomers, showing bands that are representative of their molecular weights. These bands can be used to identify and assess the purity of the protein.

2.8.6 Irreversible Thermodynamics for Biological Systems

Biological thermodynamics is the quantitative study of the energy transductions that occur in or between living organisms, structures, and cells and of the nature and function of the chemical processes underlying these transductions. Biological thermodynamics may address the question of whether the benefit associated with any particular phenotypic trait is worth the energy investment it requires.

Although evolution through natural selection has been vastly accepted in the scientific community as a fundamental law of biology, it has been criticized for being an incomplete interpretation of evolutionary processes. Natural selection cannot account for,

- The irreversibility of evolution
- The complexity-generating or anamorphic tendency of biological systems
- The self-organizing behaviour exhibited by all biological life forms

The biological evolution may be explained through a thermodynamic theory. The four laws of thermodynamics are used to frame the biological theory behind evolution. The first law of thermodynamics states that energy cannot be created or destroyed. No life can create energy but must obtain it through its environment. The second law of thermodynamics states that energy can be transformed and that occurs every day in lifeforms. As organisms take energy from their environment, they can transform it into useful energy. This is the foundation of tropic dynamics.

2.8.7 Microscopic Reversibility and Onsager's Reciprocity Relations

Onsager-Machlup time reversal properties of thermodynamic fluctuations and Onsager reciprocity relations for transport coefficients can hold also if the microscopic dynamics is not reversible.

In thermodynamics, the Onsager reciprocal relations express the equality of certain ratios between flows and forces in thermodynamic systems out of equilibrium, but where a notion of local equilibrium exists.

Reciprocal relations occur between different pairs of forces and flows in a variety of physical systems. For example, consider fluid systems described in terms of temperature, matter density, and pressure. In these systems, it is known that temperature differences lead to heat flows from the warmer to the colder parts of the system; similarly, pressure differences will lead to matter flow from high-pressure to low-pressure regions. The remarkable observation in these reactions is that, when both pressure and temperature vary, temperature differences at constant pressure can cause matter flow (as in convection) and pressure differences at constant temperature can cause heat flow. The heat flow per unit of pressure difference and the density (matter) flow per unit of temperature difference are equal. This equality was shown to be necessary by **Lars Onsager** using statistical mechanics as a consequence of the **time reversibility** of **microscopic dynamics** (microscopic reversibility). The theory developed by Onsager specify for more than two thermodynamic forces at once, with the limitation that "the principle of dynamical reversibility does not apply when (external) magnetic fields or Coriolis forces are present", in which case "the reciprocal relations break down".

Experimental verifications of the Onsager reciprocal relations were collected and analyzed by D. G. Miller for many classes of irreversible processes, namely for thermoelectricity, electrokinetics, transference in electrolytic solutions, diffusion, conduction of heat and electricity in anisotropic solids, thermomagnetism and galvanomagnetism. Therefore, chemical reactions are considered as 'Cases with Meager' and inconclusive evidence. Further theoretical analysis and experiments support the reciprocal relations for chemical kinetics with transport.

Onsager's reciprocal relations represent a further law making a thermodynamic study of irreversible processes possible. Some authors have even described Onsager's relations as the "Fourth Law of Thermodynamics".

2.9 NON-EQUILIBRIUM THERMODYNAMICS

Non-equilibrium thermodynamics is a branch of thermodynamics that deals with physical systems that are not in thermodynamic equilibrium but can be described in terms of variables (non-equilibrium state variables) that represent an extrapolation of the variables used to specify the system in thermodynamic equilibrium. Non-equilibrium thermodynamics is concerned with transport processes and with the rates of chemical reactions. It relies on what may be thought of as more or less nearness to thermodynamic equilibrium.

Almost all systems found in nature are not in thermodynamic equilibrium, for they are changing or can be triggered to change over time and are continuously and discontinuously subject to flux of matter and energy to and from other systems and to chemical reactions. Some systems and processes are, however, in a useful sense, near enough to thermodynamic equilibrium to allow description with useful accuracy by currently known non-equilibrium thermodynamics. Nevertheless, many natural systems and processes will always remain far beyond the scope of non-equilibrium thermodynamic methods due to the existence of non-variational dynamics, where the concept of free energy is lost.

The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics. One fundamental difference between equilibrium thermodynamics and non-equilibrium thermodynamics lies in the behaviour of inhomogeneous systems, which require for their study knowledge of rates of reaction which are not considered in equilibrium thermodynamics of homogeneous systems. Another fundamental and very important difference is the difficulty or impossibility, in general, in defining entropy at an instant of time in macroscopic terms for systems not in thermodynamic equilibrium; it can be done, to useful approximation, only in carefully chosen special cases, namely those that are throughout in local thermodynamic equilibrium.

Thermodynamic Criteria for Non-Equilibrium States

A profound difference separates equilibrium from non-equilibrium thermodynamics. Equilibrium thermodynamics ignores the time-courses of physical processes. In contrast, non-equilibrium thermodynamics attempts to describe their time-courses in continuous detail.

Equilibrium thermodynamics restricts its considerations to processes that have initial and final states of thermodynamic equilibrium; the time-courses of processes are deliberately ignored. Consequently, equilibrium thermodynamics allows processes that passes through states far from thermodynamic equilibrium, that cannot be described even by the variables admitted for non-equilibrium thermodynamics, such as time rates of change of temperature and pressure. For example, in equilibrium thermodynamics, a process is allowed to include explosion that cannot be described by non-equilibrium thermodynamics. Equilibrium thermodynamics does, however, for theoretical development, use the idealized concept of the 'quasi-static process'. A quasi-static process is a conceptual (timeless and physically impossible) smooth mathematical passage along a continuous path of states of thermodynamic equilibrium. It is an exercise in differential geometry rather than a process that could occur in actuality.

Non-equilibrium thermodynamics describe continuous time-courses, needs its state variables to have a very close connection with those of equilibrium thermodynamics.

Non-Equilibrium State Variables

The suitable relationship that defines non-equilibrium thermodynamic state variables when the system happens to be in states that are sufficiently close to thermodynamic equilibrium, non-equilibrium state variables are such that they can be measured locally with sufficient accuracy by the same techniques as are used to measure thermodynamic state variables, or by corresponding time and space derivatives, including fluxes of matter and energy. In general, non-equilibrium thermodynamic systems are spatially and temporally non-uniform, but their non-uniformity still has a sufficient degree of smoothness to support the existence of suitable time and space derivatives of non-equilibrium state variables.

Because of the spatial non-uniformity, non-equilibrium state variables that correspond to extensive thermodynamic state variables have to be defined as spatial densities of the corresponding extensive equilibrium state variables. When the system is sufficiently close to thermodynamic equilibrium, intensive non-equilibrium state variables, for example temperature and pressure, correspond closely with equilibrium state variables. It is necessary that measuring probes be small enough, and rapidly enough responding, to capture relevant non-uniformity. Further, the non-equilibrium state variables are required to be mathematically functionally related to one another in ways that suitably resemble corresponding relations between equilibrium thermodynamic state variables. These requirements are very demanding, and it may be difficult or practically, or even theoretically, impossible to satisfy them.

Some concepts of particular importance for non-equilibrium thermodynamics include time rate of dissipation of energy (Rayleigh 1873, Onsager 1931), time rate of entropy production (Onsager 1931), thermodynamic fields, dissipative structure, and non-linear dynamical structure.

One problem of interest is the thermodynamic study of non-equilibrium steady states, in which entropy production and some flows are non-zero, but there is no time variation of physical variables.

One initial approach to non-equilibrium thermodynamics is sometimes called 'Classical Irreversible Thermodynamics'. There are other approaches to non-equilibrium thermodynamics, for example extended irreversible thermodynamics, and generalized thermodynamics.

2.9.1 Entropy Production and Entropy Flow

For any substance subjected to Carnot cycle operating reversibly between temperatures T_2 and T_1, we have

$$\frac{W}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or $$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or $$\frac{q_2}{T_2} + \left(\frac{-q_1}{T_1}\right) = 0 \qquad ...(8.14)$$

As one isothermal and one adiabatic changes are involved, equation (8.14) is the algebraic sum of the $\frac{q}{T}$ terms where q_2 is the heat absorbed reversibly by the system at T_2 and $-q_1$, the heat absorbed at the temperature T_1. It may also be noted from equation (8.14) that the sum of the ratios $\frac{q}{T}$ around a closed path is zero.

It can be shown that any reversible cyclic process may be regarded as made up of a large number of Carnot cycles and the sum of the entropy changes for the various cycles must equal to zero. Consider for example, a reversible cyclic process being represented by *abcd* in Fig. 2.26. This may be approximated by Carnot cycles. The changes *abc* and *cda* may be regarded as a grid of isotherms and adiabatics. The grid can be used to construct a set of Carnot cycles so that the outer parts of the set trace out a curve that approximates the general Carnot cycle. If we were to carry out all these Carnot cycles the net result would be the same as performing the cyclic process *abcd*.

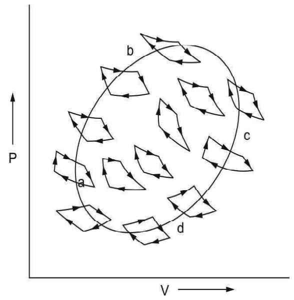

Fig. 2.26 *A cyclic process approximated by a set of Carnot cycles*

This is so because the Carnot cycles that are inside the boundary cancel out because each is traced in both forward and in the reverse direction. If one goes to the limit of an infinitely closely spaced grid, one can obtain an exact reproduction of any process. Thus, for a reversible cyclic process performed on an ideal gas, we get equation (70)

$$\sum_{\text{Cycle}} \frac{q_{rev}}{T} = 0 \qquad ...(70)$$

where q_{rev} represents the various heats absorbed divided by the temperatures at which the absorption of heat occurs. Σ means the summation of $\frac{q_{rev}}{T}$ terms in all the Carnot cycles in which the process is divided. Equation 71 can also be written as

$$\oint \frac{dq_{rev}}{T} = 0 \qquad ...(71)$$

where $\oint$ signifies the integration around a complete cycle, and dq_{rev} is the heat absorbed in an infinitesimal small process carried out reversibly.

Definition of entropy. Mathematically, it follows from equation (71) that as the cyclic integral vanishes, the integrand must be a perfect differential of some function of state of the system. This function was named 'entropy' by Clausius for the first time and denoted by the symbol S. The actual entropy of a system is not easily defined, it is rather more convenient to define the change in the entropy, dS, for an infinitesimal stage of an appreciable reversible process which takes place by taking δq_{rev} calories of heat at constant temperature as

$$dS = \frac{\delta q_{rev}}{T} \qquad ...(72)$$

where T is the temperature in absolute. If heat enters a body, δq_{rev} is positive and the entropy change is positive.

For any appreciable change, the change in entropy, ΔS, when a system goes from the initial state a to the final state b at a constant temperature T is given by

$$\Delta S = S_b - S_a = \int_a^b \frac{\delta q_{rev}}{T} \qquad ...(73)$$

Since entropy, like the energy, is a function of state, dS, like dE, is a complete differential. S is thus independent of the past history of the system and can be expressed in terms of thermodynamic parameters (P, V, T). The entropy of a system, like the energy, is an extensive property, dependent upon the amount of matter in the system.

Units. Entropy has units of calories per degree and is often stated as 'entropy unit' (e.u.).

Check Your Progress

13. State the phase rule.
14. Give the basic postulate of Maxwell-Boltzmann distribution.
15. Define the partition function.
16. What is equilibrium constant?
17. Give the types of equilibria.
18. Define the non-equilibrium state in thermodynamics.
19. What do you understand by phenomenology?
20. What is biological thermodynamics?

2.8 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for another law, i.e., the second law of thermodynamics.
2. The ***zeroth law of thermodynamics*** defines thermal equilibrium and forms a basis for the definition of temperature: If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.
3. The actual entropy of a system is difficult to define and hence defined in terms of change of entropy during change of state. The change of entropy of a system is defined as the integral of all forms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process being carried reversibly or very simply as the heat transferred during a reversible process to the absolute temperature of the system. For infinitesimal change in state of a system at constant temperature T, $dS = \frac{dq_{\text{rev}}}{T}$.
4. **Units of Entropy:** In C.G.S. units,

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\text{Calorie/mol}}{\text{Kelvin}} = \text{Cal mol}^{-1}\ \text{K}^{-1}$$

In S.I. units, $\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\text{Joules/mol}}{\text{Kelvin}} = \text{J mol}^{-1}\ \text{K}^{-1}$

5. The free energy of a system is defined as the maximum energy available to a system which can be converted into useful work. The above definition of free energy can be defined by considering 'Gibbs Free Energy'.
6. The change in free energy per mole addition of a component keeping other components fixed at a fixed temperature is called the partial molar free energy.

7. The amount of heat required to raise the temperature of one gram of a substance by 1ºC or 1 K is called the specific heat. The heat capacity (*C*) of a substance is the amount of heat required to raise the temperature by 1ºC or 1 K of one mole of substance.
8. A phase is a part of a system that is homogeneous in its composition and properties and is physically distinct from other parts of the system. Under equilibrium condition several phases can co-exist. By changing the conditions of a system (i.e., pressure, temperature and composition, etc.) the material might be transformed from one phase to another.
9. In chemical thermodynamics, the fugacity of a real gas is an effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant.
10. The Debye–Hückel equation provides a starting point for modern treatments of non-ideality of electrolyte solutions.
11. Activity of a substance in any given state is thus defined as the ratio of the fugaciy of the substance in that state to the fugacity of the same substant in the pure state.
12. Single-ion activity coefficients can be calculated theoretically, for example by using the Debye–Hückel equation. The theoretical equation can be tested by combining the calculated single-ion activity coefficients to give mean values which can be compared to experimental values.
13. Activity of a substance in any given state is thus defined as the ratio of the fugaciy of the substance in that state to the fugacity of the same substant in the pure state.

    The phase rule is a generalization which seems to explain the equilibrium existing between the heterogeneous system and was theoretically deduced by Willard Gibbs in 1876. Mathematically, it may be stated as

    $F + P = C + 2$
14. The basis postulates of MB statistics are:
    (*i*) The associated particles are distinguishable.
    (*ii*) Each energy state can contain any number of praticles.
    (*iii*) Total number of particles in the entire system is constant.
    (*iv*) Total energy of all the particles in the entire system is constant.
    (*v*) Particles are spinless.
15. In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume.
16. The equilibrium constant expressions in terms of pressure and concentration for this reaction are

$$K_p = \frac{\alpha^2 P}{1 - \alpha^2};\ K_c = \frac{n\alpha^2}{(1 - \alpha)V}$$

Let us now consider two cases:

17. There are two types of equilibria:
    - **Homogeneous equilibria** in which only one phase occurs. For example, a system containing only gases or a single liquid or solid phase.
    - **Heterogeneous equilibria** in which more than a single phase appears.

    For example, equilibrium between solid and gas, liquid and gas, solid and liquid, solid and solid, immiscible liquids, etc.
18. Non-equilibrium thermodynamics is a branch of thermodynamics that deals with physical systems that are not in thermodynamic equilibrium but can be described in terms of variables (non-equilibrium state variables) that represent an extrapolation of the variables used to specify the system in thermodynamic equilibrium.
19. Phenomenology is the application of theoretical physics to experimental data by making quantitative predictions based upon known theories. It is related to the philosophical notion of the same name in that these predictions describe anticipated behaviours for the phenomena in reality.
20. Biological thermodynamics is the quantitative study of the energy transductions that occur in or between living organisms, structures, and cells and of the nature and function of the chemical processes underlying these transductions.

2.9 SUMMARY

- The first law establishes definite relationship between the heat absorbed and the work performed by a system in a given process. But it pits no restriction on the direction of the flow of heat.
- The second law of thermodynamics helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously, that is, its own accord. It also helps us to know the equilibrium conditions.
- The second law of thermodynamics is needed because the first law of thermodynamics does not define the energy conversion process completely. The first law is used to relate and to evaluate the various energies involved in a process.
- The second law of thermodynamics is used to determine the maximum efficiency of any process. A comparison can then be made between the maximum possible efficiency and the actual efficiency obtained.
- The ***third law of thermodynamics states*** that a system's entropy approaches a constant value as the temperature approaches absolute zero. With the exception of non-crystalline solids (glasses) the entropy of a system at absolute zero is typically close to zero.
- The zeroth law of thermodynamics provides for the foundation of temperature as an empirical parameter in thermodynamic systems and establishes the transitive relation between the temperatures of multiple bodies in thermal equilibrium.

- The first law of thermodynamics is a related to the law of conservation of energy, adapted for thermodynamic processes. In general, the conservation law states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.
- At zero temperature, the system must be in the state with the minimum thermal energy, the ground state. The constant value (not necessarily zero) of entropy at this point is called the *residual entropy* of the system. Note that, with the exception of non-crystalline solids (e.g. glasses) the residual entropy of a system is typically close to zero.
- The first law of thermodynamics proclaims constancy of the total energy of isolated system for all changes, taking place in this system: energy cannot be created or destroyed. According to the second law of thermodynamics in isolated system entropy is always increasing or remaining constant.
- Removing heat from the food items in the refrigerator and throwing it away to the higher temperature atmosphere does not happen automatically. We need to supply external work via the compressor to make this happen in the refrigerator.
- Physically, entropy is a measure of molecular order. A change in entropy dS (infinitesimal change) or ΔS (finite change) corresponds to a change in the amount of molecular order of a system.
- For an irreversible process there is a net rise in entropy (ΔS_{univ} is positive). Natural processes are spontaneous and irreversible. Thus, natural process will take place in a direction in which entropy would increase or where there is no net increase in entropy process will not occur spontaneously.
- For ideal gas there is no interaction between the gaseous molecules, under such conditions γ is unity and $f = P$. For non ideal gas there is interaction between the gaseous molecules and $f = \gamma P$.
- One of the important application of Gibbs-Duhem equation is prediction of condition of equilibrium. For simplicity we consider the phase of a component in equilibrium having free energies $\bar{G}_1$ and $\bar{G}_2$.
- The heat supplied at constant pressure increases the temperature of the body by dT, i.e., increases the internal energy by dE as well as enables the gas to perform dW amount of work.
- Under equilibrium conditions the two phases have same Gibbs free energies. The Gibbs free energy is a measure of the stability of a phase.
- Accurate calculations of chemical equilibrium for real gases should use the fugacity rather than the pressure. The thermodynamic condition for chemical equilibrium is that the total chemical potential of reactants is equal to that of products.
- The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte

solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have r^{-7} dependence, and for practical purposes this can be considered ideal.

- Single **ion activity coefficients** must be linked to the activity coefficient of the dissolved electrolyte as if undissociated.
- The various methods of statistical mechanics are applied to discuss some average or most probable properties of large assemblies of electrons, atoms, molecules, etc. Before the advent of quantum mechanics, Maxwell, Boltzmann, Gibbs etc.,
- A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces.
- If an inert gas is added at constant volume, the various equilibrium concentration terms involved are not changed. Since, the concentration of an inert gas is not involved in the equilibrium constant expression, therefore, the equilibrium remains unchanged.

2.10 KEY TERMS

- **Thermodynamics:** It is the branch of physical science that deals with the relationships between heat and other forms of energy.
- **First law of thermodynamics:** The first law of thermodynamics states that, when energy passes into or out of a system (as work, heat, or matter), the system's internal energy changes in accord with the law of conservation of energy.
- **Standard entropy of substance (S^o):** The entropy of one mole of a substance in its pure state at 1 atm pressure and 25ºC is called the standard entropy of that substance and is denoted by S^o.
- **Fugacity:** In chemical thermodynamics, the fugacity of a real gas is an effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant. It is equal to the pressure of an ideal gas which has the same temperature and molar Gibbs free energy as the real gas.
- **Activity coefficient:** An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances.
- **Partition function:** In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume.

2.11 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What are the failures of first law of thermodynamics?
2. What is the need of the second law of thermodynamics?
3. Give the applications of thermodynamics.
4. Give the third law of thermodynamic.
5. Give the characteristic of entropy function.
6. What is physical significance of entropy?
7. Give the equation for entropy change for an ideal gas.
8. Define the term free energy.
9. Determine the Gibbs free energy.
10. Define the chemical potential.
11. Give the alternative method for heat capacity.
12. Define the fugacity under the condensed phase.
13. State the Debye Hückel theory.
14. What is activity coefficient?
15. Define the phase.
16. State the Maxwell-Boltzmann distribution.
17. Give the postulate the Bose-Einstein statistics.
18. What is translation partition function?
19. Define the chemical equilibria.
20. What do you understand by phenomenological equation?
21. Give the conditions of electrokinetic phenomenon.

Long-Answer Questions

1. Briefly explain the first and second laws of thermodynamics giving appropriate examples.
2. Explain in detail about the principle and applications of thermodynamics.
3. Discuss about the entropy for reversible and irreversible process.
4. Calculate the free energy for real gas, fugacity and mixture of gas.
5. Analyse the chemical potential for DA and DG.
6. Elaborate on the molar heat capacity with specific methods.
7. Interpret the fugacity and its determination.
8. Explain Debye Hückel theory of interionic attraction.
9. Calculate the activity and activity coefficient.

NOTES

10. Analyse the phase rule for the three component.
11. Elaborate on the concept of distribution in statistical thermodynamic.
12. Explain in detail about the Bose-Einstein statistics, Maxwell-Boltzmann distribution and Fermi-Dirac statistics.
13. Elaborate on the translation, rotational, vibrational and electronic partition function.
14. Discuss in detail about the heat capacity and chemical equilibria giving applications.
15. Explain in detail about the thermodynamic criteria for non-equilibrium state with examples.

2.12 FURTHER READING

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UNIT 3 CHEMICAL DYNAMICS

Structure

3.0 INTRODUCTION

Chemical dynamics is a field in which scientists study the rates and mechanisms of chemical reactions. It also involves the study of how energy is transferred among molecules as they undergo collisions in gas-phase or condensed-phase environments.

The rate law or rate equation for a chemical reaction is an equation that links the initial or forward reaction rate with the concentrations or pressures of the reactants and constant parameters. Collision theory states that the rate of a chemical reaction is proportional to the number of collisions between reactant molecules. The steric factor, usually denoted ρ, is a quantity used in collision theory. Also called the probability factor, the steric factor is defined as the ratio between the experimental value of the rate constant and the one predicted by collision theory.

Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy E_a. kinetic salt effect is used to indicate a kinetic salt effect due to a change in concentration of the reacting molecules on account of a change in the inter-ionic forces. A steady state for a differential equation is a solution where the value of y does not change over time.

A chain reaction is a sequence of reactions where a reactive product or by-product causes additional reactions to take place. A photochemical reaction is a chemical reaction triggered when light energy is absorbed by a substance's molecules. Oscillating reactions are among the most fascinating of chemical reactions. In one type of reaction, a mixture of chemicals goes through a sequence of colour changes, and this sequence repeats periodically.

Enzyme kinetics is the study of the rates of enzyme-catalysed chemical reactions. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated.

Homogeneous catalysis refers to reactions where the catalyst is in the same phase as the reactants, principally in solution. Chemical reactions that complete in a very short time, such as less than 10^{-6} seconds, they are called fast reactions. Flow method are a rapid mixing devices used to study the chemical kinetics of fast reactions in solution. Flash photolysis is a pump-probe laboratory technique, in which a sample is first excited by a strong pulse of light from a pulsed laser of nanosecond, picosecond, or femtosecond pulse width or by another short-pulse light source such as a flash lamp.

An NMR instrument allows the molecular structure of a material to be analysed by observing and measuring the interaction of nuclear spins when placed in a powerful magnetic field.

Molecular Dynamics (MD) is a computer simulation method for analysing the physical movements of atoms and molecules. Photoelectron spectroscopy of this anion probes the neutral reaction dynamics in the critical transition-state region. The dynamics of those barrier less reactions differ considerably from chemical reactions where reactants has to overcome an activation barrier [4–10]. In general barrier less reactions are very fast. The subject of unimolecular dynamics deals with the intermolecular and intramolecular microscopic details of unimolecular reactions. Theories of unimolecular dynamics are concerned with molecular motion over potential energy surfaces and the behaviour of molecular coordinates as a function of time.

In this unit, you will study about the chemical dynamics, method determination of rate law, kinetic salt effect, steady state chemical kinetics, thermodynamic or kinetic reaction control, dynamics chain reactions, photochemical reaction hydrogen chlorine and bromine, oscillatory reaction (Belousov-Zhabotinsky (BZ) reaction), homogeneous catalysis, kinetic enzyme reaction, fast reaction, flow and relaxation methods, flash photolysis, Nuclear Magnetic Resonance (NMR), probing the transition state, dynamics of barrier less chemical reactions in solution, dynamics of unimolecular reactions.

3.1 OBJECTIVES

After going through this unhit, you will be able to:

- Understand the chemical dynamics
- Know about the method determination of rate law

- Interpret the kinetic salt effect
- State the steady state chemical kinetics
- Comprehend the thermodynamic or kinetic reaction control
- Understand the dynamics chain reactions
- Discuss the photochemical reaction hydrogen chlorine and bromine
- Elaborate on the oscillatory reaction (Belousov-Zhabotinsky (BZ) reaction)
- Explain the homogeneous catalysis
- Analyse the kinetic enzyme reaction and fast reaction, flow and relaxation methods
- Determine the flash photolysis
- Understand the Nuclear Magnetic Resonance (NMR)
- Analyse the probing the transition state
- Introduce to dynamics of barrier less chemical reactions in solution
- Know about the dynamics of unimolecular reactions

3.2 METHOD DETERMINATION OF RATE LAW

The main objective of these notes is to give a simple and clear cut idea about all aspects of chemical kinetics such as various theories of reaction rates for uni, bi and termolecular reactions, complex reactions, methods for studying fast reactions. Another main objective is to explain the concepts and methodologies of various kinetic techniques in a simple manner so that the learners can easily understand the concepts.

Absolute Reaction Rate Theory (ARRT) of Bimolecular Reactions

Absolute Reaction Rate Theory (ARRT) provides an approach to explain the temperature and concentration dependence of the rate law. The colliding molecules must have sufficient energy to overcome a potential energy barrier to react.

Principles

There is a thermodynamic equilibrium between the transition state and the state of reactants at the top of energy barrier/activation energy barrier. The rate of chemical reaction is proportional to the concentration of the particles in a high-energy. transition state leading to the formation of activated complex. So this theory is also called as Transition state theory or Activated -complex theory. It takes enormous amount of free energy (G) to achieve the transition state, so the state is a high energy substance. The energy difference between the reactants and the potential energy maximum is referred to as activation energy

The bimolecular reaction

$$A + B \xrightarrow{k} C \qquad v = \frac{d(C)}{dt} = k.[A][B] \qquad ...(1)$$

is considered by 'transition state theory'.

According to the transition state model, the reactants are getting over into an unsteady intermediate state on the reaction pathway.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB^{\ddagger} \xrightarrow{k_2} C \qquad ...(2)$$

NOTES

Reaction Coordinates

There is an-'energy barrier' on the pathway between the reactants (A, B) and the product (*C*). The barrier determines a 'threshold energy' or minimum of energy necessary to permit the reaction to occur.

An **'activated complex' AB‡ or 'transition state'** is formed at the potential energy maximum. The high-energy complex represents an unstable molecular arrangement, in which bonds break and form to generate the product **C** or to degenerate back to the reactants **A** and **B**. Once the energy barrier is surmounted, the reaction proceeds downhill to the product.

There is a thermodynamic equilibrium between the transition state and the state of reactants at the top of the energy barrier. The rate of chemical reaction is proportional to the concentration of the ai1icles in the highenergy transition state. The reaction process (2) can be divided into two stages:

(i) A direct step downhill from the transition state to the product
(ii) The equilibrium between the reactants and the transition state.

The change in the concentration of the complex **AB‡**. over time can be described by the following equation,

$$\frac{d[AB^{\ddagger}]}{dt} = k_1[A][B] - k_{-1}.[AB^{\ddagger}] - k_2[AB^{\ddagger}] \qquad ...(3)$$

Due to the equilibrium between the 'activated complex' AB‡ and the reactants **A** and **B**, the components $k_1.[A].[B]$ and $k_1.[AB^{\ddagger}]$) cancel out. Thus the rate of the direct reaction is proportional to the concentration of AB‡:

$$\frac{d(C)}{dt} = -\frac{d[AB^{\ddagger}]}{dt} = k^2.\ [AB^{\ddagger}] \qquad ...(4)$$

k_2 is given by statistical mechanics:

$$k_2 = \frac{k_B.T}{h} \qquad ...(5)$$

k_B = Boltzmann's constant [$1.381 \bullet 10^{-23}$ J•K^{-1}]

T = Absolute temperature in degrees Kelvin (*K*)

h = Plank constant [$6.626 \bullet 10^{-34}$ J•s]

k_2 is called 'universal constant for a transition state'(~ $6 \bullet 10^{-12}$ sec^{-1} at room temperature).

Additionally, [AB‡] can be derived from the qua.si stationary equilibrium between **AB‡** and **A**, **B** by applying the mass action law

$$[AB^{\ddagger}] = K^{\ddagger}\ [A]\ [B] \qquad ...(6)$$

$K^{\ddagger}$ = Thermodynamic equilibrium constaint

Due to the equilibrium that will be reached rapidly, the reactants and the activated complex decrease at the same rate. Therefore, considering both **Equations (5)** and **(6), Equation (4)** becomes:

NOTES

$$-\frac{d[AB^{\ddagger}]}{dt} = \frac{k_B.T}{h}\ K^{\ddagger}[A][B] \qquad ...(7)$$

Comparing the derived rate law (1) and the expression (7) yields for the rate constant of the overall reaction

$$k = \frac{k_B.T}{h}.K^{\ddagger} \qquad ...(8)$$

Additionally, thermodynamics gives a further description of the equilibrium constant:

$$\Delta G^{\ddagger} = -R \bullet T \bullet \ln K^{\ddagger} \qquad ...(9)$$

Furthermore $\Delta G^{\ddagger}$ is given by

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - \mathrm{T} \bullet \Delta \mathrm{S}^{\ddagger} \qquad ...(10)$$

R = Universal Gas Constant = 8.3145 J/mol K

$\Delta G^{\ddagger}$ = free activation enthalpy [kJ • mo1^{-1}]

$\Delta S^{\ddagger}$ = activation entropy [J • mol^{-1} • K^{-1}]

$\Delta H^{\ddagger}$ = activation enthalpy [kJ • mol^{-1}]

$\Delta H^{\ddagger}$ is the enthalpy difference between the transition state of a reaction and the ground state of the reactants. It is called **activation enthalpy**. **S** is for the entropy, the extent of randomness or disorder in a system. The difference between the entropy of the transition state and the sum of the entropies of the reactants is called **activation entropy** $\Delta S^{\ddagger}$.

$\Delta G^{\ddagger}$ is the free activation enthalpy (Gibb's free energy). According to equation (9) $\Delta G^{\ddagger}$ is equal to the change in enthalpy $\Delta H^{\ddagger}$ minus the product of temperature T (which is in Kelvin) and the change in entropy $\Delta S^{\ddagger}$ of the system $\Delta G^{\ddagger}$ represents the determining driving power for a reaction. The sign of ΔG determmes if a reaction is spontaneous or not.

The higher the amount of negative activation entropy is, the higher the free enthalpy of activation (see equation (10)). Combining Equation (9) and the expression (10) and solvmg for 1nk yields:

$$1\mathrm{nK}^{\ddagger} = \frac{\Delta H^{\ddagger}}{R \cdot T} + \frac{\Delta S^{\ddagger}}{R} \qquad ...(11)$$

The *Eyring equation* is found by substituting Equation (11) into equation (8):

$$k = \frac{k_B \cdot T}{h} \cdot e^{-\frac{\Delta H^{\ddagger}}{R \cdot T}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}} \qquad ...(12)$$

The Hard-Sphere and Simple Collision Theory

This is the earliest theory of reaction rates. Since the reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reaction species must colloid before they react. Since, of our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase (in the later case, we speak of encounters rather than collisions), we will restricts our discussion to bimolecular reaction in the gaseous phase.

The simplest model of a bimolecular reaction is one in which the two molecules are pictured as hard spheres that do not interact at all until they collide. When they collide, if they have sufficient energy (either kinetic energy along the line of centers, or total energy, or energy in certain degrees of freedom, depending on the exact flavor of theory being used) they are assumed to react. If they have less energy, they do not react. So, we will calculate the reaction rate as

Rate = (collision rate)*(Fraction of collisions with sufficient energy to react)

The non-reactive collisions are assumed to be *elastic* - that is, both the total momentum and total kinetic energy are unchanged in the collision. An elastic collision is what we observe when macroscopic hard spheres (billiard balls or bocce balls or bowling balls or marbles) collide. In an *inelastic* collision (which could be reactive or non-reactive) the total kinetic energy changes during the collision. Momentum is conserved in any isolated collision. A simplified derivation of the collision frequency is as follows:

From the kinetic theory of gases, the number of bimolecular collisions per sec per cm^{-3}. Among molecules of one species is given by

$$Z=2n^2d^2\ (8\Delta kT / \mu)^{1/2} \tag{13}$$

For reactions involving two different gases A and B, the rate of bimolecular reactions between unlike molecules is given by

$$Z_{AB} = n_A n_B (d_{av})^2\ (8\Delta\ kT / \mu)^{1/2} \tag{14}$$

Where, n_A and n_B are numbers of A and B molecules, respectively, d_{av} is average collision diameter defined as ($dA + dB /2$) and μ is the reduced mass defined as $\mu = (m_A m_B) / (m_A + m_B)$.

The collision number Z_{AB} is given, in terms of molar masses M_A and M_B of the two gases, the expression

$$Z_{AB} = n_A n_B\ (d_{av})^2\ \left[\frac{M_A + M_B)8\prod RT}{M_A M_B}\right]^{1/2}$$

The activation energy Ea in the Arrhenius equation is thus identified with the• relative kinetic energy E along the line of centres of two colhdmg molecues which is required to cause the reaction between them.

The collision theory is applicable to simple gaseous reaction. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate, some tunes by a factor of 10^5 for reactions involving fa irly complicated molecules. The discrepancy is explained by the fact that the colliding molecules are treated as a hard sphere having no internal energy. Again, the spherical model ignores the dependence of the effectiveness of collisions on the relative orientation of the colliding molecules.

Also, the activation energy has been treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrationaj motion. For this reason, the collision theory is applicable to only to reactions between very simple gaseous molecules. The collision theory can be generalized by introducing so called steric factor, p, into the equation for the bimolecular rate constant in order to take account for the orientational requirement. Accordingly,

$$k_2 = pAe^{-Ea/RT}$$

The steric factor is supposed to be equal to the fraction of molecular collisions in which the molecules A and B posses the relative orientation necessary for the reaction. However, the steric factor cannot be reliably calculated. Perhaps its introduction oversimplifies the actual situation.

Using collision theory, the Arrhenius pre-exponential factor for unlike molecules is given by

$$A = (2.75 \times 10^{29})\, p(d_{av})^2 \left[\frac{T(M_A + M_B)}{M_A M_B}\right]^{1/2}$$

and for like molecules it is given by

$$A = (3.89 \times 1029)\, pd^2 \left(\frac{T}{M}\right)^{1/2}$$

In these equations, the molar mass is in units of gram/mole and the units of A are dm^3 /mole/sec.

Application of ARRT to Unimolecular Reactions

Lindemann / Lindemann-Hinshelwood Theory

This is the simplest theory of unimolecular reaction rates, and was the first to successfully explain the observed first-order kinetics of many unimolecular reactions. The proposed mechanism actually consists of a second order bimolecular collisional activation stop, followed by a rate-determining unimolecular step.

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

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

Applying the steady-state approximation to the concentration of A* gives

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

so that the overall rate is

$$\frac{d[P]}{dT} = k_2[A^*] = \frac{k_1 k_2[A][M]}{k_{-1}[M] + k_2}$$

This is often written as

$$\frac{d[P]}{dT} = k_{eff}\,[A]$$

where $$k_{eff} = \frac{k_1 k_2[M]}{k_{-1}[M] + k_2}$$

is an effective first-order rate constant, k_{eff} is, of course, a function of pressure. At high pressures, collisional deactivation of A^* is more likely than unimolecular reaction, k_{eff} reduces to k_1k_2/k_{-1} and the reaction is truly first order in A. At low pressures, bimolecular excitation is the rate determining step; once formed A* is more likely to react than be collisionally deactivted. The rate constant reduces to $k_{eff} = k_1$ [M] and the reaction is second order.

Lindemann Theory Breaks Down for Two Main Reasons

(i) The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom of the molecule are completely neglected, and the theory consequently underestimates the rate of activation.

(ii) The unimolecular step fails to take into account that a unimolecular reaction specifically involves one particular form of molecular motion (e.g. rotation around a double bond for cis-trans isomerization).

Subsequent theories of unimolecular reactions have attempted to address these problems. Hinshelwood theory offers a solution to problem.

Hinshelwood Theory

Hinshelwood modeled the internal modes of A by a hypothetical molecule having s equivalent simple harmonic oscillators of frequency n and using statistical methods to determine the probabality of the molecule being collisionally activated to a reactive state. The number of ways of distributing a given number of quanta, v, among the s oscillators (i.e. the number of degenerate states of the system at an energy $(v + ½)h?$) is

$$g_v = \frac{(v+s-1)!}{v!(s-1)!}$$

a handwavy explanation of where this comes from is that $(v + s\text{-}1)!$ is the number of permutations of all the quanta and all the harmonic oscillators. This has to be divided by the number of ways in which the quanta can be pennuted amongst themselves, v! , and the number of ways the oscillators can be permuted amongst themselves, (s-1)!) The fraction of molecules in state v is given by the Boltzmann distribution.

$$\frac{n_v}{N} = \frac{gve^{-vhv/kT}}{q} \text{ where } q = \left(\frac{1}{1-e^{-hu/kT}}\right)^3$$

Hinshelwood now made the strong collision assumption. He assumed that the probability of deactivation of A^* in any given collision is unity, so that the rate constant k–1 of the Lindemann mechanism is equal to the collision frequency Z. Because the collisions promote equilibrium, the probability of forming a state v in a collision is given by the Boltzmann distribution. The rate constant for activation to state v is therefore given by

$$k_1^{\,v} = Z\frac{gv^{e-vhv/kT}}{q}$$

The overall rate of activation (i.e. rate of formation of collisionally excited A^* with enough energy to react) is found by summing the k_1^v over all the energy levels which can dissociate i.e. all levels with an energy greater than the critical energy E_0 which the molecule needs to react. If the vibrational quantum number of the state with energy E_0 is m, we have

$$k_1 = \sum_{m}^{\infty} Z \frac{gv^{e-vhv/kT}}{q}$$

The energies involved are usually large, with E_0 >> hn. Hinshelwood developed equations for the case in which the energy levels can be assumed to be continuous ($kT >> hn$). The expression then becomes

$$dk_1 = Z \frac{N(E)e^{-E/kT}dE}{q}$$

where $N(E)$ is the density of states; $N(E)dE$ is therefore the number of energy levels with energy between E and $E + dE$, and dk_1 is the rate constant for activation into this energy range. The total rate of activation is found by integrating dk_1 over all energies greater than the critical energy.

$$k_1 = \frac{X}{(s-1)!}\left(\frac{E_0}{kT}\right)^{s-1} \exp\,(-E_0/kT)$$

This differs from the simple collision theory rate constant, $k_2 = Z \exp\,(-E_0/kT)$, by a factor of

$$\frac{1}{(s-1)!}\left(\frac{E_0}{kT}\right)^{s-1}$$

leading to an increased theoretical value of k_1. The increase is more pronounced for large molecules, which have more oscillators, and is exactly what is required to overcome the first failure of the Lindemann theory.

RRK Theory

A minimum amount of energy must be localised in specific modes of molecular motion in order for the unimolecular step to take place. A new step is added to the Lindemann mechanism, in which the generally excited molecule A^* is converted into the specifically excited 'activated complex' $A^‡$.

$$A^* \xrightarrow{k_{2a}} A^‡ \xrightarrow{k^‡} P$$

$k^‡$ is of the order of a vibrational frequency, and k_{2a} is generally much smaller. This means that conversion of A^* to $A^‡$ is rate determining, and k_{2a} is the overall rate coefficient for conversion of A^* to products. Because $k_{2a} << k^‡$, ($A^‡$] is very small and we can use the steady state approximation to find k_{2a}, giving

$$k_{2a} = k^‡ \frac{[A^‡]}{[A^*]}$$

RRK theory assumes that energy can flow freely from one vibrational mode to another within the molecule (this is a fairly reasonable assumption, since molecular vibrations are highly anharmonic at chemical energies and are therefore coupled). As before in the discussion of the Hinshelwood theory, for a molecule with s equivalent oscillators, the degeneracy of the 5th vibrational level is

$$\frac{(v+s-1)!}{v!(s-1)!}$$

If we have to locate at least m quanta in one particular mode for dissociation to occur (i.e., $E_0 = mh$?), this simply reduces our choice of quanta to $(v-m)$, and the total number of ways of arranging these is

$$\frac{(v-m+s-1)!}{(v-m)!(s-1)!}$$

The probability P_m v of locating at least m quanta out of v in the dissociation mode is the ratio of these two quantities.

$$= \frac{(v-m+s-1)!}{(v-m)!(s-1)!}\frac{v!(s-1)!}{(v+s-1)!} = \frac{(v-m+s-1)!v!}{(v-m)!(v+s-1)!}$$

Because the quantum numbers involved are very large (i.e., v and m are >> s) we have

$$\frac{(v-m+s-1)!}{(v-m)!} \to (v-m)s-1 \text{ and } \frac{v!}{(v+s-1)!} \to v-(s-1)$$

So that

$$Pm^{v} = (v-m)\mathrm{s}-1\ \mathrm{v}^{-(\mathrm{s}-1)} \left(\frac{v-m}{v}\right)^{s-1} = (1-m/v)s-1$$

Since $E = vh$f and $E_0 = mh$f, this expression can be rewritten in terms of energies.

$$P_{E_0}^{E} = (1-E_0/E)^{s-1}$$

$P_{E_0}^{E}$ is the probability of locating a minimum amount of energy E_0 out of the total energy E in the• dissociation mode. If energy randomization takes place rapidly enough for the vibrational energy to be distributed statistically, then

$$\frac{[A^{\ddagger}]E}{[A^*]E} = P_{E_0}^{E}\text{, and the rate constant is } k_2(E) = k^{\ddagger}\,(1-E_0/\mathrm{E})^{\mathrm{s}-1}$$

k_2 increases with energy, since the probability of localising a given amount of energy E_0 in one particular mode increases as E increases. The localisation probability decreases as a increases since there are more modes to spread the energy across. Consequently, k_2 becomes smaller as the molecule becomes more complex, in contrast to the behaviour of the rate constant for activation k_1.

RRKM Theory

Based on the results of Hinshelwood and RRK theory, the reaction mechanism can be rewritten to take account of the fact that the rates of collisional activation and unimolecular dissociation are energy dependent.

NOTES

$$A + M \; \frac{dk_1(E)}{k_{-1}} \; A^*(E) + M$$

$$A^*(E) \xrightarrow{k_2(E)} P$$

Applying the steady state approximation to [$A^*(E)$] leads to the rate expresion

$$\frac{d[P(E)]}{dt} = \frac{k_2(E)dk_1(E)[A][M]}{k_{-1}[M]+k_2(E)}$$

from which we can identify the unimolecular rate coefficient for the energy range from E to $E + dE$ as

$$k(E) = \frac{k_2(E)dk_1(E)[M]}{k_{-1}[M]+k_2(E)}$$

The thermal rate coefficient is obtained by integrating over E from E_0 to a

$$k = \int_{E_0}^{\alpha} \frac{k_2(E)dk_1(E)(M)}{k_1[M]+k_2(E)} = \int_{E_0}^{\alpha} \frac{k_2(E)dk_1(E)[M]}{k_{-1}(1+k_2(E)/k_{-1}[M]}$$

In RRKM theory, the energy of the molecule is partitioned into fixed and non-fixed components. Only the nonfixed component E^*, which can flow freely around the various modes of motion of the molecule, can contribute to reaction. The various terms of the rate expression are now evaluated using statistical mechanics.

(i) dk_1 (E^*)/k_{-1} is the equilibrium constant for energization of the A molecules into the energy rante E^* to $E^* + dE^*$, and can be calculated from the partition function ratio

QA* (E*)/QA

(ii) k_2 (E^*) is obtained by applying the steady state treatment to the activated complex $A^\ddagger$ as in RRK theory, with the modification that the overall reaction is broken down into energy, contributions from translation and from rotation/vibration. The rate constant $k^\ddagger$ and ratio of concentrations [$A^\ddagger$]/[A^*] are evaluated using partition functions ($k^\ddagger$ is treated as a translation along the reaction coordinate).

In the high pressure limit, RRKM theory reduces to transition state theory. In the general case, RRKM theory admits equilibrium between A^* and A‡, but not between A* and A. However, at high pressures A^* and A are also in equilibrium. Transition state theory assumes that the activated complex $A^\ddagger$ is in thermal equilibrium with the rectants. This is equivalent to assuming that the thermal Boltzmann distribution is maintained at all energies, which is true at sufficiently high pressures $\Rightarrow$ at high pressures the RRKM model becomes the same as the transition state theory model, and the results of the two theories coincide.

Slater Theory

As opposed to statistical theories with energy flow between the vibrations, Slater proposed a dynamic theory without energy flow. Vibrations are required to be simple harmonic, which does not allow energy flow between modes, but when different modes come in to phase, the vibrational amplitude is changed. For suitable phase relationships the vibrational amplitude may be extending beyond the critical length corresponding to the reaction.

Slater provided a classical treatment in 1939 and later a quantum mechanical derivation. The mathematical treatment is again complex but the variation of K_{uni} with [A] can be calculated. The number of vibrational modes that may contribute to the critical reaction coordinate is selected to give the best fit with the experimental data, and the result is approximately half the maximum possible modes of vibration.

Under high pressure conditions, the rate constant *Ka* may be expressed as

$$k_{\propto} = v \exp(-\in^{*}/\kappa T) \qquad (15)$$

Kintics of Third Order Reactions

A chemical reaction said to be thid order if its rate depnds on three concentration terms. In general, a third order reaction may be represented as,

I. 3A → Products

II. 2A + B → Products

III. A + B + C → Products

Type-1: Now consider a Type I in which initial concentration of all three reacting molecules is the same

$$3A \rightarrow \text{Products} \qquad (16)$$

Spppose a is the initial concentration of each reactant in gram mole/I. Suppose *x* is the concentration change of the time *t*. Then, the concentration of *A* at time *t* is $(a-x)$ gram moles/I. According to the law of mass action, the rate of such reactions at time *t* given by

$$\frac{dx}{dt} \ \alpha \ (a-x)\ (a-x)\ (a-x) \quad \text{or} \quad \frac{dx}{dt} = k_2\ (a-x)^2 \qquad (17)$$

In integrating Equation (17), we obtain

$$\frac{1}{2(a-x)^2} = k_3 + t + I_3 \qquad (18)$$

Where I_3 is know as constant of integration. Its value is determined from the initital conditions of the experiment i.e., when $t = 0, x = 0$; Equation (18) takes the form

$$I_3 = \frac{1}{2a^2} \qquad (19)$$

Substituting the value of I_3 in the Equation (19), we obtain

$$\frac{1}{2(a-x)^2} = k_3 t \ \frac{1}{2a^2}$$

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)_2} - \frac{1}{a^2}\right] \qquad (20)$$

Equation (20) is known as the kinetic equation of the third order reaction when the concentration of the three reactant is the same. Equation can be simplifed as

$$k_3 = \frac{1}{2t}\left(\frac{x(2a-x)}{a^2(a-x)^2}\right) \qquad (21)$$

Type II: We will now consider Type II in which two reactant are equal and the third one is different.

$$2A + B \rightarrow \text{Products}$$

Suppose a and b are the initial concentration of A and B respectively. Suppose x is the change of concentration after the time t from the commencement. Then the rate of the reaction is given be

$$\frac{dx}{dt} = k_3\ (a - 2x)^2\ (b - x) \qquad (22)$$

Where the amount of A decomposed at any instant in is $2x$ which is twice that of B i.e., on separating the variables and integrating the Equation (22), we obtain

$$k_3 = \frac{1}{t(a-2b)^2}\left(\frac{2x(2b-a)}{a(a-2x)} + 1n\frac{b(a-2x)}{a(b-x)}\right) \qquad (23)$$

Again, Equation (23) is know as the kinetic equation for a third order reaction.

Type III: The last case, is

$$A + B + C \rightarrow \text{Products}$$

Suppose, a, b and c are the initial concretions of A, B and C respectively. Suppose, x is the concentration change after time t from the commencement. Then, the rate of the reaction is given by

$$\frac{dx}{dt} = k_3\ (a - x)\ (b - x)\ (c - x)$$

$$\frac{dx}{(a-x)(b-x)(c-x)} = k_3 dt$$

Integrating it, we obtain

$$k_3 = \frac{1}{t}\,\frac{(b-c)\,1n\dfrac{a-x}{a} + (c-a)\,1n\dfrac{b-x}{b} + (a-b)\,1n\dfrac{c-x}{c}}{(b-c)(a-b)(c-a)}$$

Examples of Third Order Reaction

1. **Gaseous Reactions:** There only five gaseous reactions of the third order. Each of these reactions involves the nitric oxide as one of the reactants. These reactions are
   (a) $2NO + Cl_2 \rightarrow 2NOCl$

(b) $2NO + Br_2 \rightarrow 2NOBr$

(c) $2NO + O_2 \rightarrow 2NO_2$

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

(e) $2NO + D_2 \rightarrow N_2O + D_2O$

NOTES

2. **Reaction in Solution:** Noise and Cottle showed that the reduction of $FeCl_3$ by $SnCl_2$ was of the third order.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

They studied this reaction by mixing equal quantities of $SnCl_2$ and $FeCJ_3$ solution in flask which was kept in a thermostat. They with drew equal volumes of reaction mixture at regular intervals of time. The excess of $SnCl_2$ was removed by adding $HgCl_2$ to it and the $FeCl_2$ was estimated by titrating it against $K_2Cr_2O_7$ solution. It has been now proved that the reaction is of the second order only.

3. **The reaction between potassium oxalate and mercuric chloride is of 3rd order:**

$$2HgCl_2 + K_2C_2O4 \rightarrow 2KCl + 2CO_2 + Hg_2Cl_2$$

Potential Energy Surfaces (Hyper Surfaces)

Much of the microscopic theory of chemical kinetics depends on the idea of a potential energy surface (often called a potential energy hyper surface, because it usually involves more than 3 dimensions). These are based on the Born-Oppenheimer approximation of quantum mechanics. This approximation states that, because the atomic nuclei are thousands of times heavier than the electrons, we can separate the motion of the electrons from that of the nuclei. The nuclear motion is much, much slower then the motion of the electrons, so we can assume that the electron cloud responds instantaneously to any changes in the nuclear position. For now, we will consider only the *ground electronic state* of a molecule - the one in which the electrons occupy the orbitals of lowest energy.

An assembly of *N* atomic nuclei has *3N* degrees of freedom - each of the *N* molecules can move in 3 dimensions. We could describe the system using 3 Cartesian coordinates for each atom. However, if ‘the state of the system only depends on the aiTangement of the atoms relative to each other, then 6 of these degrees of freedom can be eliminated (5 for a linear molecule). That is because three degrees of freedom correspond to overall translation of the whole system (in 3 dimensions) and three degrees of freedom (2 for a linear molecule) correspond to overall rotation of the whole system. Translating or rotating the whole molecule does not change the relative positions of the atoms (the distance between any pair of atdrns). In the absence of any imposed fields (magnetic, electrical, etc.) the position and orientation of a molecule will not affect its energy.

Simple Interatomic Potentials

The potential energy surface for a molecule or a reaction is a description of the total energy of the atoms involved (all of the nuclei and all of the electrons) as a function of the positions of. the nuclei. A chemical reaction can be described in detail as motion of the atoms on this potential energy surface. We Saddle point will begin by considering the potential energy surface for a system of 2 atoms (a diatomic molecule if they form a chemical bond). The energy of this system depends on *(3N–5)* = I degree of freedom - the distance between the atoms. If we denote the potential energy as V (or $V(r)$, where r is the distance between the atoms) then the force acting on either atom is

For some types of interaction, patticularly electrostatic interactions among only two particles, we know what the interaction potential looks like: Ion-ion interaction: Ion-dipole interaction: And others for all the various combinations that we can think of - dipole-dipole, dipole-induced dipole, etc. The interaction potentials listed above (except for the interaction between charged particles of the same sign) are attractive potentials. For these, the potential keeps decreasir.g with decreasing r all the way until $r = 0$, where $V = -8$. Of course, this cannot really be the case, or everything around us would collapse into a single, very dense point. So, any realistic interaction potential must include a repulsive term (V increasing with decreasing r for sufficiently small r), and this term must doh1inate at very si1ort interparticle distances. For molecules, this term results from the Pauli exclusion principle that you learned about in chemistry. It says that multiple electrons cannot occupy the same region of space - doing so is quantum mechanically forbidden (there is a 'strictly enforced' maximum of two electrons per orbital). Of course, the electrons also repel each other through electrostatic interactions, but that is a smaller effect.

Kinetic Isotopic Effect

The term kinetic isotopic effect relates to changes in the rate of reaction. Isotopic effects are small if the isotopic substitution is far from the seat tab reaction. If the bond involving the substituted ~tom is broken or formed during the reaction the effects are much greater. The effect of changing the atom connected by the bond is referred as primary kinetic isotopic effect. Otheiwise it is described as secondary effect. Isotopic effects being influenced solely by the atomic masses or greatest when there is a large relative change in the masses. The effects are usually large when an ordinary hydrogen atom (H) is replaced by deuterium (D) or Tritium (T), the relative masses then approximately 1 :2:3. Replacement of c_{12} and c_{13} is a much small effect. Since, the ratio is only 12: 13. The kinetic isotope effects are dealt by Bigeleisen on the basis of conventional transition state theory.

When an atom is replaced by an isotope there is no change in classical potential energy surfaces, but, there are changes in vibrational frequencies and therefore, in zero point energies. At relatively low temperatures H_2 and D_2 molecules are largely at their zero point levels. Thus, as far as the initial state of reaction is concern a hydrogen molecule having 7.6k J mole^{-1} more zero point energy, will tend to react more rapidly and its reaction will tend to have a higher equilibrium constants.

In general and simplified semi classical discussion of kinetic isotopic effect in hydrogen atom transfers processes is given. Consider the abstraction reaction

$$R\text{–}H + R' \rightarrow (R \ldots. H \ldots R)^{\neq} \rightarrow R + H - R'$$

$$R\text{-}D + R' \rightarrow (R \ldots. D \ldots. R)^{\neq} \rightarrow R + D - R'$$

NOTES

The situation is pa1ticularly simple Rand R' much heavier than either H or D. The partition function s are for R–H and R–D and the practically the same, as or the partition functions for the activated complexes (R ..... H ..... R')$^{\neq}$ and (R ..... D ..... R')$^{\neq}$. Also, the relevant vibration frequencies in the activated complexes are almost same for• the two atoms.

The asymmetric vibration frequencies are different for the two isotopic forms. The zero point energies are therefore much the same for H and D. Since, the partition function for the two isotopic forms are practically the same, is semi classical ratio K^S_h/K^S_d is determined almost entirely zero point energy difference in the initial state. Thus, it is given by

$$K^S_h/K^S_d = e^{-4.5}k \text{ J mole}^{-1}/KRT$$

The main assumptions made in the Urey- Bigeleisen --Meyer treatment are as follows:

1. Conventional transition state theory is valid
2. All vibrations are purely harmonic
3. Use can be made of the limiting high temperature expression for the transitional and rotational partition functions
4. The partition function for types of motion not appreciably affected by the isotopic substitution can be taken to cancel out entirely in the rate expression
5. Quantum mechanical tunneling is neglected; i.e., the treatment is semi classical.

3.2.1 Kinetic Salt Effect

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have a $r^{”7}$ dependence, and for practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by **Coulomb's law**, which has a $r^{”2}$ dependence. Consequently, the behaviour of an electrolyte solution deviates considerably from that an ideal solution. Indeed, this is why we utilize the activity of the individual components and not the concentration to calculate deviations from ideal behaviour. In 1923, **Peter Debye** and **Erich Hückel** developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, $\gamma\pm$, and could explain how the behaviour of ions in solution contribute to this constant.

Assumptions of Debye-Hückel Theory

The **Debye-Hückel theory** is based on three assumptions of how ions act in solution:

- Electrolytes completely dissociate into ions in solution.
- Solutions of Electrolytes are very dilute, on the order of 0.01 M.
- Each ion is surrounded by ions of the opposite charge, on average.

Debye and Hückel developed the following equation to calculate the mean ionic **activity coefficient** $\gamma\pm$ **:**

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^6}{(\varepsilon T)^{3/2}} \mid z_+ z_- \mid \sqrt{I} \qquad (24)$$

Where

ε is the dielectric constant,

z_+ and z_- are the charges of the cation and anion, respectively, and

I is the ionic strength of the solution.

The Equation 24 is known as the Debye-Hückel Limiting Law. The ionic strength is calculated by the following relation:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \qquad (25)$$

Where m_i and z_i are the molality and the charge of the ith ion in the electrolyte. Since most of the electrolyte solutions we study are aqueous (ε=78.54) and have a temperature of 298 K, the Limiting Law in Equation 24 reduces to

$$\log \gamma_{\pm} = -0.509 \mid z_+ z_- \mid \sqrt{I} \qquad (26)$$

The kinetic salt effect is the effect of salts preset in solution on the rate of a reaction.

Kinetic Salt Effect

In biological systems, salts influence how well proteins and DNA (DeoxyriboNucleic Acid) function. Salts are formed by ionic bonds, between a metal and an electromagnetic atom(s). Some examples of salts include **NaCl, KCl**, and **Na_2SO_4**. Salt molecules are able to disassociate, forming cations and anions. An increase in the charge (- or +) of a transition state or an activated complex results in an increase in solvation (creating more order in the system), and causes a decrease in the change of entropy (**ΔS**). In contrast, a decrease in the charge of the transition state causes an increase in **ΔS**.

$$I^- + C^+ \rightleftharpoons E^o \rightarrow Product \qquad (27)$$

The kinetic salt effect describes the way salts stabilize reactants. For example, in the above reaction, each reactant has a charge. The negatively-charged reactant is stabilized by the positive charges from the salt, and the positively-charged reactant is stabilized by the negative charges from the salt. As a result, the rate at which the reactants come to gether decreases thus decreasesing the rate at which ***E*** forms. Because a charged intermediate is also stabilized in the solution, the half-life of the intermediate at equilibrium increases, shifting the reaction toward product formation. Because the rate of the product formation is higher due to increased amounts of the intermediate present on the solution, first order kinetics is used to derive the rate constant equation:

$$\log K_{TS} = \log K_{TS^o} + 2Z_A Z_B \sqrt{I} \qquad (28)$$

Where

Z is the charge on the cation and ion from the salt. $Z_A Z_B$ is a product value.

I is the ionic strength. **I** is also dependent on the solubility of the salt in the reaction mixture. Ionic strength is directly proportional to the solubility of the salt. Changing the ionic strength manipulates the solvation of the reactants and intermediates, thus changing **ΔS**, and affecting the reaction rate.

$logK_{TS}o$ is the rate constant without the salt in the reaction mixture.

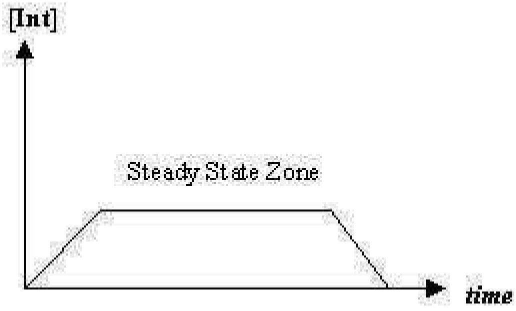
A is also a constant for the solvent the solution is in. The A value for water is 0.509 at 298 K.

3.2.2 Steady State Chemical Kinetics

When a reaction mechanism has several steps of comparable rates, the rate-determining step is often not obvious. However, there is an intermediate in some of the steps. An intermediate is a species that is neither one of the reactants, nor one of the products. The steady-state approximation is a method used to derive a rate law. The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.

When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a steady-state. The concentration of one of the intermediates, [Int], varies with time as shown in Figure . At the start and end of the reaction, [Int] does vary with time

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



Above is an example of the when an intermediate can be approximated as a steady-state.

When a reaction mechanism has several steps with comparable rates, the rate-determining step is not obvious. However, there is an intermediate in some of the steps. The steady-state approximation implies that you select an intermediate in the reaction mechanism, and calculate its concentration by assuming that it is consumed as quickly as it is generated. In the following, an example is given to show how the steady-state approximation method works.

Example 3.1

Use the steady-state approximation to derive the rate law for this reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ assuming it follows the following three-step mechanism:

NOTES

$$N_2O_5 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

Solution

In these steps, NO and NO_3 are intermediates. You have

Production rate of NO = $k_2[NO_3][NO_2]$

consumption rate of NO = $k_3[NO_3][NO]$

A steady-state approach makes use of the assumption that the rate of production of an intermediate is equal to the rate of its consumption. Thus, we have

$$k_2[NO_3][NO_2] = k_3[NO_3][NO]$$

and solving for [NO] gives the result,

$$[NO] = \frac{k_2[NO_3][NO_2]}{k_3[NO_3]} \qquad (29)$$

For the other intermediate NO_3NO_3,

Production rate of NO_3 = kf $[N_2O_5]$

consumption rate of $NO_3 = k_2[NO_3][NO_{2]}+k_3[NO_3][NO]+kb[NO_3][NO_2]$

Applying the steady-state assumption gives:

Kf $[N_2O_5] = k_2\ [NO_3]\ [NO_2]+k_3[NO_3][NO]+kb[NO_3][NO_2]$

Thus,

$[NO^3]=kf[N_2O_5]\ /\ k_2[NO_2]+k3[NO]+kb[NO_2]$ (30)

Let's review the three equations (steps) in the mechanism:

Step i. is at equilibrium and thus can not give a rate expression.

Step ii. leads to the production of some products, and the active species NONO causes further reaction in step iii. This consideration led to a rate expression from step ii. as:

$d[O_2]/dt=k_2[NO_3][NO_2$ (3)

Substituting (1) in (2) and then in (3) gives

$d[O_{2]}\ /\ dt=kfk_2[N_2O_5]\ /\ kb+2k_2=k[N_2O_5]$

A General Reaction to Show the Applicability of the Steady State Approximation

Consider the following reaction $A \rightarrow B$ (31)

Let us say that the reaction occurs in two steps

$$A \overset{k_1}{\rightarrow} I \tag{32}$$

$$I \overset{k_2}{\rightarrow} B \tag{33}$$

The differential rate laws are given by in the Equations 34, 35, 36 respectively:

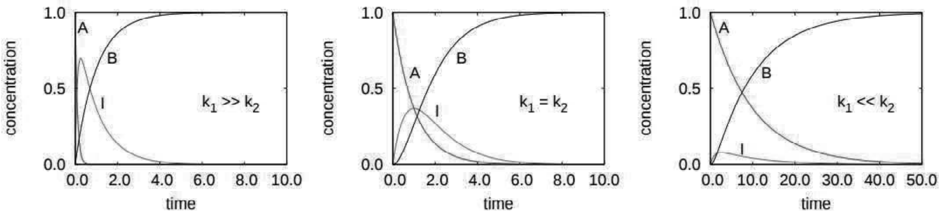
$$\begin{aligned} \frac{dc_t(A)}{dt} &= -k_1 c_t(A) \\ \frac{dc_t(I)}{dt} &= k_1 c_t(A) - k_2 c_t(I) \\ \frac{dc_t(B)}{dt} &= k_2 c_t(I) \end{aligned} \tag{34, 35, 36}$$

The integrated rate laws which are obtained by solving the coupled differential equations are given by in the Equations 37, 38, 39 below respectively:

$$\begin{aligned} c_t(A) &= c_0(A)e^{-k_1 t} \\ c_t(I) &= \begin{cases} c_0(A)\frac{k_1}{k_1-k_2}\left(e^{-k_1 t} - e^{-k_2 t}\right); & k_1 \neq k_2 \\ c_0(A)k_1 t e^{-k_1 t}; & k_1 = k_2 \end{cases} \\ c_t(B) &= c_0(A) - c_t(A) - c_t(I) \end{aligned}$$

Equation 37, 38, 39

The concentrations of the reactant, intermediate and the product for the cases i) k1 > k2, ii) k1 = k2, and iii) k1 < k2 are shown below



Clearly the steady state approximation is applicable for the case k1 < k2 where the concentration of the intermediate is small and it varies slowly and can be considered to be constant most of the time during the reaction (i.e., to a good approximation, dct(*I*) / dt = 0). The situation k1 < k2 also means that the intermediate is very reactive and this step is very fast. Also note that the first step is relatively very slow hence the first step determines the rate of the entire reaction. Now let us apply the steady state approximation for this case to derive the rate law. In most of the cases, we look for an expression for ct (*I*) in terms of the rate constants and the concentration of reactants. Let us apply dct(*I*) dt = 0 which is the steady state approximation to Equation

$$\frac{dc_t(I)}{dt} = 0 \Rightarrow c_t(I) = \frac{k_1}{k_2}c_t(A) \tag{40}$$

Using the above equation we can rewrite the rate laws (differential and integral) as follows

$$\begin{aligned}\frac{dc_t(A)}{dt} &= -k_1 c_t(A)\\ \frac{dc_t(I)}{dt} &= 0\\ \frac{dc_t(B)}{dt} &= k_1 c_t(A)\end{aligned}$$

Equation 41, 42, 43

And

$$\begin{aligned}c_t(A) &= c_0(A)e^{-k_1 t}\\ c_t(I) &= \text{constant}\\ c_t(B) &= c_0(A) - c_t(A) - \frac{k_1}{k_2}c_t(A)\\ &= c_0(A)\left\{1 - c_0(A)e^{-k_1 t} - \frac{k_1}{k_2}c_0(A)e^{-k_1 t}\right\}\\ &= c_0(A)\left\{1 - c_0(A)e^{-k_1 t}\right\}\end{aligned}$$

Equation 44, 45, 46

where in the last equation we have used $k_1 k_2 = 0$ because k_2 is large.

3.2.3 Thermodynamic or Kinetic Reaction Control

Thermodynamics Stability

The thermodynamics of metal ion complex formation provides much significant information. Basically, it is used to distinguish between enthalpic and entropic effects. Enthalpic effects depend on bond strengths and entropic effects have to do with changes in the order/disorder of the solution as a whole. The chelate effect is best explained in terms of thermodynamics.

An equilibrium constant is related to the standard Gibbs free energy change for the reaction.

$$\Delta G^{\theta} = -2.303 log\beta$$

R is the gas constant and *T* is the absolute temperature. At 25 °C, $\Delta G^{-\circ}$ = (–5.708 kJ mol^{-1}) ...log β. Free energy is made up of an enthalpy term and an entropy term.

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$

The standard enthalpy change can be determined by calorimetry or by using the Van't Hoff equation, though the calorimetric method is preferable. When both the standard enthalpy change and stability constant have been determined, then the standard entropy change is easily calculated from the equation above.

The stepwise formation constants of complexes of the type ML_n decrease in magnitude as *n* increases may be partly explained in terms of the entropy factor. Take the case of the formation of octahedral complexes.

$$\mathrm{M(H_2O)}_m\mathrm{L_{n-1}} + \mathrm{L} \leftrightharpoons \mathrm{M(H_2O)}_{m-1}\mathrm{L_n}$$

For the first step, $m = 6$, $n = 1$ and the ligand can go into one of 6 sites. For the second step, $m = 5$ and the second ligand can go into one of only 5 sites. This means that there is more randomness in the first step than the second one; $\Delta S^{\ominus}$ is more positive, so $\Delta G^{\ominus}$ is more negative and $K_1 > K_2$. The ratio of the stepwise stability constants can be calculated on this basis, but experimental ratios are not exactly same because $\Delta H^{\ominus}$ is not necessarily the same for each step.

Ionic Strength Dependence

The thermodynamic equilibrium constant, $K^{\ominus}$, for the equilibrium,

$$\mathrm{M} + \mathrm{L} \leftrightharpoons \mathrm{ML}$$

Can be defined as,

$$K^{\ominus} = \frac{\{\mathrm{ML}\}}{\{\mathrm{M}\}\{\mathrm{L}\}}$$

Where {ML} is referred as the activity of the chemical species ML, etc. $K^{\ominus}$ is dimensionless since activity is dimensionless. Activities of the products are placed in the numerator, while the activities of the reactants are placed in the denominator.

Since activity is the product of concentration and activity coefficient (γ) the definition could also be written as,

$$K^{\ominus} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \times \frac{\gamma_{\mathrm{ML}}}{\gamma_{\mathrm{M}}\gamma_{\mathrm{L}}} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \times \Gamma$$

Where [ML] represents the concentration of ML and Γ is a quotient of activity coefficients. This expression can be generalized as,

$$\beta^{\ominus}_{pq\ldots} = \frac{[\mathrm{M}_p\mathrm{L}_q\ldots]}{[\mathrm{M}]^p[\mathrm{L}]^q\ldots} \times \Gamma$$

To avoid the complications involved in using activities, stability constants are determined, where possible, in a medium consisting of a solution of a background electrolyte at high ionic strength, that is, under conditions in which Γ can be assumed to be always constant.

Temperature Dependence

All equilibrium constants vary with temperature according to the Van't Hoff equation.

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{\ominus}_{\mathrm{m}}}{RT^2}$$

Alternatively,

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H^{\ominus}}{R}$$

R is the gas constant and T is the thermodynamic temperature. Thus, for exothermic reactions, where the standard enthalpy change, $\Delta H^{-''}$, is negative, K

decreases with temperature, but for endothermic reactions, where ΔH° is positive, K increases with temperature. A complex may be quite stable to one reagent and may decompose readily in presence of another reagent.

Kinetic Stability

Kinetic stability is referred as the reactivity of the metal complexes in solution and defines the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts instead of how stable it is. It helps in determining the rate at which the reaction occurs to establish the equilibrium.

The term kinetic stability of complexes can be categorized into labile and inert based on rate of the reactions. When the rate of substitution of ligands is high, then the complex is supposed to be labile. For example, the copper complex of the formula $[\mathrm{Cu\,(NH_3)_4(H_2O)_2}]^{2+}$ is labile. In aqueous solution, the complex gives blue color, and when concentrated hydrochloric acid is added to this solution, the solution turns into green colour producing the complex $[\mathrm{CuCl_4}]^{2+}$. Alternatively, in inert complexes the rate of ligand exchange is extremely slow, and there is difficulty in the exchange of ligands, for example the cobalt complex $[\mathrm{Co\,(NH_3)_6}]^{3+}$ reacts slowly, but there is no reaction at room temperature when conc. HCl is added to the aqueous solution.

3.3 DYNAMICS CHAIN REACTIONS

There are some chemical reactions which take place by a series of successive processes involving the formation of free atoms and radicals. The kinetic laws for such reactions are considerably complex. A well known example of these types of reactions is the hydrogen-bromine reaction.

The stoichiometry for this reaction is

$$\mathrm{H_2 + Br_2 \rightarrow 2HBr}$$

but it does not follow the simple rate expression

$$\frac{d[\mathrm{HBr}]}{dt} = k\,[\mathrm{H_2}]\,[\mathrm{Br_2}]$$

analogous to that followed in the hydrogen-iodine reaction but follows the following empirical equation given by Bodenstein and Lind in 1906:

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{1 + k'\dfrac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}} \qquad ...(47)$$

k and k' are constants at a given temperature and parentheses indicate the concentration of the species. The appearance of the term [HBr] in the denominator implies that the velocity of the reaction is decreased by the product, HBr and this product acts as an inhibitor of the reaction.

The complexity of Equation (47) could not be explained until 1919 when Christiansen, Herzfeld and Polanyi independently and almost simultaneously solved the problem. They proposed a chain of reactions with the following steps:

1. $Br_2 \xrightarrow{k_1} 2\,Br$ Chain initiation
2. $Br + H_2 \xrightarrow{k_2} HBr + H$
3. $H + Br_2 \xrightarrow{k_3} HBr + Br$
4. $H + HBr \xrightarrow{k_4} H_2 + Br$ Chain inhibition
5. $Br + Br \xrightarrow{k_5} Br_2$ Chain termination

According to this mechanism, HBr is formed in reactions (2) and (3) and removed in reaction (4). Consequently, the rate of formation of HBr is given by

$$\frac{d[\text{HBr}]}{dt} = \text{k}_2\,[\text{H}_2]\,[\text{Br}] + k_3\,[\text{H}]\,[\text{Br}_2] - k_4\,[\text{H}]\,[\text{HBr}] \quad ...(48)$$

This expression involves concentrations of H atoms and Br atoms. Since these atoms are present in very small quantities, their concentrations cannot be directly measured. Thus, Equation (48) cannot be solved unless the concentrations of these atoms are expressed in terms of the concentrations of the molecules H_2, Br_2, and HBr. In order to remove this difficulty, it is assumed that the atoms H and Br are short lived intermediates and the steady-state principle can be applied to them. Thus, we get

$$\frac{d[\text{H}]}{dt} = k_2\,[\text{Br}]\,[\text{H}_2] - k_3\,[\text{H}]\,[\text{Br}_2] - k_4\,[\text{H}]\,[\text{HBr}] = 0 \quad ...(49)$$

$$\frac{d[\text{Br}]}{dt} = k_1[\text{Br}_2] + k_3\,[\text{H}]\,[\text{Br}_2] + k_4\,[\text{H}]\,[\text{Br}] - k_2\,[\text{Br}]\,[\text{H}_2] - k_5\,[\text{Br}]^2 = 0 \quad ...(50)$$

Solving these two equations simultaneously, we get

$$[\text{Br}] = \left(\frac{k_1[Br_2]}{k_5}\right)^{\frac{1}{2}} \quad ...(51)$$

and

$$[\text{H}] = \frac{k_2(k_1/k_5)^{\frac{1}{2}}[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad ...(52)$$

Substituting these values for [H] and [Br] into Equation (48) and rearranging, we get

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{\frac{1}{2}}[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + (k_4/k_3)\dfrac{[\text{HBr}]}{[\text{Br}_2]}} \quad ...(53)$$

This equation is in agreement with Equation (47) but now the constants k and k' are expressed as composites of constants for step reactions in succession.

A reaction like the above is an example of a chain reaction. Inspection of steps (1) to (5) for the hydrogen-bromine reaction leads to a number of points of interest in the mechanism. The reaction is initiated by thermal dissociation of a bromine molecule into bromine atoms. The introduction of bromine atoms produces a large number of molecules of hydrogen bromide through the sequence of reactions (2) and (3). These two stages repeat themselves until the reactants are used up.

These reactions are *chain-propagating reactions*. Step (4) accounts for the observed inhibition by HBr; since the product HBr is removed by this step, there is a decrease in the rate of formation of HBr. Step (5) results in removal of bromine atoms, and hence in chain termination. In some cases, chain termination may take place by collisions of chain propagators with the walls of the reaction vessel.

In some chain reactions, free radicals such as CH_3, C_2H_5, or CH_3CO, act as chain carriers. Consider, for example, the thermal decomposition of acetaldehyde, namely,

$$CH_3CHO \rightarrow CH_4 + CO$$

The following mechanism has been proposed for this reaction:

1. $CH_3\ CHO \xrightarrow{k_1} CH_3 + CHO$ Chain initiation
2. $CH_3\ CHO + CH_3 \xrightarrow{k_2} CH_4 + CH_3CO$ Chain propagation
3. $CH_3CO \xrightarrow{k_3} CH_3 + CO$
4. $CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$ Chain termination

Step (1) initiates the chain, steps (2) and (3) propagate the chain and step (4) terminates the chain. Applying the steady-state principle to the radicals CH_3 and CH_3CO, we get

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] + k_3\ [CH_3CO] - k_2[CH_3\ CHO]\ [CH_3] - k_4\ [CH]^2 = 0 \qquad ...(54)$$

and $$\frac{d[CH_3CO]}{dt} = k_2\ [CH_3CHO]\ [CH_3] - k_3[CH_3CO] = 0 \qquad ...(55)$$

From these two equations, we get

$$k_1[CH_3CHO] = k_4[CH_3]^2$$

or $$[CH_3] = [k_1/k_4]^{1/2}\ [CH_3CHO)^{1/2} \qquad ...(56)$$

The overall rate of reaction is determined by the production of CH_4 in step (4). The rate equation is

$$\frac{d[CH_4]}{dt} = k_2[CH_3CHO]\ [CH_3] \qquad ...(57)$$

Substituting the value of $[CH_3]$ from Equation (56) into Equation (57), we get

$$\frac{d[CH_4]}{dt} = k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \qquad ...(58)$$

The free-radical scheme thus predicts the reaction to be of the $\frac{3}{2}$ order. This is in agreement with the experimental data which shows a first order reaction gradually becoming a second order reaction.

Free radical chains play an important role in the polymerization of many unsaturated compounds, such as ethylene, styrene and vinyl compounds, to produce materials of industrial importance.

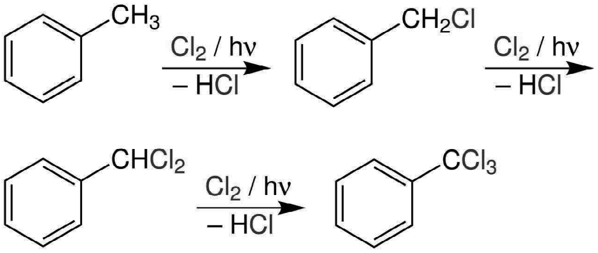
3.3.1 Photochemical Reaction

Photochemical (Hydrogen-Bromine and Hydrogen-Chlorine Reactions)

Photochlorination

Photochlorination is a chlorination reaction that is initiated by light. Generally, a C–H bond is converted to a C–Cl bond. The process is exothermic and proceeds as a chain reaction initiated by the homolytic cleavage of molecular chlorine into chlorine radicals by ultraviolet radiation. Many chlorinated solvents are produced using this method.

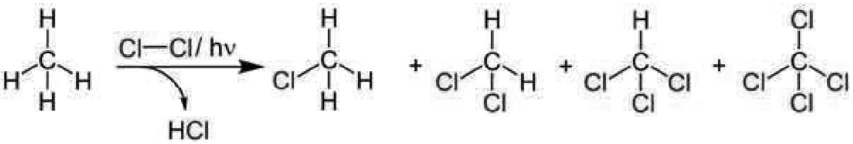
Following reaction scheme shows the photochlorination of the methyl group of toluene.



Photochlorinations are usually affected in the liquid phase, usually utilising inert solvents.

An example of photochlorination at low temperatures and under ambient pressure is the chlorination of chloromethane to dichloromethane. The liquefied chloromethane (boiling point –24 °C) is mixed with chlorine in the dark and then irradiated with a mercury-vapor lamp. The resulting dichloromethane has a boiling point of 41 °C and is later separated by distillation from methyl chloride.

Following reaction illustrates the subsequent products of photochlorination methane.



The photochlorination of methane has a lower quantum yield than the chlorination of dichloromethane. Due to the high light intensity required, the intermediate products are directly chlorinated, so that mainly tetrachloromethane is formed.

Hydrogen Bromide

Hydrogen bromide is the inorganic compound with the formula HBr. It is a hydrogen halide consisting of hydrogen and bromine. A colourless gas, it dissolves in water, forming hydrobromic acid, which is saturated at 68.85% HBr by weight at room temperature. Aqueous solutions that are 47.6% HBr by mass form a constant-boiling azeotrope mixture that boils at 124.3 °C. Boiling less concentrated solutions releases H_2O until the constant-boiling mixture composition is reached.

The hydrogen bromide (HBr) is mainly used in the production of inorganic bromides and alkyl bromides, and as a catalyst for many reactions in organic chemistry. However, reduction of bromine with red phosphorus is a more practical way to produce hydrogen bromide in the laboratory:

$$2\ P + 6\ H_2O + 3\ Br_2 \rightarrow 6\ HBr + 2\ H_3PO_3$$

$$H_3PO_3 + H_2O + Br_2 \rightarrow 2\ HBr + H_3PO_4$$

Hydrogen bromide, and its aqueous solution, are commonly used reagents in the preparation of bromide compounds.

Hydrogen bromide and hydrobromic acid are important reagents in the production of organobromine compounds. In a free radical reaction, HBr adds to alkenes as shown below:

$$RCH{=}CH_2 + HBr \rightarrow R{-}CHBr{-}CH_3$$

The resulting alkyl bromides are useful alkylating agents, for example as precursors to fatty amine derivatives. Related free radical additions to allyl chloride and styrene give 1-bromo-3-chloropropane and phenylethylbromide, respectively.

Hydrogen bromide reacts with dichloromethane to give bromochloromethane and dibromomethane, sequentially:

$$HBr + CH_2Cl_2 \rightarrow HCl + CH_2BrCl$$

$$HBr + CH_2BrCl \rightarrow HCl + CH_2Br_2$$

These metathesis reactions illustrate the consumption of the stronger acid (HBr) and release of the weaker acid (HCl).

3.3.2 Oscillatory Reaction

Oscillating reactions are chemical processes in which the reaction rate has periodic fluctuations, which may manifest itself, for example, by colour changes of the reaction mixture. These reactions have, for example, biochemical significance as biological clocks and in certain electrochemical processes.

For the occurrence of an oscillating reaction several conditions must be met, simplified: The oscillating system must be open to an exchange of energy and materials from the surroundings, several (at least two) can take steady states, with between states ***no thermodynamic equilibrium*** must have set. The system may oscillate, when a reaction step involves a feedback, such as by autocatalysis.

A ***chemical oscillator*** is a complex mixture of reacting chemical compounds in which the concentration of one or more components exhibits periodic changes; they are a class of reactions that serve as an example of ***non-equilibrium thermodynamics*** with far-from-equilibrium behaviour. The reactions are theoretically important in that they show that chemical reactions do not have to be dominated by equilibrium thermodynamic behaviour.

In cases where one of the reagents has a visible colour, periodic colour changes can be observed. Examples of oscillating reactions are the **Belousov–Zhabotinsky** (BZ), reaction the **Briggs–Rauscher reaction**, and the **Bray–Liebhafsky reaction.**

Theory

Chemical systems cannot oscillate about a position of ***final equilibrium*** because such an oscillation would violate the ***second law of thermodynamics***. For a thermodynamic system which is not at equilibrium, this law requires that the system approach equilibrium and not recede from it. For a closed system at constant temperature and pressure, the thermodynamic requirement is that the Gibbs free energy must decrease continuously and not oscillate. However it is possible that the concentrations of some reaction intermediates oscillate, and also that the rate of formation of products oscillates.

Theoretical models of oscillating reactions have been studied by chemists, physicists, and mathematicians. In an oscillating system the energy-releasing reaction can follow at least two different pathways, and the reaction periodically switches from one pathway to another. One of these pathways produces a specific intermediate, while another pathway consumes it. The concentration of this intermediate triggers the switching of pathways. When the concentration of the intermediate is low, the reaction follows the producing pathway, leading then to a relatively high concentration of intermediate. When the concentration of the intermediate is high, the reaction switches to the consuming pathway.

Different theoretical models for this type of reaction have been created, including the Lotka-Volterra model, the Brusselator and the Oregonator. The latter was designed to simulate the Belousov-Zhabotinsky reaction.

Belousov–Zhabotinsky (BZ) Reaction

A **Belousov–Zhabotinsky reaction** is one of several oscillating chemical systems, whose common element is the inclusion of bromine and an acid. An essential aspect of the BZ reaction is its so-called 'Excitability' — under the influence of stimuli, patterns develop in what would otherwise be a perfectly quiescent medium. Some clock reactions such as the Briggs–Rauscher reactions and the BZ using the chemical ruthenium bipyridyl as catalyst can be excited into self-organising activity through the influence of light.

Boris Belousov first noted, sometime in the 1950s, that in a mix of potassium bromate, cerium(IV) sulfate, propanedioic acid (another name for malonic acid) and citric acid in dilute sulfuric acid, the ratio of concentration of the cerium(IV) and cerium(III) ions oscillated, causing the colour of the solution to oscillate between a yellow solution and a colorless solution. This is due to the cerium (IV) ions being reduced by propanedioic acid to cerium(III) ions, which are then oxidized back to cerium(IV) ions by bromate(V) ions.

3.3.3 Homogeneous Catalysis

In chemistry, ***homogeneous catalysis*** is catalysis in a solution by a soluble catalyst. Homogeneous catalysis refers to reactions where the catalyst is in the same phase as the reactants, mainly in solution. In contrast, heterogeneous catalysis describes processes where the catalysts and substrate are in distinct phases, typically solid-gas, respectively. The term is used almost exclusively to describe solutions and implies catalysis by ***organometallic compounds***. Homogeneous catalysis is established technology that continues to evolve. An illustrative major application is the production of acetic acid. Enzymes are examples of homogeneous catalysts.

Advantages and Disadvantages of Homogeneous Catalysis

Advantages

- Homogeneous catalysts are generally more selective than heterogeneous catalysts.
- For exothermic processes, homogeneous catalysts dump heat into the solvent.
- Homogeneous catalysts are easier to characterize precisely, so their reaction mechanisms are amenable to rational manipulation.

Disadvantages

- The separation of homogeneous catalysts from products can be challenging. In some cases involving high activity catalysts, the catalyst is not removed from the product. In other cases, organic products are sufficiently volatile than they can be separated by distillation.
- Homogeneous catalyst have limited thermal stability compared to heterogeneous catalysts. Many organometallic complexes degrade <100 °C. Some pincer-based catalysts, however, operate near 200 °C.

3.3.4 Kinetic Enzyme Reaction

Enzyme kinetics is the study of the rates of enzyme-catalysed chemical reactions. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated.

An enzyme (**E**) is typically a protein molecule that promotes a reaction of another molecule, its substrate (**S**). This binds to the active site of the enzyme to produce an enzyme-substrate complex **ES**, and is transformed into an enzyme-product complex **EP** and from there to product **P**, via a transition state **ES*.** The series of steps is known as the mechanism:

$$\mathbf{E + S \rightleftarrows ES \rightleftarrows ES^* \rightleftarrows EP \rightleftarrows E + P}$$

This example assumes the simplest case of a reaction with one substrate and one product. Such cases exist: for example a mutase, such as ***phosphoglucomutase*** catalyses the transfer of a phospho group from one position to another, and isomerase is a more general term for an enzyme that catalyses any one-substrate one-product reaction, such as ***triosephosphate isomerase***.

General principles

The reaction catalysed by an enzyme uses exactly the same reactants and produces exactly the same products as the uncatalysed reaction. Like other catalysts, enzymes do not alter the position of equilibrium between substrates and products. However, unlike uncatalysed chemical reactions, ***enzyme-catalysed reactions*** display saturation kinetics. For a given enzyme ***concentration*** and for relatively low substrate concentrations, the reaction rate increases linearly with substrate concentration; the enzyme molecules are largely free to catalyse the reaction, and increasing substrate concentration means an increasing rate at which the enzyme and substrate molecules encounter one another. However, at relatively high substrate concentrations, the reaction rate asymptotically approaches the theoretical maximum; the enzyme active sites are almost all occupied by substrates resulting in saturation, and the reaction rate is determined by the intrinsic turnover rate of the enzyme.

The two most important kinetic properties of an enzyme are how easily the enzyme becomes saturated with a particular substrate, and the maximum rate it can achieve. Knowing these properties suggests what an enzyme might do in the cell and can show how the enzyme will respond to changes in these conditions.

3.3.5 Fast Reaction, Flow and Relaxation Methods

There are chemical reactions which take place at a very fast rate, i.e., these reactions can take place in seconds or in minutes. In general the reactions between ionic compounds are fast. For example, combustion of LPG gas in kitchen takes place in a few seconds, i.e., it takes place at a very fast rate in 10^{-15} seconds so it is a fast reaction.

The most frequently flow methods used for the study of fast reactions is the stopped-flow method. Due to the short analysis time and feasibility, flow based systems have become one of the most powerful analytical tools used for studying fast reactions. Flow methods use flow instruments which are a rapid mixing devices for studying the chemical kinetics of fast reactions in solution.

Continuous Flow Approach

For reactions that take place in milliseconds, the continuous flow technique is used, for example to study fast gas-phase reactions in which one of the reactants is a free radical, such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.

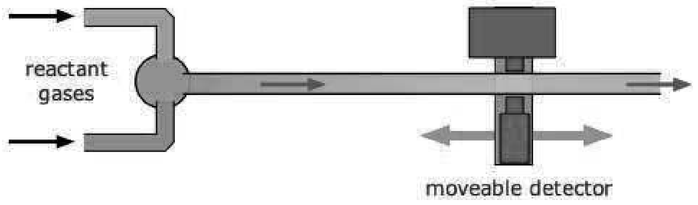


Fig. 3.1 A Continuous Flow Fast Kinetic System

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined.

Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

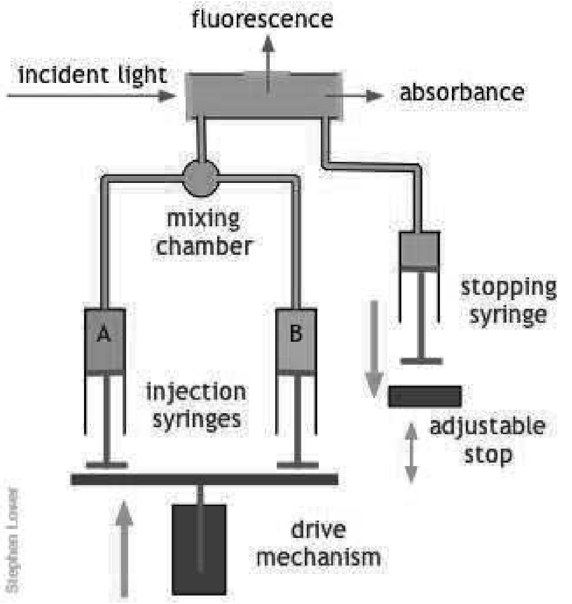


Fig. 3.2 *A Stop Flow Fast Kinetic System*

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.

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).

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.

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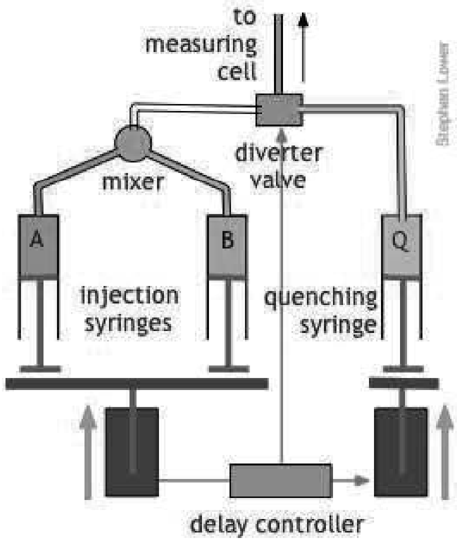

Fig. 3.3 *A Quench Flow Fast Kinetic System*

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.

Relaxation Methods

Many chemical reactions are complete in less than a few seconds, which makes the rate of reaction difficult to determine. In these cases, the relaxation methods can be used to determine the rate of the reaction.

The term relaxation is used to describe a reaction's return to equilibrium. An equilibrium system is subjected to an external perturbation, such as temperature change. When the change is applied suddenly, the lagging time it takes the system to reach the new equilibrium position is related to the k_f and k_r constants and is called relaxation time, τ. To determine the relaxation, the method can be utilized by reactions with half-lives of 1 s to 1010 s.

The rate constants of reversible reactions can be measured using a temperature jump 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. For example, if the reaction,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

is endothermic, then according to the Le Chatelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.

3.3.6 Flash Photolysis

In 1967 the Nobel Prize in Chemistry was awarded to Manfred Eigen, Ronald George, George Porter and Wreyford Norrish for their co-discovery of 'Flash Photolysis' in 1949. Flash photolysis is used extensively to study reactions that happen extremely quickly, even down to the femtosecond depending on the laser that is used. The technique was used to take pictures of fast-moving planes, rockets, and missiles.

Flash photolysis techniques and experiments use flash lamps to provide short (millisecond to microsecond) pulses of light and are often used to study photolysis.

Flash photolysis is often used to study reactions that are light dependent, such as photosynthesis and reactions in the cones on the retina of the our eyes, but the method can also be applied to other reactions. The light in the form of a laser excites a molecule into a reactive state, usually in the form of a free radical. From there it is possible to measure the reaction spectroscopically, using the flash as a light source to measure absorbance. The laser pulse must be approximately half the length of the reaction, and of sufficient energy to induce the reaction to take place. Further the flash must cover the spectrum of frequencies which are being studied because not only is the flash producing intermediates of the reaction that are usually not observed, but it is also producing the source for spectroscopic analysis. Intermediates of most reactions are rarely observed, this technique isolates even low concentrations.

Flash photolysis is a pump-probe laboratory technique, in which a sample is first excited by a strong pulse of light from a pulsed laser of nanosecond, picosecond, or femtosecond pulse width or by another short-pulse light source, such as a flash lamp. This first strong pulse is called the pump pulse and starts a chemical reaction or leads to an increased population for energy levels other than the ground state within a sample of atoms or molecules. Typically, the absorption of light by the sample is recorded within short time intervals to monitor relaxation or reaction processes initiated by the pump pulse

3.3.7 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like IR and UV spectroscopy this method is non-destructible one and permits the recovery of the sample for further evaluation.

As implied in the name, nuclear magnetic resonance is concerned with the magnetic properties of certain nuclei, notably the nucleus of the hydrogen atom– the proton. Studying an organic molecule by NMR spectroscopy enables us to record difference in the magnetic properties of the various nuclei present, and to deduce in large measure what are the positions of these nuclei with in the molecule.

We can for proton NMR deduce how many different kinds of hydrogen environments there are in the molecule, and also which hydrogen atoms are present an neighbouring carbon atoms. We can also measure how many hydrogen atoms are present in each of these environments.

Nuclei are characterized by nuclear spin quantum, *I*, which have the values 1/2, 1, 3/ 2... expressed in units of $\frac{h}{2\pi}$. For a given nucleus with spin number *I*, there are 2/+ 1 orientations possible in a magnetic field. It has been found that the nuclei with even atomic numbers and even mass numbers, i.e., both *p* and *n* even have zero nuclear spins. Such nuclei do not exhibit nuclear magnetic resonance. The nuclei with zero spin are ^{4}He, ^{12}C and ^{16}O. Nuclei with both *p* and *n* odd, i.e., with charge odd and mass even, have integral spins. The examples are ^{2}H, ^{14}N (spin 1) and ^{10}B (spin 3). The nuclei with odd mass have half integral spin. The examples are ^{1}H, ^{15}N, ^{13}C and ^{17}O. However, very commonly one consider the hydrogen nuclei (^{1}H).

The proton behaves like a spinning magnet and it precesses like a top around the axis of an applied magnetic field and can do so in two principal orientations, either aligned with the field (low energy) or opposed to the field (high energy) as shown in Figure 3.4, where, B_0 is the external magnetic field. The spinning frequency of the nucleus does not change, but the speed of precession does. The precessional frequency, *v*, is directly proportional to the strength of the external field B_0; that is

$$v \propto B_0'$$

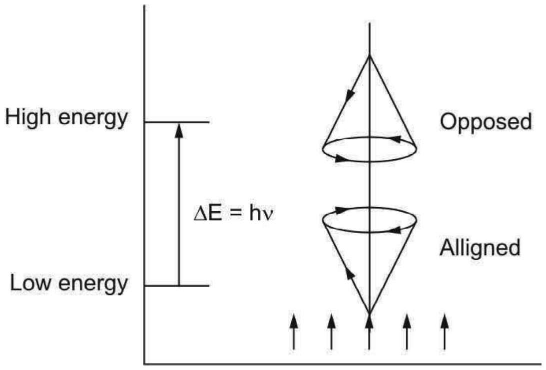

Fig. 3.4 *NMR Study of Hydrogen Nuclei*

For example a proton when exposed to an external magnetic field of 1.4 *T* (≡ 14.000 gauss) will precess ~60 million times per second, so that *v* = 60 MHz: in doing so it will take up one of the two orientations with respect to the axis of the external field–aligned or opposed. If a proton is precessing in the aligned orientation, it can absorb energy and pass to the opposed orientation; subsequently it can lose this extra energy and relax back into the aligned position. If we irradiate the precessing nuclei with a beam of radio-frequency energy of the correct frequency, the low-energy nuclei may absorb this energy and move to a higher energy state. The precessing proton will only absorb energy from the radio-frequency source if the precessing frequency is the same as the frequency of the radio-frequency beam; when this occurs, the nucleus and the radio-frequency beam are said to be in resonance; hence the term nuclear magnetic resonance (NMR). In an applied magnetic nuclei like the proton precess at a frequency v, which is proportional to the strength of the applied field. The exact frequency is given by

$$v = \mu\beta_N B_0/ht \qquad ...(59)$$

where B_0 = strength of the applied external field

h = Planck's constant

μ = magnetic moment of the particular nucleus

I = spin quantum number

β_N = nuclear magneton constant.

Experimental Arrangement

The experimental method for the determination of nuclear magnetic resonance was developed independently by F M Purcell and Bloch in 1946. A simplified diagram of a nuclear magnetic resonance spectrometer is shown in Figure 3.5. A magnetic field B varying from 0 to 10.000 gauss is applied and this field produces an equidistant splitting of the nuclear energy levels. Transitions between the energy levels are stimulated by radiation from the radio frequency transmitter which sends out electromagnetic radiation from the transmitter coil. The sample will absorb the radiation if the frequency of the oscillating field satisfies. The transitions are detected in the indicator. Usually, a cathode ray oscillograph is used as indicator.

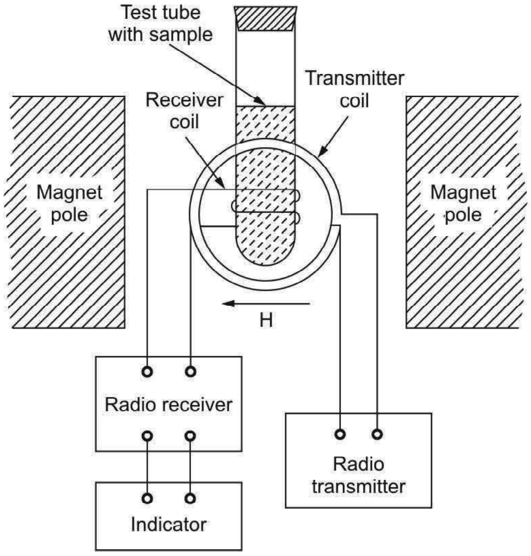

Fig. 3.5 *Schematic Representation of An NMR Spectrometer*

The resonance condition is achieved by superimposing a small variable magnetic field. The low resolution NMR spectrum of ethyl alcohol or ethanol is shown in Figure 3.7. This absorption spectrum is historically significant because it was the first compound which was studied by Packard in 1951. He was able to detect three different values for the precessional frequencies of the protons. He thus, demonstrated that these corresponded to three different chemical environments for the protons an ethanol (CH_3, CH_2 and OH).

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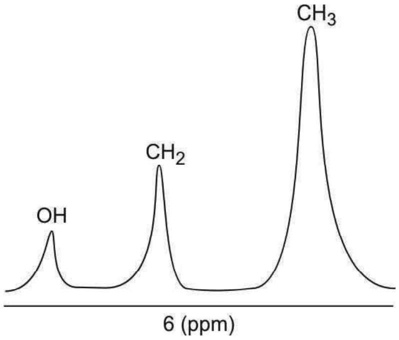

Fig. 3.6 NMR Spectrum of Eethanol

The NMR spectra helps us to know the types of hydrogen atoms in the molecule, which is given by the number of peaks in the NMR spectra. Secondly the number of hydrogen atoms of each type can be determined by finding the ratio of the relative area under each peak. The area under the peaks in ethanol molecule is in the ratio of 1: 2: 3.

Spin-spin Splitting: When the NMR spectrum of ethanol is recorded at high resolution, the CH_2 peak is split into four lines and that for CH_3 into three lines. This splitting is not a chemical shift is proved by the fact the observed splitting does not depend on the strength of the applied field. The effect is caused by the interaction of the nuclear spins of one set of equivalent protons with those of another set. This is called spin-spin coupling. Further the splitting of an NMR line due to interaction of the spins is measured by the spin-spin coupling constant J.

Let us consider a proton A which has another Proton X in its neighbourhood. Now the proton X can have either its nuclear magnet aligned with proton A or opposed to it. Thus, the proton X can either increase the net magnetic field experienced by A (X aligned) or decrease it (X opposed). The two spin orientations of X create two different magnetic fields around proton A. Therefore, the proton A comes to resonance not once but twice thus producing doublet as shown in Figure 3.7.

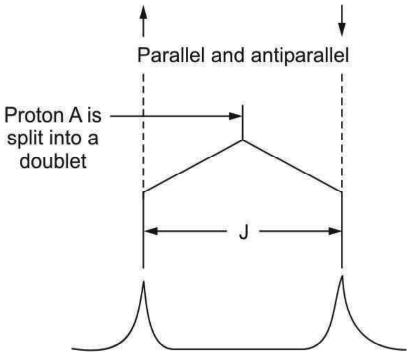

Fig. 3.7 Spin compling be hower neighbour proton x

Similarly a proton A sees two neighbouring protons X and X' the A can see three different possible combinations of spins (*i*) the nuclear spins X and X' both be parallel to A (↑↑); (*ii*) both can be anti-parallel to A (↓↓) (*iii*) one can be parallel and another anti-parallel and this can arise in two ways–X parallel with

X' anti-parallel (↑↓) or X antiparallel and X' parallel (↓↑). Three distinct situations are thus created. The probability of the first two states arising is equal while the third state since it can occur in two ways has twice the probability to occur than the first two. This is shown in Figure 3.8.

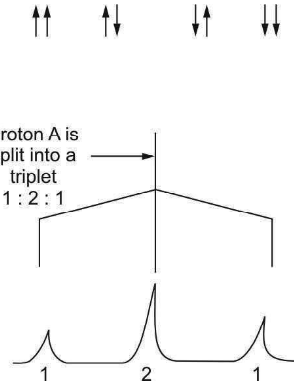

Fig. 3.8 *Spin coupling between Proton and Two Neighbour Protons X and X′*

In general if there are n number of equivalent protons interacting with the neighbouring proton the absorption will be split into $n + 1$ lines and their relative intensities will be proportional to the coefficients of the binomial expansion of $(1 + x)^m$ where $m = n - 1$. Alternatively these coefficients can also be calculated using Pascal's triangle.

1

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

1 6 15 20 15 6 1

Pascal's triangle

A high resolution NMR spectrum of ethanol is more complicated than the ordinary low resolution spectrum. With higher resolution the lines in the spectrum are split into multiplets. The absorption line due to methyl (CH_3) protonts is split into three components (1 : 2 : 1) because the neighbouring methylene group (CH_2) contains two protons each with spin $\frac{1}{2}$. We can think of the first methylene proton splitting the methyl proton resonance into a doublet as shown in Figure 3.9.

Then the second methylene proton splits the doublet into a triplet with the center line twice as intense as the other two. The two methylene protons produce the same spin-spin splitting because there is rapid rotation of around the C–C bond.

The absorption line due to methylene protons is split into four components by three protons of the neighbouring CH_3 group. The relative intensities will be 1 : 3 : 3 : 1.

In the high resolution spectrum recorded in presence of trace amounts of acid the proton in the hydroxyl group does not cause splitting because it undergoes chemical change so rapidly with protons in other molecules that it does not produce splitting effect.

Fig. 3.9 *High resolution NMR Spectra Ethanol*

3.4 MOLECULAR DYNAMIC

Molecular Dynamics (MD) is a computer simulation method for analysing the physical movements of atoms and molecules. The atoms and molecules are allowed to interact for a fixed period of time, giving a view of the dynamic 'Evolution' of the system. In the most common version, the trajectories of atoms and molecules are determined by numerically solving ***Newton's equations*** of motion for a system of interacting particles, where forces between the particles and their potential energies are often calculated using interatomic potentials or molecular mechanics force fields. The method is applied mostly in chemical physics, materials science, and biophysics.

Because molecular systems typically consist of a vast number of particles, it is impossible to determine the properties of such complex systems analytically; MD simulation circumvents this problem by using numerical methods. However, long MD simulations are mathematically ill-conditioned, generating cumulative errors in numerical integration that can be minimized with proper selection of algorithms and parameters, but not eliminated entirely.

For systems that obey the ergodic hypothesis, the evolution of one molecular dynamics simulation may be used to determine macroscopic thermodynamic properties of the system: the time averages of an ergodic system correspond to microcanonical ensemble averages. MD has also been termed ***statistical mechanics by numbers*** and **Laplace's vision of Newtonian mechanics** of predicting the future by animating nature's forces and allowing insight into molecular motion on an atomic scale.

First used in ***theoretical physics***, the MD method gained popularity in materials science soon afterward, and since the 1970s is also common in biochemistry and biophysics. MD is frequently used to refine 3-dimensional structures of proteins and other macromolecules based on experimental constraints from ***X-ray crystallography or NMR spectroscopy***. In physics, MD is used to examine the dynamics of atomic-level phenomena that cannot be observed directly, such as thin-film growth and ***ion-subplantation***, and also to examine the physical properties of ***nanotechnological devices*** that have not or cannot yet be created. In biophysics and structural biology, the method is frequently applied to study the motions of macromolecules such as proteins and nucleic acids, which can be useful for interpreting the results of certain biophysical experiments and for modeling interactions with other molecules, as in ligand docking. In principle MD can be used for ab initio prediction of protein structure by simulating folding of the polypeptide chain from random coil.

Design Constraints

The design of a molecular dynamics simulation should account for the available computational power. Simulation size (***n*** = number of particles), time step, and total time duration must be selected so that the calculation can finish within a reasonable time period. However, the simulations should be long enough to be relevant to the time scales of the natural processes being studied. To make statistically valid conclusions from the simulations, the time span simulated should match the kinetics of the natural process. Otherwise, it is analogous to making conclusions about how a human walks when only looking at less than one footstep. Most scientific publications about the dynamics of proteins and DNA use data from simulations spanning nanoseconds ($10^{"9}$ s) to microseconds ($10^{"6}$ s). To obtain these simulations, several CPU-days to CPU-years are needed. Parallel algorithms allow the load to be distributed among CPUs; an example, is the spatial or force decomposition algorithm.

During a classical MD simulation, the most CPU intensive task is the evaluation of the potential as a function of the particles' internal coordinates. Within that energy evaluation, the most expensive one is the non-bonded or non-covalent part. In Big O notation, common molecular dynamics simulations scale by $\mathbf{O}n^2$ if all pair-wise electrostatic and van der Waals interactions must be accounted for explicitly. This computational cost can be reduced by employing electrostatics methods, such as particle mesh Ewald summation

O(nlog(n)), particle–particle-particle–mesh (P3M), or good spherical cutoff methods $\mathbf{O}(n)$.

3.4.1 Probing the Transition State

The $\mathbf{H_3O^{-}}$ anion has stable and metastable structures that resemble configurations in the vicinity of the transition state for the neutral reactions $\mathbf{OH} + \mathbf{H_2} \leftrightarrow \mathbf{H_2O} + \mathbf{H}$. ***Photoelectron spectroscopy*** of this anion probes the neutral reaction dynamics in the critical transition-state region. Accurate ***quantum dynamics*** calculations of the photoelectron intensity and photo dissociation product energies are shown to provide a quantitatively reliable means of interpreting such experimental observations and reveal a detailed picture of the reaction dynamics.

Since the first detailed studies of elementary chemical reactions at the molecular level, both experimentalists and theoreticians have attempted to probe and understand the dynamics of the critical transition state that separates reactants and products. For several molecules, the stable anion has an ***equilibrium geometry*** that resembles the geometry of the transition state for a reaction involving the corresponding neutral molecule—for example, FH^{-}_{2} and the transition state for the reaction $\mathbf{F + H_2 \rightarrow FH + H}$. ***Photoemission*** of an electron therefore creates, according to the ***Franck–Condon principle***, the neutral molecule in the vicinity of the transition state. Photoelectron spectroscopy measures the kinetic energy distribution of the ejected electron and thereby probes the molecular states in the transition state region. The combination of such experiments with accurate ab initio calculation of the Potential Energy Surfaces (PESs) of the neutral specie and anion, and with exact quantum scattering calculations of the motion of the atomic nuclei, resulted in a quantitative understanding of the transition-state dynamics for the $\mathbf{F + H_2}$ reaction.

Since this work, a number of relevant advances have been made in both theory and experiment. In an important paper, the Berkeley group combined with Gunion and Lineberger to report independent measurements of the photoelectron spectroscopy of the polyatomic anions $\mathbf{H_3O^-}$ and $\mathbf{D_3O^-}$. These experiments probed the transition state for the reactions:

$$\mathbf{OH + H_2 \leftrightarrow H_2O + H}$$

3.4.2 Dynamic of Barrierless Chemical Reaction in Solution

These reactions are characterized by a potential energy surface lacking a potential energy barrier along the reaction coordinate from reactants to products.

Barrierless chemical reactions have often been modelled as a ***Brownian motion*** on a one-dimensional harmonic potential energy surface with a position-dependent reaction sink or window located near the minimum of the surface. This simple (but highly successful) description leads to a non-exponential survival probability only at small to intermediate times but exponential decay in the long-time limit. However, in several reactive events involving proteins and glasses, the reactions are found to exhibit a strongly non-exponential (power law) decay kinetics even in the long time. In order to address such reactions, here, we introduce a model of barrierless chemical reaction where the motion along the reaction coordinate sustains dispersive diffusion. A complete analytical solution of the model can be obtained only in the frequency domain, but an asymptotic solution is obtained in the limit of long time. In this case, the asymptotic long-time decay of the survival probability is a power law of the **Mittag–Leffler functional** form. When the barrier height is increased, the decay of the survival probability still remains non-exponential, in contrast to the ordinary Brownian motion case where the rate is given by the Smoluchowski limit of the well-known **Kramers' expression**. Interestingly, the reaction under dispersive diffusion is shown to exhibit strong dependence on the initial state of the system, thus predicting a strong dependence on the excitation wavelength for photo isomerization reactions in a dispersive medium. The theory also predicts a fractional viscosity dependence of the rate, which is often observed in the reactions occurring in complex environments.

3.4.3 Dynamic of Unimolecular Reaction

Unimolecular reaction: An elementary reaction in which the rearrangement of a single molecule produces one or more molecules of product.

The subject of ***unimolecular dynamics*** deals with the intermolecular and intramolecular microscopic details of unimolecular reactions. Theories of

unimolecular dynamics are concerned with molecular motion over potential energy surfaces and the behaviour of molecular coordinates as a function of time. Most studies of unimolecular reactions have involved measurements and predictions of the rate at which an energized molecule will undergo a uni-molecular reaction. The basic postulate of all unimolecular theories is the rapidity of intramolecular vibrational energy relaxation. Experimentalists were awarded a rare opportunity to test two conflicting assumptions regarding this postulate by the simultaneous advent of the Slater and Rice-Ramsperger-Kassel-Marcus (RRKM) theories in the 1950s. Slater's theory, which is dynamical, pictures a molecule as an assembly of harmonic oscillators. Within this framework vibrational energy relaxation between the normal modes is forbidden, and reaction occurs only when some coordinate, the reaction coordinate, reaches a critical extension by superposition of the various normal modes. The experimental tests overwhelmingly endorsed the RRKM theory, and the controversy involving intramolecular vibrational energy relaxation was seemingly laid to rest. It also appeared as though dynamical treatments of unimolecular reactions were unnecessary.

Check Your Progress

1. State the ARRT.
2. What is activation entropy?
3. Give the assumptions of how ions act in solution.
4. What do you understand by the steady state approximation?
5. Define the kinetic stability.
6. Give the hydrogen-bromine reaction.
7. State the photochemical reaction.
8. Define the oscillating reaction.
9. Give the advantages of homogeneous catalysis.
10. What is enzyme kinetics?
11. What is flow method?
12. State the NMR.
13. Define MD.
14. State the unimolecular reaction.

3.5 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Absolute Reaction Rate Theory (ARRT) provides an approach to explain the temperature and concentration dependence of the rate law. The colliding molecules must have sufficient energy to overcome a potential energy barrier to react.
2. $\Delta H^{\ddagger}$ is the enthalpy difference between the transition state of a reaction and the ground state of the reactants. It is called **activation enthalpy**. **S** is for

the entropy, the extent of randomness or disorder in a system. The difference between the entropy of the transition state and the sum of the entropies of the reactants is called **activation entropy** $\Delta S^{\ddagger}$.

NOTES

3. The **Debye-Hückel theory** is based on three assumptions of how ions act in solution:
    - Electrolytes completely dissociate into ions in solution.
    - Solutions of Electrolytes are very dilute, on the order of 0.01 M.
    - Each ion is surrounded by ions of the opposite charge, on average.
4. The steady-state approximation is a method used to derive a rate law. The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.
5. Kinetic stability is referred as the reactivity of the metal complexes in solution and defines the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts instead of how stable it is. It helps in determining the rate at which the reaction occurs to establish the equilibrium.
6. There are some chemical reactions which take place by a series of successive processes involving the formation of free atoms and radicals. The kinetic laws for such reactions are considerably complex. A well known example of these types of reactions is the hydrogen-bromine reaction.

    The stoichiometry for this reaction is

    $$H_2 + Br_2 \rightarrow 2HBr$$
7. Photochlorination is a chlorination reaction that is initiated by light. Generally, a C H bond is converted to a C Cl bond. The process is exothermic and proceeds as a chain reaction initiated by the homolytic cleavage of molecular chlorine into chlorine radicals by ultraviolet radiation. Many chlorinated solvents are produced using this method.
8. Oscillating reactions are chemical processes in which the reaction rate has periodic fluctuations, which may manifest itself, for example, by colour changes of the reaction mixture. These reactions have, for example, biochemical significance as biological clocks and in certain electrochemical processes.
9. Advantages of Homogeneous catalysts are:
    - Homogeneous catalysts are generally more selective than heterogeneous catalysts.
    - For exothermic processes, homogeneous catalysts dump heat into the solvent.
    - Homogeneous catalysts are easier to characterize precisely, so their reaction mechanisms are amenable to rational manipulation.
10. Enzyme kinetics is the study of the rates of enzyme-catalysed chemical reactions. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated.

11. The most frequently flow methods used for the study of fast reactions is the stopped-flow method. Due to the short analysis time and feasibility, flow based systems have become one of the most powerful analytical tools used for studying fast reactions. Flow methods use flow instruments which are a rapid mixing devices for studying the chemical kinetics of fast reactions in solution.
12. Nuclear Magnetic Resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like IR and UV spectroscopy this method is non-destructible one and permits the recovery of the sample for further evaluation.
13. Molecular Dynamics (MD) is a computer simulation method for analysing the physical movements of atoms and molecules. The atoms and molecules are allowed to interact for a fixed period of time, giving a view of the dynamic 'Evolution' of the system.
14. An elementary reaction in which the rearrangement of a single molecule produces one or more molecules of product.

3.6 SUMMARY

- There is a thermodynamic equilibrium between the transition state and the state of reactants at the top of energy barrier/activation energy barrier. The rate of chemical reaction is proportional to the concentration of the particles in a high-energy. transition state leading to the formation of activated complex.
- An **'activated complex' $AB^{\ddagger}$ or 'transition state'** is formed at the potential energy maximum. The high-energy complex represents an unstable molecular arrangement, in which bonds break and form to generate the product **C** or to degenerate back to the reactants **A** and **B**. Once the energy barrier is surmounted, the reaction proceeds downhill to the product.
- The simplest model of a bimolecular reaction is one in which the two molecules are pictured as hard spheres that do not interact at all until they collide. When they collide, if they have sufficient energy (either kinetic energy along the line of centers, or total energy, or energy in certain degrees of freedom, depending on the exact flavor of theory being used) they are assumed to react.
- The non-reactive collisions are assumed to be *elastic* - that is, both the total momentum and total kinetic energy are unchanged in the collision. An elastic collision is what we observe when macroscopic hard spheres (billiard balls or bocce balls or bowling balls or marbles) collide.
- The collision theory is applicable to simple gaseous reaction. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate, some tunes by a factor of 10^5 for reactions involving fa irly complicated molecules.

- The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom of the molecule are completely neglected, and the theory consequently underestimates the rate of activation.
- The overall rate of activation (i.e. rate of formation of collisionally excited A^* with enough energy to react) is found by summing the k_1^v over all the energy levels which can dissociate i.e. all levels with an energy greater than the critical energy E_0 which the molecule needs to react.
- Based on the results of Hinshelwood and RRK theory, the reaction mechanism can be rewritten to take account of the fact that the rates of collisional activation and unimolecular dissociation are energy dependent.
- he term kinetic isotopic effect relates to changes in the rate of reaction. Isotopic effects are small if the isotopic substitution is far from the seat tab reaction.
- Quantum mechanical tunneling is neglected; i.e., the treatment is semi classical.
- When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a steady-state.
- Clearly the steady state approximation is applicable for the case $k1 < k2$ where the concentration of the intermediate is small and it varies slowly and can be considered to be constant most of the time during the reaction (i.e., to a good approximation, $dct(I) / dt = 0$).
- Free radical chains play an important role in the polymerization of many unsaturated compounds, such as ethylene, styrene and vinyl compounds, to produce materials of industrial importance.
- If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate.
- Many chemical reactions are complete in less than a few seconds, which makes the rate of reaction difficult to determine. In these cases, the relaxation methods can be used to determine the rate of the reaction.
- Nuclei are characterized by nuclear spin quantum, I, which have the values 1/2, 1, 3/ 2... expressed in units of $\frac{h}{2\pi}$.
- The NMR spectra helps us to know the types of hydrogen atoms in the molecule, which is given by the number of peaks in the NMR spectra. Secondly the number of hydrogen atoms of each type can be determined by finding the ratio of the relative area under each peak. The area under the peaks in ethanol molecule is in the ratio of 1: 2: 3.
- The absorption line due to methylene protons is split into four components by three protons of the neighbouring CH_3 group. The relative intensities will be 1 : 3 : 3 : 1.

- In the high resolution spectrum recorded in presence of trace amounts of acid the proton in the hydroxyl group does not cause splitting because it undergoes chemical change so rapidly with protons in other molecules that it does not produce splitting effect.

3.7 KEY TERMS

- **Reaction Rate**: The Reaction Rate for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time.
- **Activation enthalpy:** The standard enthalpy of activation is the enthalpy change that appears in the thermodynamic form of the rate equation obtained from conventional transition state theory.
- **Activation entropy:** The entropy of activation'of a reaction is one of the two parameters (along with the enthalpy of activation) which are typically obtained from the temperature dependence of a reaction rate constant, when these data are analyzed using the Eyring equation.
- **Steady-state approximation:** The steady-state approximation is a method used to derive a rate law. The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.
- **Nuclear Magnetic Resonance (NMR):** Nuclear Magnetic Resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like ir and uv spectroscopy this method is non-destructible one and permits the recovery of the sample for further evaluation.

3.8 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define reaction rate.
2. What is ARRT?
3. Give any two principles of ARRT.
4. What is Hinshelwood theory?
5. What do you understand by kinetic salt effect?
6. State the steady chemical kinetic.
7. What is dynamics chain reaction?
8. What is branched chain explosive reaction?
9. What is homogeneous catalysis?

10. State the kinetic enzyme reaction.
11. What is flow method?
12. State the dynamic of unimolecular chain reaction.

Long-Answer Questions

1. Explain in detail about the ARRT and RRKM theory with examples.
2. Discuss about the kinetic salt effect giving examples.
3. Discuss in detail about the steady state approximation.
4. Elaborate on the thermodynamic and kinetic control reactions with various types of examples.
5. Describe the dynamic chain reaction with appropriate examples.
6. Analyse the photochemical reaction hydrogen chlorine and bromine and oscillatory reaction (Belousov-Zhabotinsky (BZ) reaction).
7. Interpret the fast reaction, flow and relaxation methods giving examples.
8. Briefly describe the NMR.
9. Analyse the molecular dynamic and probing the transition state.
10. Explain in detail about the dynamic of barrier less chemical reaction and unimolecular reaction.

3.9 FURTHER READING

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UNIT 4 SURFACE CHEMISTRY

NOTES

Structure

4.0 INTRODUCTION

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. Absorption is a chemical or physical phenomenon in which the molecules, atoms and ions of the substance getting absorbed enters into the bulk phase (gas, liquid or solid) of the material in which it is taken up.

The Gibbs adsorption isotherm for multicomponent systems is an equation used to relate the changes in concentration of a component in contact with a surface with changes in the surface tension, which results in a corresponding change in surface energy. Surface film tension is the property of a liquid by which it acts as if its surface is a stretched elastic membrane. The catalytic activity is localised on the surface of the catalyst. The mechanism involves diffusion of reactants to the surface of the catalyst and adsorption of reactant molecules on the surface of the catalyst.

A micelle or micelle is an aggregate (or supramolecular assembly) of surfactant phospholipid molecules dispersed in a liquid, forming a colloidal suspension (also known as associated colloidal system). In colloidal and surface chemistry, the Critical Micelle Concentration (CMC) is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system will form micelles. A microemulsion is a thermodynamically stable fluid that differs from kinetically stable emulsions, which will separate into oil and water over time.

Reverse micelles are nanometer-sized (1-10 nm) water droplets dispersed in organic media obtained by the action of surfactants. Surfactant molecules organize with the polar part to the inner side able to solubilize water and the polar part in contact with the organic solvent.

A macromolecule is a very large molecule, such as a protein. They are composed of thousands of covalently bonded atoms. A polymer is any of a class of natural or synthetic substances composed of very large molecules, called macromolecules, which are multiples of simpler chemical units called monomers. Conductive polymers or, more precisely, Intrinsically Conducting Polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. Fire-safe polymers are polymers that are resistant to degradation at high temperatures. There is need for fire-resistant polymers in the construction of small, enclosed spaces such as skyscrapers, boats, and airplane cabins. Liquid Crystal Polymers (LCPs) are polymers with the property of liquid crystal, usually containing aromatic rings as mesogens. The distribution of molecular weights in a polymer sample is often described by the ratio of the weight average molecular weight to the number average molecular weight. The sedimentation rate is proportional to the difference in density between the particle and the medium.

In this unit, you will study about the surface chemistry, absorption, surface area determination, Gibbs adsorption isotherm, surface films on liquid, catalytic activity at surfaces, micelles, counter ion binding to micelles, thermodynamic of micellization, micellar solubilisation, microemulsion, reverse micelles, macromolecule, kinetic and mechanism of polymerization, electrical conductive polymers, fire resistance polymers, molecular mass and its determination, chain configuration of macromolecules.

4.1 OBJECTIVES

After going through this unit, you will be able to:

- Know about the surface chemistry
- Define the absorption
- Determine the surface area
- Calculate the Gibbs adsorption isotherm
- Interpret the surface films on liquid
- Discuss the catalytic activity at surfaces
- Explain about the micelles
- Elaborate on the counter ion binding to micelles
- Analyse the thermodynamic of micellization
- Comprehend the micellar solubilisation
- Understand the microemulsion
- Introduce the reverse micelles

- Describe the macromolecule
- Know about the kinetic and mechanism of polymerization
- Analyse the electrical conductive polymers
- Discuss about the fire resistance polymers
- Explain the molecular mass and its determination
- Illustrate the chain configuration of macromolecules

4.2 ADSORPTION

When solids are allowed to remain in contact with a gas, a film of gas molecules accumulates on the surface. It was pointed out in the discussion of surface tension that the molecular forces at the surface of a liquid are unbalanced or unsaturated than in the bulk. Similarly, molecules or ions at the surface of a solid have unsaturated or residual forces. Solid and liquid surfaces, therefore, have a tendency to satisfy their residual forces by attracting onto and retaining on their surfaces, molecules of gases or other substances with which they come in contact. This results in higher concentration of molecules on the surface of a solid or liquid than in the bulk of the medium. This phenomenon is known as *adsorption*.

The substance on which the adsorption takes place is known as the *adsorbent* and the substance which is adsorbed in known as *adsorbate*.

The phenomenon of adsorption should not be confused with *absorption* which refers to one material passing into the bulk of another. For example, water is adsorbed by a sponge and water vapours are adsorbed by anhydrous calcium chloride. On the other hand, water vapours are adsorbed by silica gel and acetic a particular process is adsorption or absorption, the term *sorption* is used which includes both absorption and adsorption. Figure 4.1 shows the adsorption of a gas on a solid surface.

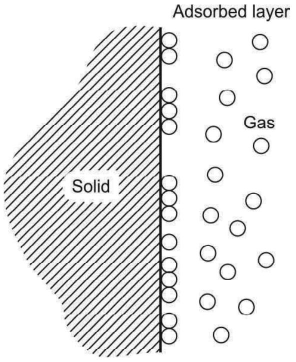

Fig. 4.1: *Adsorption of a Gas on a Solid Surface*

Adsorption of Gases by Solids

All solids adsorb gases to some measurable extent. The magnitude of adsorption of gases by solids depends on the nature of the solid and the gas being adsorbed, the state of subdivision (area) of the solid the temperature and the pressure of the gas.

It has been observed that those solids which have the largest possible surface areas are very good adsorbing agents. In fact, larger is the surface area, greater will be the amount of gas adsorbed. The best adsorbents used in practice are various kinds of specially prepared carbon (wood, bone and blood charcoals, etc). They have large surface areas due to their exceptionally high porosity. In addition to various kinds of carbon, other good adsorbing substances are silica gel, alumina, kaolin and certain alumino silicates. The adsorption power of these substances can further be enhanced by a process called activation. During activation, the adsorbent is heated in steam or air atmosphere to about 1500ºC. Heating drives out all impurities gasified at that temperature from the pores and leads to larger free surface for adsorption. Thus, activated charcoal at 24ºC adsorbs 1.48 gram of carbon tetrachloride per gram of charcoal whereas before activation it, could adsorb only 0.011 gram per gram of charcoal.

Gases which condense more easily are much more strongly adsorbed. Since it is difficult to determine the surface area of adsorbing agents directly, the mass of adsorbent is generally taken as a measure of the surface available for adsorption. Hence adsorption is generally expressed as the amount of substance adsorbed per unit mass of adsorbing agents.

The amount of adsorbed gas, as a rule, decreases with increase of temperature at a constant pressure and increases with a fall in temperature. Hence, according to Le-Chatelier Braun principle, adsorption of a gas by a solid is accompanied by evaluation of heat which is known as the *heat of adsorption*. This has been confirmed by direct experimental evidence. For every gas and solid, there is some definite heat of adsorption. The extent of adsorption increases with increase of pressure.

Types of Adsorption

The type of force that holds the adsorbed molecules on the surface has a considerable effect on certain characteristics, in particular how tightly the molecules are held and whether the solid will adsorb certain substance more strongly than others. There are two types of adsorption:

- Physical or Van der Waals Adsorption.
- Chemisorption or Activated Adsorption.

Physical Adsorption: It is characterised by low heats of adsorption of the order of 5 to 10 kcal per mol of the gas. The process of adsorption is similar to the condensation of gas on liquid. This suggests that the forces by which the adsorbed gas molecules are held to the surface of the solid, are similar to the forces of cohesion of molecules in the liquid state. A rise in temperature will increase the kinetic energies of molecules and the molecules will leave the surface thus lowering the extent of adsorption. Another characteristic of physical adsorption is that the adsorption equilibrium is reversible and is established rapidly. Physical adsorption is generally observed in the adsorption of various gases on charcoal and is independent of the chemical nature of the substance being adsorbed.

Chemisorption: In chemisorption adsorption occurs by chemical force and a chemical bond is formed between the adsorbed molecule and the surface. Chemisorption is thus highly selective since only certain types of molecules will be adsorbed by a particular solid. This depends on the chemical properties of gas and the adsorbent. Chemisorption is accompanied by much higher heat changes from 10 kcals to 100 kcals per mole. These heat changes are of the same order as those involved in chemical reactions. Unlike physical adsorption, chemical adsorption is not reversible. Hydrogen is strongly adsorbed by metals—nickel, iron and platinum.

In many cases, it has been observed that adsorption is neither physical nor chemical but a combination of the two. Some systems show physical adsorption at low temperatures but as the temperature is raised, physical adsorption changes into chemical adsorption.

Adsorption Isotherms

A plot obtained between the amount of substance adsorbed per unit mass of the adsorbent and the equilibrium (in case of a gas) or concentration (in case of solution) at constant temperature is known as the adsorption isotherm. Five different types of adsorption isotherms have been observed in the adsorption of gases on solids. These are shown in Figure 4.2.

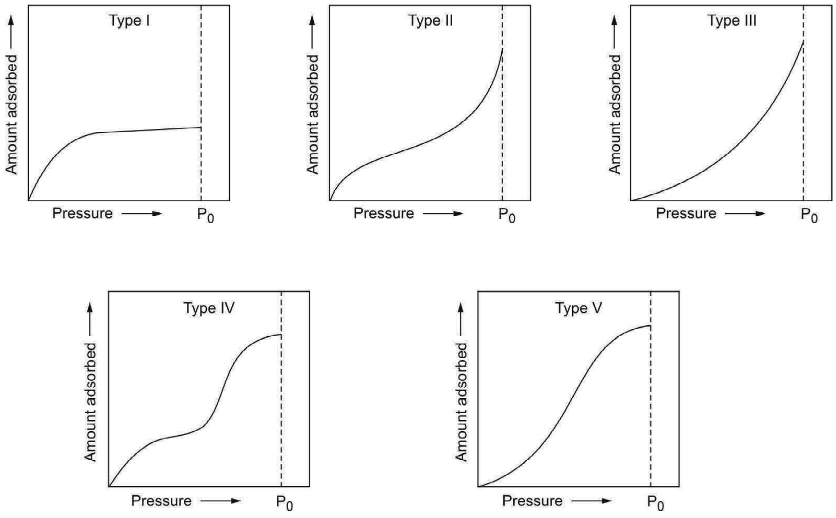

Fig. 4.2: *Five Types of Adsorption Isotherms*

p^0 = Pressure required to condense the gas to liquid.

Type I. Adsorption of nitrogen on charcoal at — 183°C.

Type II. Adsorption of nitrogen on iron or silica gel at — 195°C.

Type III. Adsorption of bromine or iodine on silica get at 83°C.

Type IV. Adsorption of benzene vapours on ferric oxide gel at 50°C.

Type V. Adsorption of water vapours on charcoal at 100°C.

In case of chemisorption, only Type I curves are obtained while in case of physical adsorption all the five isotherms are observed.

Explanation of Type I Isotherm

The Freundlich Adsorption Isotherm: To show the variation of the amount of gas adsorbed per unit mass of the adsorbent with pressure at constant temperature, Freundlich suggested an empirical equation which is known as Freundlich's adsorption isotherm. The equation is

$$\frac{x}{m} = KP^{1/\mathrm{m}} \qquad \text{...(1)}$$

where x is the mass of gas adsorbed, m the mass adsorbent, p is the equilibrium pressure and k and n are constants which depend on the nature of the adsorbate and adsorbent and on the temperature. This equation is applicable only at low pressures.

In order to test Equation (1), take the logarithms of both sides, when it will take the form

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \text{...(2)}$$

According to Equation (2), a plot of $\log \frac{x}{m}$ against $\log p$ should be a straight line with slope equal to $\frac{1}{n}$ and intercept $\log k$ as shown in Figure 4.3.

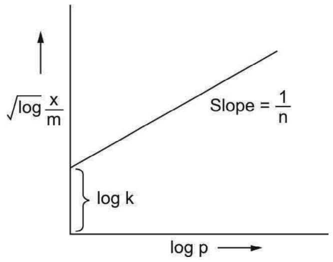

Fig. 4.3: *Freundlich's Adsorption Isotherm*

It was found that the actual plots were straight lines only at low pressures and showed a slight curvature at higher pressure, especially at low temperatures. This indicates that Equation (1) is approximate and cannot be regarded an equation of general applicability to explain adsorption of gases on solids.

The Langmuir Adsorption Isotherm: Langmuir derived an equation from theoretical considerations for type I isotherms. He was the first to point out that in the chemical adsorption of a gas on a solid surface, a layer single molecule in thickness is formed. He proposed that adsorption process consists of two opposing actions—(*i*) condensation of molecules from the gas phase on the surface and (*ii*) evaporation of molecules from the surface back into the body of the gas. At equilibrium the two rates become equal. He derived an equation based on the following assumptions:

- An adsorbent side adsorbs a layer single molecule in thickness.
- Adsorption of other molecules on this side is restricted.
- There is no interaction between the adsorbed molecules.

Consider an adsorbing surface exposed to a gas. Molecules of the gas will strike the surface and stick for an appreciable time due to condensation while other gas molecules will evaporate from the surface due to thermal agitation.

Let a fraction θ of adsorbing surface be covered by the adsorbed gas molecules at any instant. Then the fraction $(1 - \theta)$ of the surface will be bare and available for adsorption.

If p is the pressure of the gas, then from kinetic theory of gases, rate of adsorption of gas molecules

$$= k_1 p(1 - \theta) \qquad ...(3)$$

where k_1 is proportionality constant.

The rate at which gas molecules evaporate from the surface will depend on the fraction of the surface covered by the gas molecules.

Therefore, rate of evaporation of gas molecules

$$= k_2\theta \qquad ...(4)$$

where k_2 is another proportionality constant.

At equilibrium, the two rates must be equal so that

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

or

$$\theta = \frac{k_1 p}{k_2 + k_1 p} \qquad ...(5)$$

Dividing the numerator and denominator of the right hand side of equation (5) by k_2,

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

$$\theta = \frac{bp}{1 + bp} \qquad ...(6)$$

where b is another constant and is equal to k_1/k_2.

Since the amount of the gas adsorbed per unit mass of the adsorbent, y, is proportional to the fraction θ of the surface covered, i.e.,

$$y = k\theta$$

where k is proportionality constant.

Substituting the value of θ from equation (6)

$$y = \frac{kbp}{1 + bp}$$

$$= \frac{ap}{1 + bp} \qquad ...(7)$$

where the constant $a = kb$.

Equation (7) relates the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as the Langmuir adsorption isotherm. The constants a and b depend on the nature of the system and on the temperature.

In order to test this isotherm, Equation (7) is rearranged so as to give

$$\frac{p}{y} = \frac{1}{a} + \left(\frac{b}{a}\right)p \qquad ...(8)$$

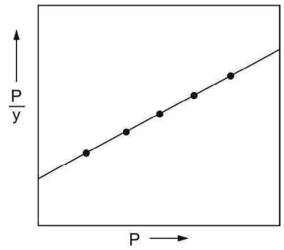

Fig. 4.4 Langmuir Adsorption Isotherm

This equation is similar to an equation for a straight line. Hence, if p/y is plotted against p, a straight line should be obtained with a slope equal to b/a and intercept equal to $1/a$ as shown in Figure 4.4.

It was observed in numerous cases that actual curves were straight lines thus verifying Langmuir adsorption equation.

Consider two extreme cases of Langmuir isotherm:

Case I: *When the gas pressure p is very small.*

Under these conditions, the factor bp is negligibly small as compared to unity in the denominator of Equation (7). This equation, therefore, becomes

$$y = ap$$

$$y \propto p \qquad ...(9)$$

which means that at *very low pressures*, *the amount of gas adsorbed is directly proportional to the pressure*.

Case II: *When the gas pressure p is very high.*

Under these conditions, unity can be neglected in comparison to bp in the denominator of Equation (7) and this equation becomes

$$y = \frac{a}{b} \qquad ...(10)$$

which means that at very high pressure, the amount of gas adsorbed reaches a constant limiting value.

This situation arises when the surface is nearly completely covered with a monomolecular layer at high pressures so that change in pressure has a little effect on the amount of gas adsorbed.

Restriction: Langmuir equation is applicable for smooth, non porous surfaces, which are not very good adsorbents, and for low values of pressure. If the surface is a very good adsorbent and pressure is very high, there are chances of multilayer formation.

Type II–V Isotherms

It was pointed out earlier that in physical adsorption, all the five types of adsorpsion isotherms are observed. Although Langmuir isotherm can satisfactorily explain type I isotherm, it altogether fails to explain all the five types of curves. It was proposed that in types II and III, multilayer formation takes place especially the gas pressure is increased. On this assumption, Brunauer, Emmett and Teller derived the BET equation for types II and III isotherms. The equation is

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \frac{(C-1)}{(v_m C)} \cdot \frac{p}{p_0} \qquad \text{...(11)}$$

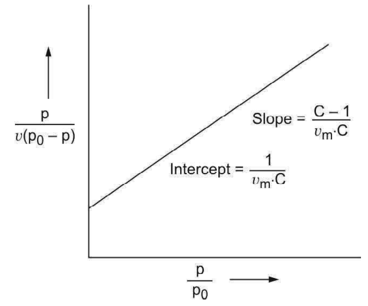

Fig. 4.5 *Isotherm Plot according to BET Equation*

where v and v_m are the volumes, reduced to standard conditions, of the gas adsorbed at pressure p and when the surface is covered with a monomolecular layer respectively at temperature T, p_0 the saturated vapour pressure of the gas at temperature T and C is a constant approximately equal to $\delta(E_1 - E_L)/RT$ where E_1 is the heat of adsorption of the first layer and E_L is the heat of condensation of the gas to liquid. If $E_1 > E_L$, isotherms of type II are observed and if $E_1 < E_L$ isotherms of type III are observed.

Equation (11) can be tested by plotting $\frac{p}{v(p_0 - p)}$ versus $\frac{p}{p_0}$. The plot should be a straight line with slope $\frac{C-1}{v_m C}$ and intercept $\frac{1}{v_m C}$ as shown in Figure 4.5.

To explain type IV and V isotherms, it was suggested that in addition to the multilayer adsorption, condensation of the gas molecules also takes place in the small pores and capillaries of the adsorbent even at pressure below p_0. The distinction between these two types is again based on the relative magnitudes of E_1 and E_L. If $E_1 > E_L$, types IV isotherms are observed and if $E_1 < E_L$ type V isotherms are observed.

Adsorption from Solution

Solid surfaces can also adsorb solutes from the solution. An application of adsorption from solution is the use of activated charcoal for decolorising sugar solutions. Activated characoal can adsorb colouring impurities on its surface. Other examples of this type of adsorption are the adsorption of ammonia from ammonium hydroxide, phenolphthalein from solutions of acids or bases and acetic acid from its solution in water, etc. by activated charcoal.

It has been observed that carbon adsorbs non-electrolytes more readily from a solution than electrolytes and inorganic solids adsorb electrolytes in preference to non-electrolytes. This behaviour of adsorbents to attract certain substances in preference to other substances leads to a phenomenon of *negative adsorption*.

Adsorption from solution in most of the cases leads to the formation of layer single molecule in thickness on the surface of the solid as was observed in the chemisorption of gas on a solid.

NOTES

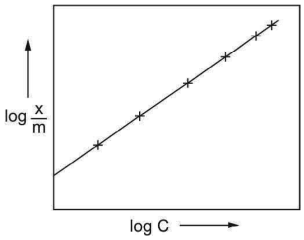

Fig. 1.6 *Adsorption of Acetic Acid by Charcoal*

This type of adsorption is also affected by temperature and concentration. The extent of adsorption decreases with increase of temperature and increases with increase of concentration. In order to represent the variation of extent of adsorption with concentration, Freundlich suggested an empirical isotherm similar to Equation (1). This equation is,

$$\frac{x}{m} = kC^{l/n} \qquad ...(12)$$

where x and m are the masses of the substance adsorbed and of adsorbent respectively, C is the equilibrium concentration of the adsorbed substance in the solution, k and n are empirical constants. Taking logarithms of Equation (12), we get,

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log \mathrm{C} \qquad ...(13)$$

Equation (13) implies that a plot of log $\frac{x}{m}$ against log C should be a straight line with slope $\frac{1}{n}$ and intercept log k. Figure 1.6 shows such a plot of a data for the adsorption of acetic acid from aqueous solution at 25ºC.

Temkin Isotherm

Temkin adsorption isotherm model contains a factor that explicitly taking into the account of adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than in logarithmic manner with the coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energy (up to some maximum binding energy). The fitting was carried out by plotting the quantity sorbed q_e against ln C_e. The constants were determined from the slope and the intercept. The model is given by the following Equations

$$q_e = \frac{RT}{b_T}\ln\left(A_T C_e\right)$$

$$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e$$

$$B = \frac{RT}{b_T}$$

$$q_e = B \ln A_T + B \ln C_e$$

where:

A_T = Temkin isotherm equilibrium binding constant ($L \cdot g^{-1}$)
b_T = Temkin isotherm constant
R = Universal gas constant ($8.314\ J \cdot mol^{-1} \cdot K^{-1}$)
T = Temperature at 298 K.
B = Constant related to heat of sorption ($J \cdot mol^{-1}$)

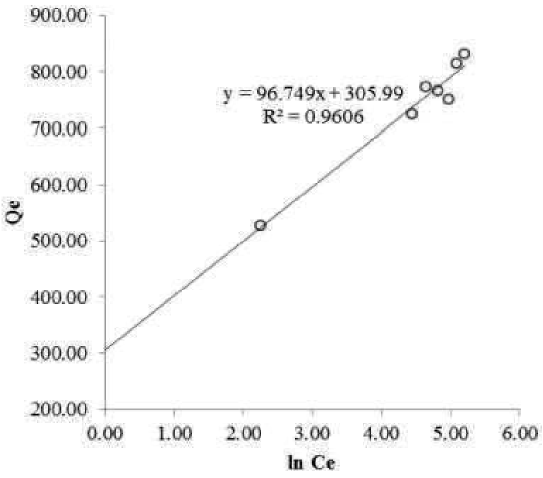

Fig. 4.7 *Temkin Adsorption Isotherm.*

From the Temkin plot shown in Figure 4.7, the following values were estimated: $A_T = 0.484\ L.g^{-1}$, $B = 96.749\ J.mol^{-1}$ which is an indication of a physical adsorption and the $R^2 = 0.9606$.

Hutson and Yang applied Temkin isotherm model to confirm that the adsorption of cadmium ion onto nanozero-valent iron particles follows a chemisorption process. Similarly, Elmorsi *et al*. used the Temkin isotherm model in their investigation of the adsorption of methylene blue onto miswak leaves.

Applications of Adsorption

Adsorption finds extensive applications both in the laboratory and in the industry. Some of the important applications are:

- Adsorption of gases on solids is employed for creating a high vacuum between the walls of Dewar containers designed for storing liquid air or liquid hydrogen. This is achieved by placing activated charcoal between the walls which has already been exhausted to the maximum extent using a vacuum pump. The activated charcoal will adsorb any gas which may appear due to glass imperfection or diffusion through the glass.

- Adsorption of gases on solids is also utilized in gas masks which contain an adsorbent or a series of adsorbents. These adsorbents purify the air for breathing by adsorbing all the poisonous gases from the atmosphere. In the same manner, suitable adsorbents can also be employed in the industry for recovering the solvent vapours from air or particular solvents from the mixture of other gases.
- Charcoal finds an extensive application in the sugar industry. It is used as a decolorizer for the purification of sugar liquors. It can also be used for removing coloring matter from various other types of solutons.
- Adsorption is employed for the recovery and concentrations of vitamins and other biological substances.
- Adsorption finds extensive applications in chromatography which is based on selective adsorption of a number of constituents present together in a solution or gas.
- Adsorption also plays an important role in catalysis.

4.2.1 Surface Area Determination

The surface area of a solid object is a measure of the total area that the surface of the object occupies. The mathematical definition of surface area in the presence of curved surfaces is considerably more involved than the definition of arc length of one- dimensional curve, or of the surface area for polyhedral, i.e., objects with flat polygonal faces, for which the surface area is the sum of the areas of its faces. Smooth surfaces, such as a sphere, are assigned surface area using their representation as parametric surfaces. This definition of surface area is based on methods of infinitesimal calculus and involves partial derivatives and double integration.

A general definition of surface area was sought by Henri Lebesgue and Hermann Minkowski in the twentieth century. Their work defined geometric measure theory which studies various notions of surface area for irregular objects of any dimension.

In chemistry, the surface area is considered significant in chemical kinetics. Increasing the surface area of a substance generally increases the rate of a chemical reaction. For example, iron in a fine powder will combust, while in solid blocks it is stable enough to use in structures. For different applications a minimal or maximal surface area may be desired. For example, when we cut up a piece of a solid, we increase its surface area. By doing this, we expose more of its particles to attack by other reactant particles. Therefore we increase the chance of collisions between reactant particles. Because the collisions become more frequent, the rate of reaction increases.

Hence, the greater the surface area of a solid reactant, the faster its rate of reaction.

Thus, as we increase the surface area of the reactants, we increase the rate of reaction.

Surface Tension

Consider a molecule, *A*, in the interior of a liquid. It is being attracted by neighbouring molecules equally in all directions and thus the resultant force on it is zero. Now consider another molecule, *B* at the surface. It is experiencing a resultant force downward because of greater attraction for molecules in the liquid than for molecules in the vapour above the liquid. This is the case with all the molecules at the surface. As a result of this inward pull, all the molecules at the surface tend to go down and in doing so make the liquid behave as if it were enclosed by a membrane or skin. Thus the surface of the liquid tends to contract to have the minimum surface area possible. This force in the surface of a liquid is called *surface tension* and is defined as the force per unit length exerted at right angles upon a line of unit length in the surface. The units of surface tension are force per unit length or is the CGS system dyne per centimeter. It is because of surface tension that falling water droplets in vacuum and the mercury particles on a smooth surface acquire spherical shape (a sphere occupies a smallest area for the given volume).

Since every liquid has a tendency to decrease its surface area, therefore, it is necessary to do work against the inward pull and to bring molecules from the interior of the liquid in the surface in order to increase the surface area of the liquid. To obtain an expression for this work, consider a film of liquid stretched on a rectangular wire frame, one side of which is movable.

Let a force, *F* is applied perpendicular to the movable side to move it against the force of surface tension. If the wire moves a distance, *dx* the work done, *W* is given by

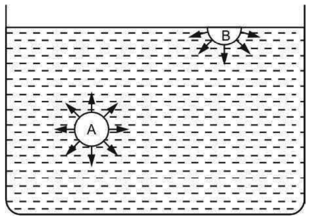

Fig. 2.1 Force acting on a molecule in a liquid

$$W = Fdx \qquad ...(14)$$

This causes an increase in the surface area of the film given by

$$\Delta A = 2(l \times dx) \qquad ...(15)$$

where *l* is length of the film. The factor 2 is introduced because there are two sides of the film.

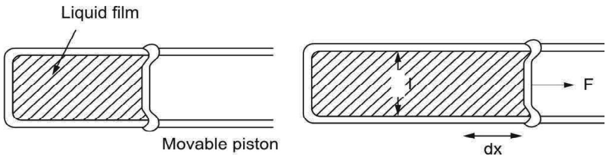

Fig. 4.9 Calculation of force on a liquid surface

Since the force *F* is applied against the force of surface of tension acting on the film, therefore, if γ is the force per centimeter along the movable wire, then

$$F = \gamma \times 21 \qquad ...(16)$$

$$\gamma = \left(\frac{F}{2l}\right) = \frac{\text{Force}}{\text{Unit length}}$$

Therefore, $W = g \cdot 2ldx$

$$= \gamma \times \Delta A$$

or $$\gamma = \frac{W}{\Delta A} = \frac{\text{Work}}{\text{Area}} \qquad \text{...(17)}$$

From equation (16), surface tension is defined as the force in dynes acting per unit length and from Equation (17), it can be defined as the work in ergs required to generate a unit increase in surface area. The units of surface tension are dynes/cm or ergs/cm^2. SI units of surface tension is newton/m.

Measurement of Surface Tension

The various methods which are commonly employed to determine the surface tension of a liquid are:

1. The Capillary Rise Method: This method is based on the fact that any liquid such as water which wets the walls of the glass capillary tube will rise in the tube when the tube is placed in the liquid. On the other hand, if a liquid, such as mercury which does not wet the walls of the capillary tube will not rise and show a depression in the level of the liquid in the capillary tube. The rise or falls of a liquid in a capillary tube is based on the surface tension.

The word capillary means hair in Latin. If the tube were hair thin in the rise would be large.

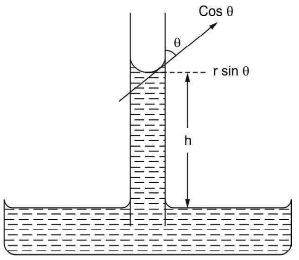

Fig. 4.9 Capillary Rise Method for Measuring Surface Tension

Consider a find capillary tube of uniform radius, r, placed in a liquid that wets the walls of the tube. Because of force of surface tension, γ, which acts along the innercircumference of the liquid, liquid will rise. The liquid keeps on rising until upward force, F_1, due to surface tension is balanced by the downward force, F, due to the weight of the liquid.

Since the force due to surface tension is acting at an angle θ, known as *contact angle,* the upward force F_1, is given by

$$F_1 = 2\pi r \cdot \gamma \cos\theta \qquad \text{...(18)}$$

If the liquid rises a height h in the tube above the level of the liquid outside, the downward force, F_2 is given by

$$F_2 = \pi r^2 hdg \qquad \text{...(19)}$$

where d is the density of the liquid and g is the gravitational force. At equilibrium the two forces are equal.

Therefore, $F_1 = F_2$

From Equations (18) and (19)

$$2\pi r\,\gamma \cos\theta = \pi r^2 \cdot hdg$$

or $$\gamma \approx \frac{1}{2\cos\theta}.rh\,dg \qquad ...(20)$$

For most liquids $\theta = 0$, $\cos\theta = 1$

$$\therefore \qquad \gamma = \frac{1}{2}rhdg \qquad ...(21)$$

A liquid making an angle of 90º, cos 90 = 0

$$h = \frac{2\gamma\cos\theta}{rdg} = 0$$

would show no capillary rise at all. Mercury whose contact angle again glass is about 140º shows a capillary depression, i.e.,

$$h = \frac{2\gamma\text{ (-ve value)}}{rdg}$$

The capillary rise phenomenon is not only the basis for an absolute and accurate means of measuring surface tension but is also one of its major manifestations. The phenomenon accounts for the general tendency of wetting liquids to enter pores and fine cracks. The absorption of vapours by porous solids to fill their capillary channels and the displacement of oil by gas or water in petroleum formations constitute specific examples of capillary effects. The water proofing of fabrics involves a direct application of capillary effects. Fabrics are porous materials the space between amounting to small capillary tubes. If the fibres are coated with material on which water has contact angle greater than 90º it will oppose the entry or rise of water into the fabric.

$$h = \frac{2\gamma\text{(-ve value)}}{rdg}$$

Example 4.1

The radius of a given capillary is 0.0355 cm. A liquid whose density is 0.866 gram/cm^2 rises to a height of 2.0 cm in the capillary when it is dipped in the liquid. Calculate the surface tension of the liquid.

Solution: Since $\gamma = 1/2\ r\ h\ dg$

Here $r = 0.03335$ cm, h = 2.0 cm

$d = 0.866$ gram/cm^2 and $g = 981$

Therefore $\gamma = 1/2 \times 0.0335 \times 2.0 \times 0.866 \times 981$

$= 28.46$

Thus, surface tension of the liquid = 28.46 dynes/cm.

Example 4.2

At 20ºC, the surface tension of chloroform is 16.2 dynes/cm. The densities of liquid and gas at the same temperature are 0.1988 gm/cm^2 and 0.0110 gram/cm^3. If the radius capillary is 0.105 mm, what would be the height of the liquid in the capillary, angle of contact being zero?

Solution:

$$\gamma = \frac{1}{3}\left(h + \frac{r}{3}\right)(d_l - d_v)gr.$$

NOTES

Here γ =162; h = ?

d_l = 0.9l88, d_v = 0.0110

g = 981

and r = 0.0105 cm

Substituting these values,

$$16.2 = \frac{1}{2}\left[h + \frac{0.0105}{3}\right] (0.9188 - 0.0110)\ 931 \times 0.0105$$

or h = 3.46

Thus, liquid rises to height of 3.46 cm in the capillary.

2. The Drop-Weight Method: This method is mainly employed to be compare the surface tensions of two liquids.

In this method, the liquid whose surface tension is to be determined, is allowed to pass drop by drop through a capillary tube held vertically. Every drop coming out of the capillary tube grows spherically in size and attains some definite weight. When the weight of the drop becomes equal to the force of surface tension, acting along the circumference of the capillary tube, it falls.

The relationship between the weight of the falling drop (W) and surface tension (γ) is given by the expression

$$\gamma = \frac{W_g}{2\pi r f} \qquad \text{... (22)}$$

where f is a correction factor which is equal to $\frac{r}{v^{1/3}}$, v being the volume of the drop and r its radius.

In actual practice it is difficult to determine all the factors on the right hand side of Equation (9). Thus, for convenience, surface tension of two liquids flowing separately through the same capillary tube, is compared.

If γ_1 is the surface tension of one liquid and γ_2 is the surface tension of another liquid, the two are related by the expression.

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2} \qquad \text{...(23)}$$

where W_1 and W_2 are the weights of drops of liquids 1 and 2 respectively.

The detached drop thus leaves behind a considerable residue of liquid. Table 4.1 gives some values of f.

Table 4.1: *Correction Factors* f, *for the Drop Weight Method*

$\frac{r}{v^{1/3}}$	f	$\frac{r}{v^{1/3}}$	f
0.30	0.7256	0.80	0.600
0.40	0.6828	0.90	0.5998
0.50	0.6515	1.00	0.6098
0.60	0.6250	1.10	0.6280
0.70	0.6093	1.20	0.6535

Note that the correction is considerable. In practice one forms the drops within a closed space to avoid evaporation and in sufficient number that the weight per drop can be determined accurately. It is only necessary to form each drop slowly during the final stages of its growth.

The instrument used for the purpose is known as the stalagmometer and consists of a bubbled capillary tube as shown in the Figure 4.10. The tube, after it has been thoroughly washed and dried, is filled by sucking upto some certain mark X with the liquid whose surface tension is to be determined. The liquid is then allowed to fall very slowly upto mark Y in the form of drops which are collected in a weighing bottle. The number of drops falling at the rate of one to two seconds is counted and their weight is determined. If W_1 and W_2 are the mean weights of drops of the two liquids and γ_1 and γ_2 are their surface tension respectively, they are related to each other by Equation (23).

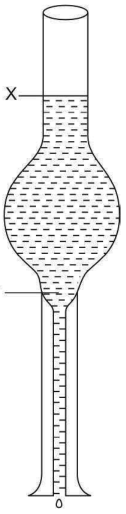

Fig. 4.10 Stalagmometer

It is more convenient to determine the number of drops formed by a definite volume of a liquid than to determine the weight of the drop.

Let n_1 and n_2 be the number of drops of equal volumes (say V) of two liquids 1 and 2 of densities d_1 and d_2 respectively.

The mean weight of drops of liquid 1 is given by

$$W_1 = \frac{V}{n_1} \times d_1 \qquad \text{...(24)}$$

and the mean weight of drops of liquid 2 is given by

$$W_2 = \frac{V}{n_2} \times d_2 \qquad \text{...(25)}$$

(∴ weight of drop = volume of drop × density)

Therefore, equation (4.22) becomes

$$\gamma_1 = \frac{W_1}{W_2} = \frac{\frac{V}{n_2} \times d_1}{\frac{V}{n_2} \times d_2}$$

or $$\frac{\gamma_1}{\gamma_2} = \frac{d_1 n_2}{d_2 n_1} \quad ...(26)$$

From Equation (26), knowing the surface tension of one liquid, usually called the reference liquid, the surface tension o the other liquid can be calculated simply by knowing their densities and the number of drops formed by the equal volume of the two liquids.

3. The Tensiometric or Torsion Balance Method: In this method, a platinum ring about 4 cm in circumference is immersed in the liquid to be tested from the end of the beam of a torsion balance and the force required to separate the ring from the surface of the liquid is then measured. The force f, required for this separation, is related to the surface tension of the liquid by the expression.

$$f = \gamma \times 2(2\pi r) \quad ...(27)$$

where $(2\pi r)$ is the circumference of the ring of radius r. The factor 2 is introduced because the force due to surface tension is acting at both the inner and the outer circumference of the ring.

From Equation (27)

$$\gamma = \frac{f}{4\pi r} \quad ...(28)$$

So knowing f and r, γ can be easily calculated.

This is the quickest method for determining the surface tension of a liquid and requires only small amounts of liquid.

Table 4.2: *Surface tension of liquids at 20ºC*

Liquid	$\gamma(10^{-3}$ *N/m*$)$	*Liquid*	$\gamma(10^{-3}$ *N/m*$)$
Acetone	23.70	Ethyl Ether	17.01
Benzene	28.85	n-Hexane	18.43
Carbon tetrachloride	26.95	Methyl alcohol	22.61
Ethyl acetate	23.90	Toluene	28.50
Ethyl alcohol	22.75	Water	72.75

Example 4.3:

In the determination of surface tension of a liquid, A, by the drop weight method using a stalagmometer, A gave 55 drops while water gave 25 drops volume of the two liquids being the same. The densities of water and A are 0.996 and 0.800 gm/cm^2 respectively and the surface tension of water is 72.0 dynes/cm. What is the surface tension of A?

Solution:

Since $$\frac{\gamma_1}{\gamma_2} = \frac{d_1 n_2}{d_2 n_1}$$

Here $\gamma_2 = 72.0$ dynes/cm

$d_2 = 0.996$

$n_2 = 25$

$\gamma_1 = ?$

$$d_1 = 0.800$$

and $$n_1 = 55 \text{ drops}$$

Substituting these values in the equation, we have

$$\gamma_1 = 72 \times \frac{0.800 \times 25}{0.996 \times 55} = 26.3$$

NOTES

Therefore, surface tension of liquid A = 26.3 dynes/cm.

Variation of Surface Tension with Temperature: The surface tensions of all liquids decrease with increasing temperature and become zero at the critical temperature because at the critical temperature, there is no surface of separation between the liquid and the vapours. To represent the variation of surface tension of a liquid with temperature, many equations have been proposed. Some of them are given below:

1. Eötvös Equation (1886): According to this equation,

$$\gamma\left(\frac{M}{d_l}\right)^{2/3} = K(t_c - t) \qquad ...(29)$$

where γ is the surface tension of the liquid at temperature t and K is a constant independent of temperature, M, d_t and t_c are the molecular weight, density and the critical temperature of the liquid. Since $\left(\frac{M}{d_l}\right)$ is the molar volume, the factor $\left(\frac{M}{d_l}\right)^{2/3}$ is proportional to the molar surface area of the liquid and the product, $\gamma\left(\frac{M}{d_l}\right)$ gives the molar surface energy.

From Equation (28), molar surface energy varies with temperature in a linear manner and becomes zero at the critical temperature.

2. Ramsay-Shields Equation (1893): The equation proposed by W Ramsay and J Shields, is a modification over the Evötvös equation and is expressed as:

$$\gamma\left(\frac{M}{d_l}\right)^{2/3} = (t_c - t - 6) \qquad ...(30)$$

This equation holds good for many liquids. According to this equation, γ will be zero at a temperature 6° below the critical point and will become negative at the critical point.

3. Katayama's equation: Katayama replaced $(t_c - 6)$ by t_c in the Ramsay-Shields equation to obviate the difficulty that γ is zero at $t = t_c - 6$ and proposed in equation (23).

$$\gamma\left(\frac{M}{d_l - d_v}\right)^{2/3} = K(t_c - t) \qquad ...(31)$$

Here d_v is the density of vapour above the liquid at temperature t.

4. MacLeod's Equation (1923): The equation is

$$\gamma = C(d_t - d_v)^4 \qquad ...(32)$$

NOTES

where d_t is the density of the liquid and d_v is the density of the vapour—both measured at the same temperature. C is a constant, characteristic of each liquid but is independent of temperature.

This equation holds good with accuracy over a large temperature range for liquids which do not associate or dissociate.

In Equations (29), (30) and (31), the value of the constant, K, was found to be 2.12 for all liquids that behave normally. However, those liquids such as water, alcohol, carboxylic acids, etc., which are associated, gave not only abnormally low values of K but also showed variation of K with temperature. For some liquids which dissociate, the value of K was found to be higher than 2.12.

Interfacial Tension: The surface tension measures against another immiscible or partially miscible liquid is referred to as interfacial tension. Consider two immiscible liquids A and B in contact with each other. If γ_A and γ_B are their respective surface tensions then the interfacial tension γ_{AB} exists at the boundary between the two layers. Interfacial tension can be measured by the pure liquids. For instance, in the drop weight method, the drops of the liquid may be counted in the liquid against which the interfacial tension is to be measured, the interfacial tension value γ_{AB} is generally intermediate between the surface tensions of the two liquids, γ_A and γ_B. It is given $\gamma_{AB} = \gamma_A - \gamma_B$. Sometimes the interfacial tension may be lower than the surface tension of the either liquid. For example at 20°C, the surface tensions of water and carbon tetrachloride are 72.75 and 26.8 respectively. Their interfacial tension is equal to 45.0, which is very nearly equal to the difference of their surface tensions. But in the case of water and ethyl ether, the interfacial tension at 20°C is 10.7 which is lower than the surface tensions of water and ethyl ether at the same temperature (surface tensions of water and ethyl ether at 20°C are 72.75 and 17.0 respectively). The phenomena of interfacial tension is of considerable importance in connection with the properties of emulsions, detergents, foams, etc.

The dirty clothes containing dirt and grease can not be cleaned by washing with water. This is because water does not wet grease. On adding the detergent or soap to water the molecules of detergent which are hair pin shaped with one end attracted to water and the other end to molecules of grease oil or wax, tend to form water oil interfaces. This results in the removal of dirt and greasy matter and clean the clothes.

Example 4.4:

From the following data

ºC	d_t g/cm^2	γ dynes/cm
°C	0.927	4.5
20°C	0.772	1.16

Calculate t_c for carbon dioxide using Ramsay equation.

Solution. According to Ramsay equation

$$\gamma\left(\frac{M}{d_i - d_l}\right)^{2/3} = K(t_c - t - 6)$$

$$M = 44$$

Substituting the various values from the data at 0°C (273.16 K)

$$4.5\left(\frac{44}{0.927}\right)^{2/3} = K[t_c - (273.16 + 6)]$$

or $$36.31 = K(t_c - 279.16)$$

Similarly, substituting the various values at 20°C (293.16 K)

$$1.16\left(\frac{44}{0.722}\right)^{2/3} = K[t_c - (293.16 + 6)]$$

or $$140.85 = K[t_c - (299.16)]$$

Taking the ratio of the two equations

$$\frac{140.85}{36.31} = \frac{(t_c - 279.16)}{(t_c - 299.16)}$$

or $$t_c = 306.1\text{ K}$$
$$= 33°\text{C}.$$

Pressure Difference Curved Surface (Laplace Equation)

The Laplace pressure is the pressure difference between the inside and the outside of a curved surface that forms the boundary between a gas region and a liquid region. The pressure difference is caused by the surface tension of the interface between liquid and gas.

The Laplace pressure is determined from the Young–Laplace equation given as

$$\Delta P \equiv P_{\text{inside}} - P_{\text{outside}} = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

Where R_1 and R_2 are the principal radii of curvature and γ (also denoted as σ) is the surface tension. Although signs for these values vary, sign convention usually dictates positive curvature when convex and negative when concave.

The Laplace pressure is commonly used to determine the pressure difference in spherical shapes, such as bubbles or droplets. In this case, $R_1 = R_2$:

$$\Delta P = \gamma\frac{2}{R}$$

For a gas bubble within a liquid, there is only one surface. For a gas bubble with a liquid wall, beyond, which is again gas, there are two surfaces, each contributing to the total pressure difference. If the bubble is spherical and the outer radius differs from the inner radius by a small distance, $R_o = R_i + d$, we find

$$\Delta P = \Delta P_i + \Delta P_o = 2\gamma\left(\frac{1}{R_i} + \frac{1}{R_i + d}\right) = \frac{2\gamma}{R_i}\left(1 + \frac{R_i}{R_i + d}\right) = \frac{2\gamma}{R_i}\left(1 + \frac{R_i + d}{R_i + d} - \frac{d}{R_i + d}\right) = \frac{4\gamma}{R_i}\left(1 - \frac{1}{2}\frac{d}{R_i + d}\right) \approx \frac{4\gamma}{R_i} + O(d).$$

The Kelvin equation describes the change in vapour pressure due to a curved liquid–vapour interface, such as the surface of a droplet. The vapour pressure at a convex curved surface is higher than flat surface. The Kelvin equation is dependent upon ***thermodynamic principles*** and does not allude to special properties of materials. It is also used for determination of pore size distribution of a ***porous***

medium using ***adsorption porosimetry***. The equation is named in honor of William Thomson, also known as Lord Kelvin.

The Kelvin equation may be written in the form

$$\ln \frac{p}{p_{\mathrm{sat}}} = \frac{2\gamma V_{\mathrm{m}}}{rRT},$$

Where p is the actual vapour pressure, p_{sat} is the saturated vapour pressure when the surface is flat, γ is the liquid/vapour surface tension, V_m is the molar volume of the liquid, R is the universal gas constant, r is the radius of the droplet, and T is temperature.

Equilibrium vapour pressure depends on droplet size according following conditions.

- If the curvature is convex, r is positive, then $p > p_{sat}$
- If the curvature is concave, r negative, then $p < p_{sat}$

As r increases, p decreases towards p_{sat} and the droplets grow into bulk liquid.

If we now cool the vapour, then T decreases, but so does p_{sat} This means p / p_{sat} increases as the liquid is cooled. We can treat γ and V_m as approximately fixed, which means that the critical radius r must also decrease. The further a vapour is super cooled, the smaller the critical radius becomes. Ultimately it gets as small as a few molecules, and the liquid undergoes homogeneous nucleation and growth.

The change in vapour pressure can be attributed to changes in the Laplace pressure. When the Laplace pressure rises in a droplet, the droplet tends to evaporate more easily.

When applying the ***Kelvin equation***, two cases must be distinguished: A drop of liquid in its own vapour will result in a convex liquid surface, and a bubble of vapour in a liquid will result in a concave liquid surface.

4.2.2 Gibbs Adsorption Isotherm

Surface excess is the difference between the amount of a component actually present in the system, and that which would be present in a reference system if the bulk concentration in the adjoining phases were maintained up to the arbitrary chosen but precisely determined in position dividing surface.

Gibbs Isotherm

The Gibbs adsorption isotherm for multi component systems is an equation used to relate the changes in concentration of a component in contact with a surface with changes in the surface tension, which results in a corresponding change in surface energy. For a binary system, the Gibbs adsorption equation in terms of surface excess is:

$$-\mathrm{d}\gamma = \Gamma_1 \mathrm{d}\mu_1 + \Gamma_2 \mathrm{d}\mu_2 ,$$

Where

γ is the surface tension,

Γ_i is the surface excess of component i,

μ_i is the chemical potential of component i.

Different influences at the interface may cause changes in the composition of the near-surface layer. Substances may either accumulate near the surface or, conversely, move into the bulk. The movement of the molecules characterizes the phenomena of adsorption. Adsorption influences changes in surface tension and colloid stability. Adsorption layers at the surface of a liquid dispersion medium may affect the interactions of the dispersed particles in the media and consequently these layers may play crucial role in colloid stability. The adsorption of molecules of liquid phase at an interface occurs when this liquid phase is in contact with other immiscible phases that may be gas, liquid, or solid.

Conceptual Explanation of Equation

Surface tension describes how difficult it is to extend the area of a surface (by stretching or distorting it). If surface tension is high, there is a large free energy required to increase the surface area, so the surface will tend to contract and hold together like a rubber sheet.

There are various factors affecting surface tension, one of which is that the composition of the surface may be different from the bulk. For example, if water is mixed with a tiny amount of surfactants (for example, hand soap), the bulk water may be 99% water molecules and 1% soap molecules, but the topmost surface of the water may be 50% water molecules and 50% soap molecules. In this case, the soap has a large and positive 'surface excess'. In other examples, the surface excess may be negative: For example, if water is mixed with an inorganic salt like sodium chloride, the surface of the water is on average less salty and more pure than the bulk average.

Consider again the example of water with a bit of soap. Since the water surface needs to have higher concentration of soap than the bulk, whenever the water's surface area is increased, it is necessary to remove soap molecules from the bulk and add them to the new surface. If the concentration of soap is increased a bit, the soap molecules are more readily available (they have higher chemical potential), so it is easier to pull them from the bulk in order to create the new surface. Since it is easier to create new surface, the surface tension is lowered. The general principle is:

When the surface excess of a component is positive, increasing the chemical potential of that component reduces the surface tension.

Next consider the example of water with salt. The water surface is less salty than bulk, so whenever the water's surface area is increased, it is necessary to remove salt molecules from the new surface and push them into bulk. If the concentration of salt is increased a bit (raising the salt's chemical potential), it becomes harder to push away the salt molecules. Since it is now harder to create the new surface, the surface tension is higher. The general principle is:

When the surface excess of a component is negative, increasing the chemical potential of that component increases the surface tension.

The Gibbs isotherm equation gives the exact quantitative relationship for these trends.

Location of Surface and Defining Surface Excess

In the presence of two phases (α and β), the surface (Surface Phase) is located in between the phase α and phase β. Experimentally, it is difficult to determine the exact structure of an inhomogeneous surface phase that is in contact with a bulk liquid phase containing more than one solute. Inhomogeneity of the surface phase is a result of variation of mole ratios. A model proposed by Josiah Willard Gibbs proposed that the surface phase as an idealized model that had zero thickness. In reality, although the bulk regions of α and β phases are constant, the concentrations of components in the interfacial region will gradually vary from the bulk concentration of α to the bulk concentration of β over the distance x. This is in contrast to the idealized Gibbs model where the distance x takes on the value of zero. The diagram to the right illustrates the differences between the real and idealized models.

Definition of Surface Excess

In the idealized model, the chemical components of the α and β bulk phases remain unchanged except when approaching the dividing surface. The total moles of any component (Examples include: water, ethylene glycol, etc.) remains constant in the bulk phases but varies in the surface phase for the real system model as shown below in Figure 4.11.

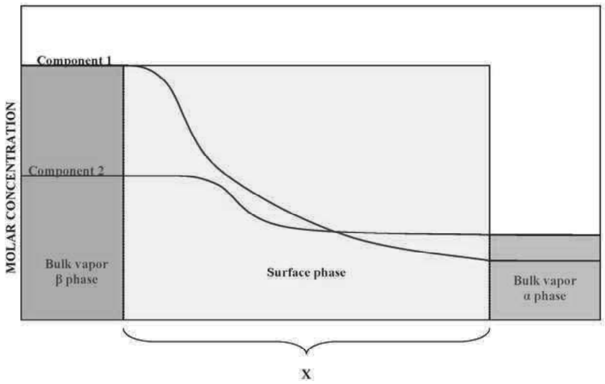

***Fig. 4.11** Variation in the Concentration of Components in the Surface Phase of the Real Model*

In the real system, however, the total moles of a component varies depending on the arbitrary placement of the dividing surface. The quantitative measure of adsorption of the i-th component is captured by the surface excess quantity. The surface excess represents the difference between the total moles of the i-th component in a system and the moles of the i-th component in a particular phase (either α or β) and is represented by: $\Gamma_i = \dfrac{n_i^{\mathrm{TOTAL}} - n_i^{\alpha} - n_i^{\beta}}{A}$,

where Γ_i is the surface excess of the i-th component, n are the moles, α and β are the phases, and A is the area of the dividing surface.

Γ represents excess of solute per unit area of the surface over what would be present if the bulk concentration prevailed all the way to the surface, it can be positive, negative or zero. It has units of mol/m^2.

Relative Surface Excess

Relative Surface Excess quantities are more useful than arbitrary surface excess quantities. The Relative surface excess relates the adsorption at the interface to a solvent in the bulk phase. An advantage of using the relative surface excess quantities is that they don't depend on the location of the dividing surface. The relative surface excess of species i and solvent 1 is therefore:

$$\Gamma_i^1 = \Gamma_i - \Gamma_1 \left(\frac{C_i{}^{\alpha} - C_i{}^{\beta}}{C_1{}^{\alpha} - C_1{}^{\beta}} \right).$$

The Gibbs Adsorption Isotherm Equation for α and β Phase

Derivation of the Gibbs adsorption equation:

For a two-phase system consisting of the α and β phase in equilibrium with a surface S dividing the phases, the total Gibbs free energy of a system can be written as: $G = G^{\alpha} + G^{\beta} + G^{S}$,

Where G is the Gibbs free energy.

The equation of the Gibbs Adsorption Isotherm can be derived from the particularization to the thermodynamics of the Euler theorem on homogeneous first-order forms. The Gibbs free energy of each phase α, phase β, and the surface phase can be represented by the equation:

$$G = U + pV - TS + \sum_{i=1}^{k} \mu_i \, \mathrm{n}_i \,,$$

Where

U is the internal energy

p is the pressure

V is the volume

T is the temperature

S is the entropy

μ_i is the chemical potential of the i-th component.

By taking the total derivative of the Euler form of the Gibbs equation for the α phase, β phase and the surface phase:

$$\mathrm{d}G = \sum_{\alpha,\beta,S} \left(\mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T + \sum_{i=1}^{k} \mu_i \, \mathrm{d}n_i + \sum_{i=1}^{k} \mathrm{n}_i \, \mathrm{d}\mu_i \right) + A\mathrm{d}\gamma + \gamma \mathrm{d}A \,,$$

where A is the cross sectional area of the dividing surface, and γ is the surface tension.

For reversible processes, the first law of thermodynamics requires that:

$$\mathrm{d}U = \delta q + \delta w \,,$$

where q is the heat energy and w is the work.

$$\delta q + \delta w = \sum_{\alpha,\beta,S} \left(T\mathrm{d}S - p\mathrm{d}V - \delta w_{\text{non-pV}} \right) .$$

Substituting the above equation into the total derivative of the Gibbs energy equation and by utilizing the result γdA is equated to the non-pressure volume work when surface energy is c considered: $\mathrm{d}G = \sum_{\alpha,\beta,S}\left(V\mathrm{d}p - S\mathrm{d}T + \sum_{i=1}^{k}\mu_i\,\mathrm{d}n_i + \sum_{i=1}^{k}\mathrm{n}_i\,\mathrm{d}\mu_i\right) + A\mathrm{d}\gamma,$

by utilizing the fundamental equation of Gibbs energy of a multi component system:

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_{i=1}^{k}\mu_i\,\mathrm{d}n_i\,.$$

The equation relating the α phase, β phase and the surface phase becomes: When considering the bulk phases (α phase, β phase), at equilibrium at constant temperature and pressure the Gibbs–Duhem equation requires that: $\sum_{i=1}^{k}\mathrm{n_i}^{\alpha}\,\mathrm{d}\mu_i = \sum_{i=1}^{k}\mathrm{n_i}^{\beta}\,\mathrm{d}\mu_i = 0\,.$

The resulting equation is the Gibbs adsorption isotherm equation:

$$\sum_{i=1}^{k}\mathrm{n_i}^{\mathrm{S}}\,\mathrm{d}\mu_i + A\mathrm{d}\gamma = 0\,.$$

The Gbbs adsorption isotherm is an equation which could be considered an adsorption isotherm that connects surface tension of a solution with the concentration of the solute.

For a binary system containing two components the Gibbs Adsorption Equation in terms of surface excess is: $-\mathrm{d}\gamma = \Gamma_1\mathrm{d}\mu_1 + \Gamma_2\mathrm{d}\mu_2\,.$

Relation between Surface Tension and the Surface Excess Concentration

The chemical potential of species *i* in solution depends on the activity a using the following equation: $\mu_i = \mu_i{}^{o} + RT\ln a_i$

where μ_i is the chemical potential of the i-th component, μ_i^{o} is the chemical potential of the i-th component at a reference state, *R* is the gas constant, *T* is the temperature, and a_i is the activity of the i-th component.

Differentiation of the chemical potential equation results in: $\mathrm{d}\mu_i = RT\frac{\mathrm{d}a_i}{a_i} = RT\mathrm{d}\ln fC_i\,,$

where *f* is the activity coefficient of component *i,* and *C* is the concentration of species *i* in the bulk phase.

If the solutions in the α and β phases are dilute (rich in one particular component i) then activity coefficient of the component *i* approaches unity and the Gibbs isotherm becomes: $\Gamma_i = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ln C_i}\right)_{T,p}.$

Gibbs Adsorption Isotherm

In the study of adsorption, changes in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are significant for equilibrium constant. The equilibrium constants for thermodynamic calculation can be derived in different ways. The values of ΔG°, ΔH°, and ΔS° of adsorption varies because it depends on the method employed. If the equilibrium constants are derived from other adsorption isotherm equations or distribution constants for determination of $\Delta G°$ then it requires thorough analysis.

As per standard derivations, if Gibb's free energy values are negative then the adsorption process is spontaneous and if it is positive then the adsorption process is non-spontaneous.

The magnitude of $\Delta G°$ measures how distant a reaction is from the equilibrium. If the value of $\Delta G°$ is larger, then the reaction is far from the equilibrium and thus the reaction must shift to reach equilibrium state. In reactions in which the enthalpy is favourable and entropy is unfavourable, the reaction becomes less spontaneous ($\Delta G°$ increases) until eventually the reaction is not spontaneous (when $\Delta G° > 0$).

//Gibbs derived a thermodynamic relationship between the surface or interfacial tension γ and the surface excess Γ (adsorption per unit area). At constant temperature, in the presence of adsorption, the Gibbs adsorption equation is $d\gamma = -\sum(ni/A)d\mu I = -\sum \Gamma id\mu I$, , where $(ni/A) = \Gamma i$ is the number of moles of component I adsorbed per unit area and μI is the chemical potential of the surfactant solution. For a single surfactant component, the Gibbs adsorption equation is simply $d\gamma/d\log C$ = "2.303 Γ RT, where C is the surfactant concentration, R is the gas constant, and T is the absolute temperatures. The Gibbs adsorption equation allows one to determine the amount of surfactant adsorption Γ (moles m"2) from a plot of log γ (the surface tension at the air/water interface or interfacial tension at the liquid/liquid interface) versus log C.

In thermodynamics, the Gibbs free energy (IUPAC recommended name, Gibbs energy or Gibbs function, also known as free enthalpy to distinguish it from Helmholtz free energy) is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric). The Gibbs free energy ($\Delta G^o = \Delta H^o - T\Delta S^o$) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system (one that can exchange heat and work with its surroundings, but not matter); this maximum can be attained only in a completely reversible process. When a system transforms reversibly from an initial state to a final state, the decrease in Gibbs free energy equals the work done by the system to its surroundings, minus the work of the pressure forces.

The Gibbs energy (also referred to as G) is also the thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system vanishes at the equilibrium point. As such, a reduction in G is a necessary condition for the spontaneity of processes at constant pressure and temperature.

Properties of Gibbs Free Energy (G)

This function is defined by

$$G = E - TS + PV \qquad ...(33)$$

This definition may be written in two alternative but equivalent forms which are frequently employed. First, since H it equivalent to $E + PV$, hence

$$G = H - TS \qquad ...(34)$$

Second, since $A = E - TS$, it follows that

$$G = A + PV \qquad ...(35)$$

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For a process taking place at constant pressure, the change in free energy is given by

$$\Delta G = \Delta A + P\,\Delta V \qquad ...(36)$$

If, in addition, the temperature is constant, $\Delta A = -W_m$ as seen from Equation, so that Equation (36) becomes

$$\Delta G = -(W_m - P\,\Delta V) \qquad ...(37)$$

The quantity W_m represents maximum work obtainable in the given change and includes all types of work, such as electrical or surface work, in addition to work of expansion. The latter is equal to $P\,\Delta V$ and so $W_m - PdV$ represents the reversible work, exclusive of work of expansion, that can be obtained from a given change in state. The quantity $W_m - PdV$ is referred to as *net work.*

Thus, $-\Delta G$ = Net work

Three decrease in free energy at constant T and P is equal to the maximum net work available for the given change in state which the process accompanies.

Again, from complete differential of Equation we get

$$dG = dH - TdS - SdT \qquad ...(38)$$

But $H = E + PV$, which on differentiation becomes

$dH = dE + PdV + VdP$. Also $TdS = dE + PdV$.

Making use of these identities into Equation (6),

We get

$$dG = dE + PdV + VdP - dE - PdV - SdT$$

$$= -SdT + VdP \qquad ...(39)$$

At constant pressure, $dP = 0$ and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad ...(40)$$

At constant temperature, $dT = 0$ and

$$\left(\frac{\partial G}{\partial T}\right)_T = V \qquad ...(41)$$

An alternate equation which shows the variation of G with T is obtained by differentiating the quantity G/T with respect to T at constant P, namely,

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P = \frac{T\left(\frac{\partial G}{\partial T}\right)_P - G}{T^2}$$

$$= -\frac{(G + TS)}{T^2}$$

But $G + TS = H$.

Therefore,

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P = -\frac{H}{T^2} \qquad ...(42)$$

Isothermal Changes in Free Energy Function: At constant temperature, $dT = 0$ and Equation becomes:

$$dG = VdP \qquad ...(43)$$

For 1 mole of a perfect gas, $PV = RT$

or $V = \frac{RT}{P}$

Substituting this into Equation, we get

$$dG = \frac{RT}{P}\,dP \qquad ...(44)$$

Integrating between limits, Equation (12) takes the form:

$$\int_{G_1}^{G_2} dG = RT\int_{P_1}^{P_2}\frac{dP}{P} \qquad ...(45)$$

$$G_2 - G_1 = RT\ln\frac{P_2}{P_1} \qquad ...(46)$$

or

$$\Delta G = RT\ln\frac{P_2}{P_1} \qquad ...(47)$$

Generally, the free energy of a gas is related to the standard free energy $G°$. This is defined as the free energy of one mole of the gas at one atmosphere pressure. Equation (47) then becomes

$$G - G° = RT\ln\frac{P}{1} = RT\ln P$$

or

$$G = G° + RT\ln P \qquad ...(48)$$

The Gibbs–Helmholtz Equation

Since $G = H - TS$

Substituting the value of S from Equation (8), we get

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \qquad ...(49)$$

Similarly, substituting the value of S from Equation (6) into equation $A = E - TS$, we get

$$A = E + T\left(\frac{\partial A}{\partial T}\right)_V \qquad ...(50)$$

These two equations are usually regarded as different forms of the Gibbs-Helmholtz equation. There are also other forms of the Gibbs-Helmholtz equation which are most widely used.

They are deduced as shown below:

For a given reaction of the type,

$$\text{Reactants} \rightarrow \text{Products}$$

$$\Delta G = G_p - G_r$$

where G_p is the sum total of the free energies of all the products and G_r is the sum total of the free energies of all the reactants.

From Equation (34), we have

$G_p = H_p - TS_p$ and $G_r = H_r - TS_r$, so that by substitution

$$\Delta G = (H_p - TS_p) - (H_r - TS_r)$$
$$= (H_p - H_r) - T(S_p - S_r)$$

or
$$\Delta G = \Delta H - T\Delta S \qquad ...(51)$$

where ΔS and ΔH are respectively the entropy and enthalpy change of the given isothermal reaction. Further, from Equation

$$-\Delta S = -(S_p - S_r) = \left(\frac{\partial G_p}{\partial T}\right)_P - \left(\frac{\partial G_r}{\partial T}\right)_P$$

or
$$\left[\frac{\partial(G_p - G_r)}{\partial T}\right]_p = \left[\frac{\partial(\Delta G)}{\partial T}\right]_p \qquad ...(52)$$

Substituting this result into equation (19), we get

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad ...(53)$$

Similarly, we can deduce the analogous expression

$$\Delta A = \Delta E + T\left[\frac{\partial(\Delta A)}{\partial T}\right] \qquad ...(54)$$

Equations (53) and (54) are alternate forms of the Gibbs-Helmholtz equation. These equations find numerous practical applications.

Still another form of the Gibbs-Helmholtz equation is obtained by differentiating $\frac{\Delta G}{T}$ with respect to T at constant P as given below:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = \frac{T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P - \Delta G}{T^2} \qquad ...(55)$$

But according to Equation,

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

Therefore, Equation becomes

$$\left[\frac{\frac{\partial(\Delta G)}{T}}{\partial T}\right]_P = \frac{\Delta G - \Delta H - \Delta G}{T^2}$$

$$= -\frac{\Delta H}{T^2} \qquad ...(56)$$

Example 4.5: One mole of a perfect gas at 27ºC expands isothermally and reversibly from 10 atm to 1 atm against a pressure that is gradually reduced. Calculate q and W and each of the thermodynamic quantities, ΔE, ΔG, ΔH, ΔA and ΔS.

Solution: Since the process is carried out isothermally and reversibly from 10 atm to 1 atm against a pressure that is gradually reduced.

$$W_{max} = -RT \ln\frac{V_2}{V_1} = -2.303\,RT \log\frac{V_2}{V_1}$$

$$= -2.303\ RT \log \frac{P_1}{P_2}$$

$$= -(2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 300.1\ \text{K}) \log 10/1$$

$$= -5746\ \text{J mol}^{-1}.$$

$$\Delta A = W_{max} = -5746\ \text{J mol}^{-1}$$

Since the internal energy of a perfect gas is not affected by a change in volume,

$$\Delta E = 0,$$

$$q = \Delta E - W = 0 + 5746 = 5746 \text{ J mol}^{-1}$$

$$\Delta H = \Delta E + \Delta(PV) = 0 + 0 = 0$$

Since PV is constant for a perfect gas at constant temperature

$$\Delta G = \int_{10}^{1} VdP = RT \ln \frac{1}{10} = 2.303\, RT \log \frac{1}{10}$$

$$= -2.303\ (8.314\ JK^{-1} \text{ mol}^{-1})\ (300.1 \text{ K})$$

$$= -5746 \text{ J mol}^{-1}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{5746 \text{ J mol}^{-1}}{300.1 \text{ K}} = 19.15 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{0 - (-5746 \text{ J mol}^{-1})}{300.1 \text{ K}}$$

$$= 19.15 \text{ JK}^{-1} \text{ mol}^{-1}$$

The Gibbs–Duhem Equation

Since $$dG = VdP - SdT + \sum_i \mu_i\, dn_i$$

At constant temperature and pressure, this becomes

$$dG = \sum_i \mu_i\, dn_i$$

By integrating this Equation, we have

$$G = \sum \mu_i\, n_i \qquad ...(57)$$

Differentiating Equation (57), we obtain

$$dG = \sum (n_i d\mu_i + u_i dn_i) \qquad ...(58)$$

Subtracting Equation (58) from equation (24), we get

$$\sum n_i d\mu_i = VdP - SdT \qquad ...(59)$$

This is known as the Gibbs-Duhem equation.

At constant temperature and pressure, if the only variation in composition takes place, Equation (59) takes the form

$$\sum n_i d\mu_i = 0\ (T, P \text{ constant}) \qquad ...(60)$$

This equation shows that with variations in compositions, the chemical potentials do not change independently but in a related way. Consider, for example, a system of two constituents of compositions n_1 and n_2 respectively. For such a system, Equation (60) becomes

$$n_1 d_{\mu_1} + n_2 d_{\mu_2} = 0\ (T, P \text{ constant})$$

or $$d\mu_2 = -\left(\frac{n_1}{n_2}\right) d\mu_1 \qquad ...(61)$$

With the help of this equation it is possible to find the change in the chemical potential d_{μ_2} of the second constituent by knowing a change in the chemical potential d_{μ_1} of the first constituent that results due to the variation in composition. Table 4.2 gives various thermodynamic quantities.

Table 4.2 *Various Thermodynamic Functions*

Definition	*Function*	*Name*
$dE = dq + dw$	E	Internal Energy
$dS = \frac{dq_{rev}}{T}$	S	Entropy
$H = E + PV$	H	Enthalpy
$G = H - TS$	G	Gibbs free Energy
$A = E - TS$	A	Helmholtz free energy (work function)
$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, nj}$	μ_i	Chemical potential
$C_p = \left(\frac{\partial H}{\partial T}\right)_P$	C_P	Heat capacity at constant pressure
$C_v = \left(\frac{\partial E}{\partial T}\right)_V$	C_V	Heat capacity at constant volume

Estimation of Surface Area (BET Equation)

Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. The observations are very often referred to as physical adsorption or ***physisorption***. BET theory applies to systems of multilayer adsorption that usually utilizes a probing gas (called the ***adsorbate***) that do not react chemically with the adsorptive (the material upon which the gas attaches to and the gas phase is called the adsorptive) to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate for probing surface(s). For this reason, standard BET analysis is most often conducted at the boiling temperature of $\mathbf{N_2}$ (77 K). Other probing adsorbates are also utilized, albeit less often, allowing the measurement of surface area at different temperatures and measurement scales. These include argon, carbon dioxide, and water. Specific surface area is a scale-dependent property, with no single true value of specific surface area definable, and thus quantities of specific surface area determined through BET theory may depend on the adsorbate molecule utilized and its adsorption cross section.

Concept

The concept of the theory is an extension of the **Langmuir theory**, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses:

1. Gas molecules physically adsorb on a solid in layers infinitely;
2. Gas molecules only interact with adjacent layers;
3. The Langmuir theory can be applied to each layer
4. The enthalpy of adsorption for the first layer is constant and greater than the second (and higher).

5. The enthalpy of adsorption for the second (and higher) layers is the same as the enthalpy of liquefaction.

   The resulting BET equation is

$$\theta = \frac{cp}{(p_o - p)(p_o + p(c-1))}$$

Where **c** is referred to as the **BET** C-constant, p_o is the vapour pressure of the adsorptive bulk liquid phase which would be at the temperature of the adsorbate and **θ** is the "surface coverage, defined as:

$$\theta = n_{ads}/n_m$$

Here n_{ads} is the amount of adsorbate and n_m is called the monolayer equivalent. The n_m is the entire amount that would be present as a monolayer (which is, theoretically impossible for physical adsorptionwould cover the surface with exactly one layer of adsorbate. The above equation is usually rearranged to yield the following equation for the ease of analysis:

$$\frac{1}{v\left[(p_0/p) - 1\right]} = \frac{c-1}{v_{\mathrm{m}}c}\left(\frac{p}{p_0}\right) + \frac{1}{v_{\mathrm{m}}c},$$

Where p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, respectively; v is the adsorbed gas quantity (for example, in volume units) while v_m is the monolayer adsorbed gas quantity. **c** is the BET constant,

$$c = \exp\left(\frac{E_1 - E_{\mathrm{L}}}{RT}\right),$$

Where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction or heat of ***vaporization***.

4.2.3 Surface Films on Liquids (Electrokinetic Phenomena)

Whenever a drop of liquid is placed on the surface of a substrate, the liquid is expected to evolve until it reaches an equilibrium state. This may require the drop to either spread and cover the surface or remain as a drop or in some cases even try to leave the surface. Such a process depends on properties of the surfaces involved as well as the external conditions such as temperature. This field is broadly categorized as wetting and spreading phenomena and aims to determine how a liquid behaves on the surface of a substrate.

Wetting phenomena are widespread in nature and occur whenever a surface is exposed to an environment. Understanding why and when a liquid decides to wet a surface can greatly improve our knowledge of everyday events. Further, this information can help in designing new materials and technology. This review is aimed at providing a basic analysis of wetting and the different phase transitions

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that arise during the process. The topics presented here are directly related to the material covered in phase transitions course during the semester and ties concepts of discontinuous and continuous phase transitions, and critical exponents to an excellent real life scenario. Further, this is also a topic of current and growing interest for both theorists and experimentalists. New developments and recent experiments are constantly improving our understanding in this field.

Basics of Wetting and Spreading Surface Thermodynamics

When considering a liquid on a surface, there are three systems that come into play; the liquid, the surface and the surrounding atmosphere which is referred to as the vapor. The relation between the various surface tensions and the contact angle was given by Young in Equation (62).

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos\theta_{eq} \qquad \text{... (62)}$$

Here S, V and L refer to the substrates surface, the vapor and the liquid respectively. θ is the contact angle as shown in Figure 4.12. Young's equation in the above form describes the equilibrium situation when the surface tension forces balance each other.

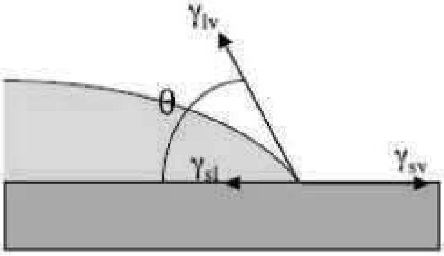


Fig. 4.12 *Young's Equation Equates the Surface Tension Forces at Equilibrium*

For a given set of surfaces, the corresponding θ_{eq} can be obtained from the surface tensions involved. If, for instance $\gamma SV = \gamma SL + \gamma LV$, then $\theta_{eq} = 0$ and equilibrium corresponds to when the liquid is spread across the surface of the substrate. This situation is referred to as wetting. The other two phases that arise are the dewetting phase and the partial wetting phase. Though in practice dewetting is rare, from a thermodynamic point of view both wetting and dewetting are similar under exchange of surface and the vapor systems. Thus, it suffices to consider and study the wetting state, which is characterized by a macroscopically thick layer. In the partial wetting state, the drops on a surface are surrounded by a microscopically thin film adsorbed at the surface. The three wetting states are shown in Figure 4.13. In typical experiments film thickness may range from a molecule to several molecules.

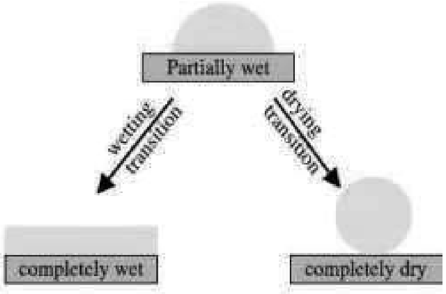


Fig. 4.13 *The Three Different Wetting Phases*

One can define an equilibrium spreading coefficient Seq to help classify the different wetting states.

$$S_{eq} \equiv \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) = \gamma_{LV}(cos\theta_{eq} - 1) \quad ...(63)$$

NOTES

S_{eq} above measures the difference between the surface free energy γSV and its value in the case of complete wetting. Notice that in general Seq d" 0 and Seq = 0 only in the case of complete wetting. When a drop of liquid first encounters a surface, it is far from the equilibrium state. An initial spreading coefficient may be defined as follows,

$$S_i = \gamma_{S0} - (\gamma_{SL} + \gamma_{LV}) \quad ... (64)$$

Where γ so is the surface tension of the dry solid substrate. If $S_i < 0$, the drop will have a finite contact angle θ_i and prefer to remain in a partial wetting state. On the other hand, if Si > 0 the drop will tend to spread out and wet the surface. An analysis of the adsorption equation shows that in general $S_i > S_{eq}$. This implies, whenever $S_i < 0$, this ensures that $S_{eq} < 0$. Nothing definite can be said about the sign of S_{eq}, if $S_i > 0$.

Drop Spreading

This part covers some basics of drop spreading. As discussed above, when a drop is generally placed on a surface, it is far from equilibrium$(S_i \neq S_{eq})$ Consider the simple case of a small viscous droplet on a surface. Here small implies that the drop radius is less than the capillary length l_c, given by

$$l_c = \sqrt{\gamma/\rho g} \quad (65)$$

The capillary number gives the ratio of the viscous and surface tension forces.

$$Ca = U\eta/\gamma \quad (66)$$

Ca≈10^{-}5–10^{-}3 in most spreading experiments, η is the liquid viscosity and $U = R^1$ is the contact line speed. Combining these results one can obtain a relationship between drop radius and time as give by Tanner's law Equation (67).

$$R(t) \approx \left[\frac{10\gamma}{9B\eta}\left(\frac{4V}{\pi}\right)^3\right]^{1/10} \propto t^n \quad (67)$$

The rate at which a drop spreads is determined by the interplay between the surface energies, gravity and dissipation. For small drops the surface free energy also plays a role

$$F_s = 4V^2\gamma/\pi R^4 - \pi S_i R^2 \quad (68)$$

The first term in this expression corresponds to the liquid-vapor interface due to the curved nature of the drop and the second term arises due the base area of the drop being covered by fluid. By inspection of the above equation, it appears that when $S_i > 0$, spreading would lead to a reduction in the surface free energy. However, in practice this reduction in free energy is not always converted to macroscopic motion of the drop. Instead only some of the molecules near the contact line may spread out creating a sort of thin precursor film around the drop. This process uses up the energy that could have gone toward spreading the entire drop. As F_s reduces, the effective radius *R* still increases. This causes spreading coefficient to approach an equilibrium value slowing down the rate of spreading.

In order to compute the power *n* in Tanner's equation Equation (67) , one has to measure the rate of energy dissipation near the contact line

Contact Angle

Contact angle is one of the common ways to measure the wettability of a surface or material. Wetting refers to the study of how a liquid deposited on a solid (or liquid) substrate spreads out or the ability of liquids to form boundary surfaces with solid states. The wetting, as mentioned before is determined by measuring the contact angle, which the liquid forms in contact with the solids or liquids. The wetting tendency is larger, the smaller the contact angle or the surface tension is. A wetting liquid is a liquid that forms a contact angle with the solid which is smaller then 90º. A non-wetting liquid creates a contact angle between 90º and 180º with the solid.

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces. Wetting deals with the three phases of materials: gas, liquid, and solid. It is now a center of attention in nanotechnology and nanoscience studies due to the advent of many nanomaterials in the past two decades.

Wetting is important in the bonding or adherence of two materials. Wetting and the surface forces that control wetting are also responsible for other related effects, including capillary effects. There are two types of wetting: non-reactive wetting and active wetting

A contact angle gives us an indication of how well (or how poorly) a liquid will spread over a surface. While formulating an ink, contact angles provide a useful indicator of how a modification to the ink will affect its spreading. A contact angle can be large or small, depending on the physical properties of the materials being investigated. Figure 4.14 shows three different droplets on a surface. The left-most droplet has a large contact angle, as it does not spread over the solid surface. The right-most droplet has a low contact angle, as it has spread well. This spreading is know as 'wetting', and a droplet either 'wets' or 'dewets' when deposited on a surface.

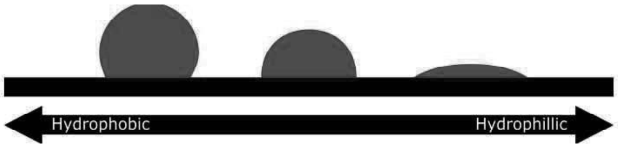


Fig. 4.14 *A Varying Contact Angle*

Figure 4.15 shows a 2D cross-section of a droplet on a solid surface. Locate the point at which the droplet outline intersects the solid surface. The angle between the droplet outline and the solid surface is the contact angle.

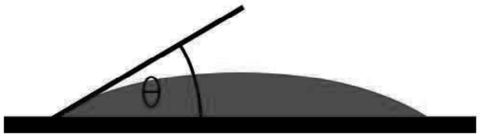


Fig. 4.15 *A Contact Angle* 'θ'

Explanation of Contact Angle

Adhesive forces between a liquid and solid cause a liquid drop to spread across the surface. Cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface.

The contact angle (θ), as seen in Figure 4.15 is the angle at which the liquid–vapor interface meets the solid-liquid interface. The contact angle is determined by the balance between adhesive and cohesive forces. As the tendency of a drop to spread out over a flat, solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability.

A contact angle less than 90° (low contact angle) usually indicates that wetting of the surface is very favorable, and the fluid will spread over a large area of the surface. Contact angles greater than 90° (high contact angle) generally means that wetting of the surface is unfavorable, so the fluid will minimize contact with the surface and form a compact liquid droplet.

For water, a wettable surface may also be termed hydrophilic and a nonwettable surface hydrophobic. Superhydrophobic surfaces have contact angles greater than 150°, showing almost no contact between the liquid drop and the surface. This is sometimes referred to as the Lotus effect. The table describes varying contact angles and their corresponding solid/liquid and liquid/liquid interactions. For non water liquids, the term lyophilic is used for low contact angle conditions and lyophobic is used when higher contact angles result. Similarly, the terms omniphobic and omniphilic apply to both polar and apolar liquids.

High-Energy vs. Low-Energy Surfaces

Liquids can interact with two main types of solid surfaces. Traditionally, solid surfaces have been divided into high-energy solids and low-energy types. The relative energy of a solid has to do with the bulk nature of the solid itself. Solids such as metals, glasses, and ceramics are known as ‘hard solids’ because the chemical bonds that hold them together (for example, covalent, ionic, or metallic) are very strong. Thus, it takes a large input of energy to break these solids (alternatively large amount of energy is required to cut the bulk and make two separate surfaces so high surface energy), so they are termed ‘high energy’. Most molecular liquids achieve complete wetting with high-energy surfaces.

The other type of solids is weak molecular crystals (for example, fluorocarbons, hydrocarbons, etc.) where the molecules are held together essentially by physical forces (for example, van der Waals and hydrogen bonds). Since these solids are held together by weak forces, a very low input of energy is required to break them, thus they are termed ‘low energy’. Depending on the type of liquid chosen, low-energy surfaces can permit either complete or partial wetting.

Dynamic surfaces have been reported that undergo changes in surface energy upon the application of an appropriate stimuli. For example, a surface presenting photon-driven molecular motors was shown to undergo changes in water contact angle when switched between bistable conformations of differing surface energies.

Wetting of Low-Energy Surfaces

Low-energy surfaces primarily interact with liquids through dispersion (van der Waals) forces. William Zisman produced several key findings:

Zisman observed that cos θ increases linearly as the surface tension (γLV) of the liquid decreased. Thus, he was able to establish a linear function between cos θ and the surface tension (γLV) for various organic liquids.

A surface is more wettable when γLV and θ is low. Zisman termed the intercept of these lines when cos θ = 1, as the critical surface tension (γc) of that surface. This critical surface tension is an important parameter because it is a characteristic of only the solid.

Knowing the critical surface tension of a solid, it is possible to predict the wettability of the surface. The wettability of a surface is determined by the outermost chemical groups of the solid. Differences in wettability between surfaces that are similar in structure are due to differences in the packing of the atoms. For instance, if a surface has branched chains, it will have poorer packing than a surface with straight chains. Lower critical surface tension means a less wettable material surface.

4.2.4 Catalytic Activity at Surfaces

Although there are various types of catalyzed reactions, but in spite of their many differences, they show the following characteristic properties:

1. **The Catalyst Remains Unchanged in Chemical Composition at the End of the Reaction:** The amount of the catalyst recovered at the end of the reaction is found to be the same as the amount taken at the start of the reaction. Hence, a catalyst does not undergo any chemical change although, its physical form may change completely. Thus, manganese dioxide, used as a catalyst in the decomposition of potassium chlorate, changes from coarsely powdered form to fine powder at the end of the reaction. Similarly, a smooth platinum gauze, used as a catalyst in the oxidation of ammonia, becomes rough after some time.
2. **Only a Small Amount of the Catalyst is Required to Bring about a Reaction:** There are many cases known where a very small amount of the catalyst is sufficient to convert large quantities of the reactants into the products, for example, one gram of platinum is sufficient to cause decomposition of 10^8 litre of hydrogen peroxide.

   This is not invariably true. There are some homogeneous catalyzed reactions where the rate of the reaction increases with the increase in the concentration of the catalyst as, for example, the inversion of cane sugar in presence of hydrochloric acid which acts as a catalyst. There are also some heterogeneous reactions where the rate proportionally increases with the increase in the area of the surface of the catalyst.

   Attempts have been made to determine the exact quantity of the catalyst required for a reaction, but it has not been very successful.
3. **A Catalyst does not Alter the Final Position of Equilibrium in a Reversible Reaction and hence does not Modify the Value of the Equilibrium Constant:** It has been found from thermodynamics that whether

a reversible reaction takes place in the presence of a catalyst or not, the free energy of the process is same. A catalyst accelerates equally the rates of both forward and reversible reactions and helps to establish equilibrium quickly.

This has been found to be true where the amount of the catalyst used is small. If the catalyst is present in large quantity, the magnitude of the equilibrium constant changes. For example, in the hydrolysis of ethyl acetate in presence of large quantity of the catalyst, HCl, the equilibrium constant is affected.

4. **A Catalyst does not Start or Initiate a Reaction, but it Merely Increases or Decreases its Speed:** A catalyst simply changes the speed of a reaction which is already proceeding, though very slowly. The function of the catalyst is to help a reaction to attain an alternative path which requires minimum energy of activation.
5. **A Catalyst is Specific in Action:** This implies that a given catalyst can catalyze only particular reaction and cannot be used to bring about every reaction. For example, manganese dioxide will catalyze only decomposition of potassium chlorate and will fail to catalyze other reactions. Similarly, enzymes are also specific in action.

   Thus, a proper catalyst for a particular reaction is chosen after numerous experiments.
6. **A Catalyst has an Optimum Temperature:** The temperature at which the catalyst is most active.
7. **A Catalyst is Poisoned by the Presence of Small Quantities of Certain Substances Called Catalytic Poisons:** Some of the most powerful catalytic poisons are arsenious oxide, hydrogen cyanide and carbon monoxide. The presence of these substances makes the catalyst inactive.
8. **The Activity of a Catalyst is Enhanced by the Presence of a Substance called Promoter:** For example, in Haber's process for the manufacture of ammonia, molybdenum is used as a promoter to the catalyst iron.

Types of Catalysis

There are generally two types of catalysis: (i) Homogeneous Catalysis, and (ii) Heterogeneous Catalysis.

1. Homogeneous Catalysis: In this type, the catalyst is present in the same phase as the reactants. There can be gaseous or liquid phase.

Examples of Homogeneous Catalysis in Gas Phase: Catalyzed homogeneous gas reactions are very rare. A common example of this is the oxidation of sulphur dioxide to sulphur trioxide in the presence of nitric oxide in the lead-chamber process of sulphuric acid.

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

Nitric oxide can also catalyze the combination of carbon monoxide and oxygen and the decomposition of nitrous oxide to nitrogen and oxygen.

$$2CO + O_2 \xrightarrow{NO} 2CO_2$$

$$2N_2O \xrightarrow{NO} 2N_2 + O_2$$

Another example is the decomposition of methyl-ethyl, diethyl and disopropyl ethers in the presence of iodine vapours which acts as a catalyst.

Iodine vapours also act as a catalyst in the decomposition of acetaldehyde.

$$CH_3CHO \xrightarrow{I_2 \text{ vapours}} CH_4 + CO$$

It is found to be of second order and the reaction rate is given by,

$$\frac{dx}{dt} = k\, C_{CH_3CHO}.C_{I2}$$

To account for this, it is said that the reaction takes place in two steps:

1. $CH_3CHO + I_2 \rightarrow CH_3\ I + HI + CO$
2. $CH_3\ I + HI \rightarrow CH_4 + I_2$

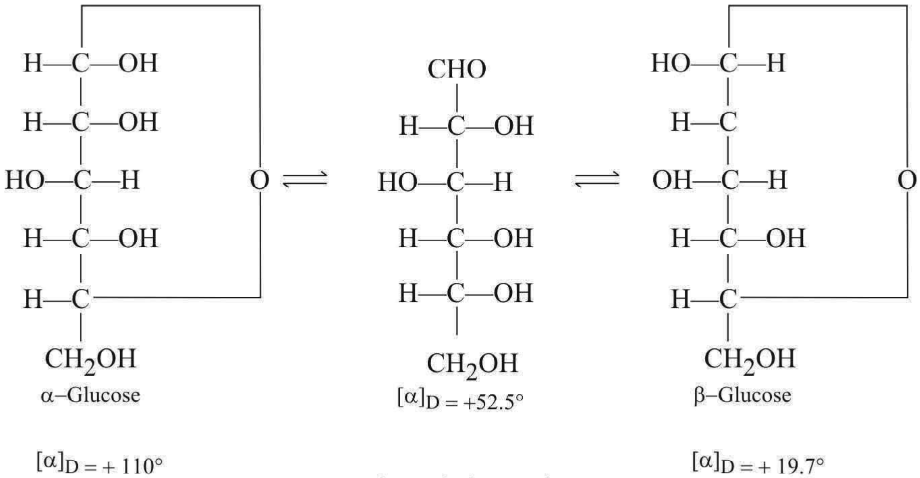
The first reaction being slower determines the rate of the reaction.

Examples of Homogeneous Catalysis in Liquid Phase: There are many examples of homogeneously catalyzed reactions in solution. The most common are catalyzed by hydrogen or hydroxyl ions and are generally included under the heading of **acid-base catalysis**. Hydrogen ions are found to catalyze reactions such as the inversion of sucrose and hydrolysis of esters. For such reactions, the rate is proportional to the concentration of hydrogen ions and the concentration of the substrate, i.e., reacting molecule or ion.

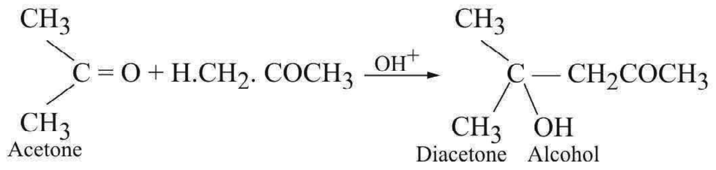
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Ethyle Acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Similarly, hydroxyl ions are found to have catalytic effect for reactions, such as the mutarotation of glucose and the conversion of acetone into diactone alcohol.



Mutarotation of glucose by OH⁻



$$(CH_3)_2C=O + H.CH_2.COCH_3 \xrightarrow{OH^+} (CH_3)_2C(OH)-CH_2COCH_3$$

It has been observed that for many reactions which are catalyzed by hydrogen ions, any other substance which is an acid in the Bronsted sense (proton donor) can act as a catalyst for the reaction. This is called **general acid catalysis**. Similarly **general base catalysis** refers to reactions which are catalyzed by all bases (proton acceptor).

There are some reactions, for example, the mutarotation of glucose and the enolization of acetone which are catalyzed by both acids and base and are known as general acid-base catalysis.

For such reactions, the general expression for the measured specific rate constant (K) for the overall reaction may be written as:

$$K = K_0 + \sum K_{\text{acid}} C_{\text{acid}} + \sum K_{\text{base}} C_{\text{base}}$$

Where K_0 is the rate constant for the non-catalyzed reaction, such as occurs in neutral solution and K_{acid} and K_{base} are the catalytic coefficients of each species of acid and base, in accordance with the Lowry's concept of acid and base) of concentrations C_{acid} and C_{base}, respectively. The value of K_{acid} can be measured from solutions which are strongly acidic (C_{base} is extremely small) and that of K_{base} from solutions which are strongly basic (C_{acid} is small). By knowing K_{acid} and K_{base}, one can easily compare the catalytic effects of various acids and bases.

In considering the mechanism of acid or base catalyzed reactions, addition or removal of a proton by a catalyst must be taken into consideration.

This can be illustrated by the following few examples:

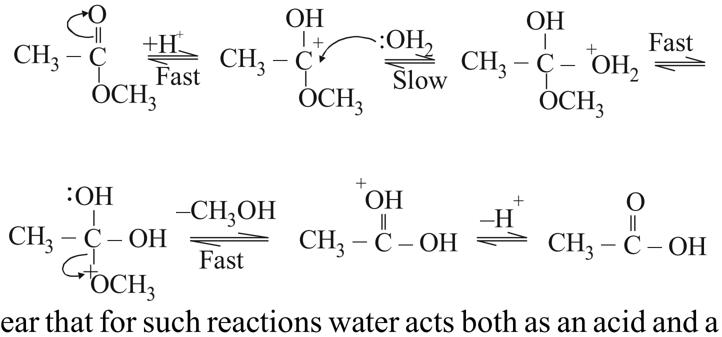
(*i*) Mutarotation of Glucose: This is presented as:

$$\underset{\alpha\text{-glucose}}{GH} + H_3O^+ \rightleftharpoons \underset{\text{(Intermediate Compound)}}{HGH^+} + H_2O$$

$$HGH^+ + H_2O \rightleftharpoons \underset{\beta\text{-glucose}}{HG} + H_3O^+$$

Here the first step involves addition of proton, supplied by acid, H_3O^+ to a glucose molecule and leads to the formation of an intermediate compound which is unstable. This decomposes to give β-glucose and proton discarded is taken by a water molecule.

(*ii*) The Hydrolysis of Methyl Acetate:



It is clear that for such reactions water acts both as an acid and a base as it supplies as well as accepts a proton.

2. Heterogeneous Catalysis: In this type, catalyst constitutes a separate phase from the reactions. The catalyst is generally solid and reactants are mostly gases and sometimes liquids. The catalysts which are frequently used here are the metals, such as platinum, nickel, copper and iron and sometimes oxides of metals such as ferric oxide, zinc oxide, molybdenum oxide, etc. These catalysts are used in a state of fine powder so as to give a large surface area.

In heterogeneous catalysis, we have number of reactions which are of commercial importance. Some important example are given below:

(*i*) Haber's Process for the manufacture of ammonia: Combination of nitrogen and hydrogen (Ratio 1:3) is catalyzed by iron in the presence of a promotor (Molybdenum).

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

(*ii*) Contact process for the manufacture of sulphuric acid: Combination of sulphur dioxide and oxygen in the presence of platinum.

$$2SO_2(g) + P_2 \rightleftharpoons 2SO_3(g)\ \Delta H - 197\ kJmol^{-1}$$

(*iii*) Formation of water is brought about by combining hydrogen and oxygen in the presence of platinum.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

(*iv*) In the manufacture of nitric acid, oxidation of ammonia is done in the presence of a mixture of ferric oxide and bismuth oxide.

$$4NH_3 + 5O_2 \xrightarrow[Bi_2O_3]{Fe_2O_3} 4NO + 6H_2O$$

(*v*) Hydrogenation of unsaturated hydrocarbons in the presence of nickel.

$$\underset{\text{Unsaturated Oil}}{X—CH{=}CH—Y + H_2} \xrightarrow{Ni} \underset{\text{Saturated Fat}}{X—CH_2—CH_2—Y}$$

(*vi*) In the preparation of hydrogen, combination of carbon monoxide and water gas is done in the presence of ferric oxide.

$$CO + H_2O \xrightarrow{Fe_2O_3} CO_2 + H_2$$

(*vii*) Hydrochloric acid can be manufactured by passing a mixture of hydrogen and chlorine over activated charcoal prepared from wood.

$$H_2 + Cl_2 \xrightarrow{Charcoal} 2HCl$$

Application of Catalysts and Miscellaneous Examples

Almost the whole of modern chemical industry depends on the development, selection, and application of catalysts, and all we can attempt to do here is to give an indication of the breadth of application rather than going into the details of technological applications.

Table 4.3 *Catalysts and Their Applications*

Catalyst	*Function*	*Example*
Metals	Hydrogenation Dehydrogenation	Fe, Ni, Pt, Ag
Semiconducting Oxide and Sulphides	Oxidation Dehydrogenation Desulphurization	NiO, ZnO, MgO, Bi_2O_3/MoO_3
Insulating Oxides	Dehydration	Al_2O_3, SiO_2, MgO
Acids	Polymerization Isomerization Cracking Alkylation	$H_3PO_4.H_2SO_4$, SiO_2/Al_2O_3

The choice of a catalyst depends on the job to be done, the danger of it being poisoned by products or impurities in the reaction mixture, and economic considerations relating to its cost and life time.

The activity of a catalyst depends on the strength of chemisorption in a way that can be represented by a ‘Volcano’ curve, Figure 4.16. In order to have significant activity the catalyst should be extensively covered by the adsorbate, and this requires moderately strong adsorption. On the other hand, if the adsorption strength increases beyond what is required for significant amount of coverage, the strength of the adsorption bonds is so great that the catalytic activity declines either because the incoming species cannot react or because the adsorbed molecules are immobilized on the surface. This indicates that the activity increases with strength of adsorption (as measured, for example, by the enthalpy of adsorption), and then falls: the greatest activity is for catalysts lying in the regions close to the mouth of the volcano.

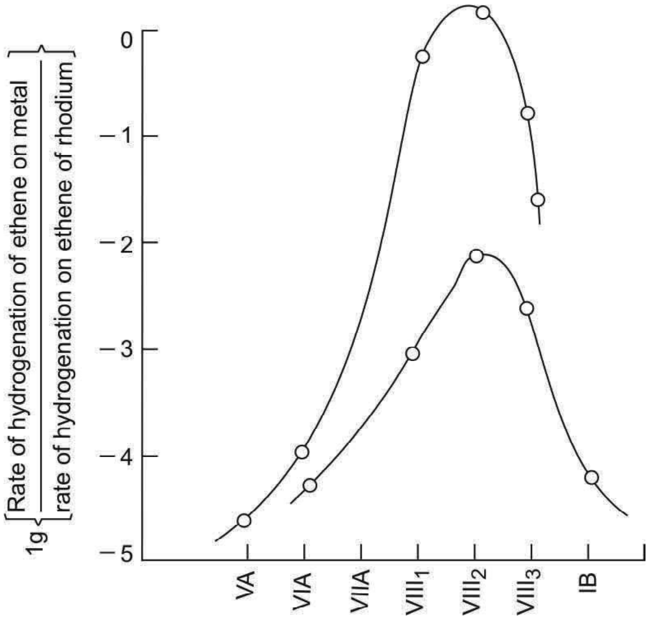


Fig. 4.16 A Volcano Curve of Catalytic Activity. Lower Curve: First Row Metals; Upper Curve: Second Third Row Metals

Many metals are suitable for adsorbing gases, and the general sequence of adsorption strengths is O_2, C_2H_2, C_2H_4, CO, H_2, CO_2, N_2, with oxygen usually the most strongly adsorbing molecule, and nitrogen the least. Some of these molecules adsorb dissociatively (such as hydrogen). Transition metals such as iron, vanadium, and chromium show strong activity for all these gases, but metals like manganese and copper are unable to adsorb nitrogen and carbon dioxide, and adsorb hydrogen only weakly. Metals towards the left of the periodic table (such as magnesium and lithium), are able to adsorb only the most active gas, oxygen.

Hydrogenation: A major industrial application of catalysed hydrogenation reactions is the formation of edible fats from vegetable and animal oils. Raw oils obtained from sources, such as the soyabean have the structure + indicates strong chemisorption; ±weak chemisorption –no chemisorption.

Table 4.4 Chemisorption Abilities

	O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	–
Pd, Pt	+	+	+	+	+	–	–
Mn, Cu	+	+	+	+	±	–	–
Al, Au	+	+	+	+	–	–	–
Li, Na, K	+	+	–	–	–	–	–
Mg, Ag, Zn, Pb	+	–	–	–	–	–	–

$CH_2(O_2CR_1)$. $CH(O_2CR_2)_2$ $C(O_2CR_3)_3$, where R_1, R_2, and R_3 are long chain hydrocarbons with several double bonds. One disadvantage of the presence of many double bonds is that they make the oils susceptible to atmospheric oxidation, which turns the oil rancid. The geometrical configuration of chains containing rigid double bonds is responsible for the liquid nature of the oil, and in many applications (such as on sandwiches) a solid fat is at least much better, and often necessary. Controlled, partial hydrogenation of an oil with a catalyst carefully selected so that hydrogenation is incomplete and so that the chains do not isomerize, is used on a wide scale to produce edible fats. The process, and the industry, is not made any easier by the seasonal variation of the number of double bonds in the oils.

Oxidation: Catalytic oxidation is also widely used in industry, and increasingly in pollution control. Although in some instances it is desirable to achieve complete oxidation, as in the elimination of nitrogen oxides from engine emissions, in others incomplete oxidation is the aim. For example, the complete oxidation of propene to carbon dioxide and water is wasteful, but its partial oxidation to acrolein (CH_2=CHCHO) is the start of important industrial processes. Likewise, the controlled oxidations of ethene to ethanol, ethanal (acetaldehyde), and in the presence of acetic acid or chlorine, to vinyl acetate (CH_2=$CHCOOCH_3$) or vinyl chloride (CH_2=CHCl), are the initial stages of really important chemical industries.

Not all the reactions mentioned in the last paragraph proceed under the influence of simple metal catalysts, although platinum in exhaust emission control and palladium in the formation of vinyl acetate are two exceptions. A number depend on solid oxides of various kinds, and the physical chemistry of these complex surfaces in often very obscure. Some of the problems can be indicated by considering the oxidation of propene to acrolein. This is brought about by a bismuth molybdate surface which acts by adsorbing the propene with loss of a hydrogen atom to form the allyl radical CH_2=$CHCH_2$. The oxygen in the surface can transfer to the allyl, leading to the formation of acrolein and its desorption from the surface. The hydrogen atom also charges with a surface oxygen, with the formation of water. The surface is left with the charges of the oxide ions, and these are centres of attack for oxygen molecules in the surrounding atmosphere. These oxygens chemisorb on to the surface as oxide ions, and the catalyst is thereby reformed. This type of reaction obviously involves quite dramatic upheavals of the surface, and some materials break up under the stress of the conditions.

Cracking and Reforming: Many of the small organic molecules used in the preparation of all kinds of chemical products, from pharmaceuticals to explosives and from perfumes to polymers, come from oil. Not only are chemicals constructed by catalytic oxidation, hydrogenation, chlorination, and long chain hydrocarbons squeezed out of the earth. The catalytically induced destruction of hydrogen chains to smaller, more volatile fragments, is called **cracking**, and has been brought about on silica-alumina catalysts. These operate by forming carbonium ions, which are unstable, fall apart, and isomerize to a more highly branched chain form internal combustion engines than their linear isomers, and are the basis of the higher 'octane' fuels.

Catalytic cracking has been largely superseded by **catalytic reforming** using a **dual-function catalyst**, such as a mixture of platinum and treated alumina. The former is the **metal function**, and brings about dehydrogenation hydrogenation. The latter is the **acidic function**, being able to form a carbonium ion. The sequence of events at this catalyst shows very clearly the complications that have to be unravelled if a reaction as important as this is to be fully understood, and the understanding used to develop an even better catalyst.

The first step is the attachment of the long chain hydrocarbon by chemisorption to the platinum: in the process first one, and then a second hydrogen atom is lost, and the olefin is formed. This olefin then migrates to an acidic site, where it accepts a proton, and attaches to the surface as a carbonium ion. This carbonium ion can undergo a variety of reactions. It can break in two, isomerize into a more highly branched structure (branched chain carbonium ions are more stable than straight chain ions), or undergo various types of ring closure. Then it loses a proton, escapes from the surface, and migrates as an olefin in (possibly through the gas) to a metallic part of the catalyst where it is hydrogenated. We end up with a rich selection of smaller molecules which can be withdrawn, separated by fractionation, and then used as raw materials in other processes.

Check Your Progress

1. Define the absorbent
2. What is chemisorption?
3. State the Freundlich adsorption isotherm.
4. Define the Temkin isotherm.
5. How will you measure of surface area?
6. Give the unit of surface tension.
7. What is capillary rise method?
8. Define the Gibbs adsorption isotherm.
9. What do you understand by relative surface excess?
10. Define the contact angle.
11. What is homogeneous catalysis?

4.3 MICELLES

Surfactant, also called surface-active agent, substance such as a detergent that, when added to a liquid, reduces its surface tension, thereby increasing its spreading and wetting properties. In the dyeing of textiles, surfactants help the dye penetrate the fabric evenly. They are used to disperse aqueous suspensions of insoluble dyes and perfumes. A term surfactant comes from the word surface active agent. They are amphiphilic molecules and are thus absorbed in the air-water interface. At the interface, they align themselves so that the hydrophobic part is in the air and hydrophilic part is in water. This causes the decrease in surface or interfacial tensions.

The surface-active molecule must be partly hydrophilic (water-soluble) and partly lipophilic (soluble in lipids, or oils). It concentrates at the interfaces between bodies or droplets of water and those of oil, or lipids, to act as an emulsifying agent, or foaming agent. Other surfactants that are more lipophilic and less hydrophilic may be used as defoaming agents, or as demulsifiers. Certain surfactants are germicides, fungicides, and insecticides.

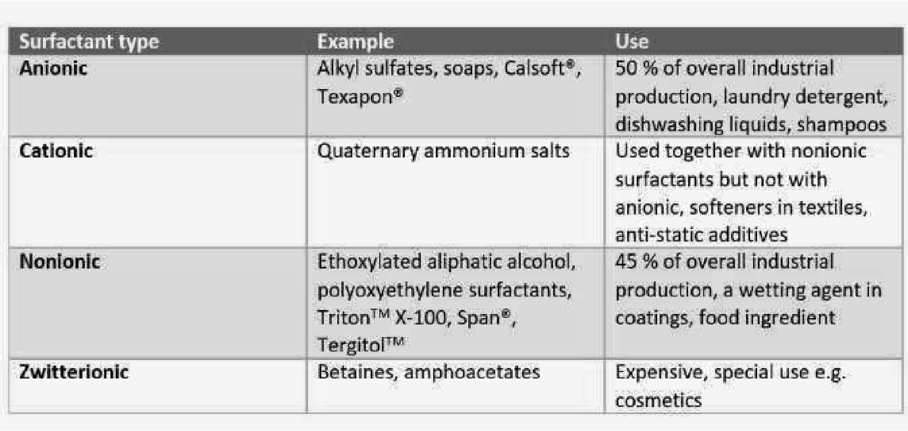
Surfactants are used in corrosion inhibition, in ore flotation, to promote oil flow in porous rocks, and to produce aerosols. Surfactants are the most versatile products of the chemical industry. They are utilized in every industrial area ranging from household detergents to drilling muds and food items to pharmaceuticals.

Surfactant Basics

Surfactants are amphiphilic molecules that have hydrophobic and hydrophilic parts. The hydrophobic tail is a hydrocarbon, fluorocarbon or siloxane. Surfactants are typically classified based on their polar head as the hydrophobic tails are often similar. If the head group has no charge, the surfactant is called **non-ionic**. If the head group has negative or positive charge, it is called **anionic or cationic**, respectively. If it contains both positive and negative groups, then the surfactant is called **zwitterionic**.

Anionic and non-ionic surfactants are by far the most used surfactant types in industry. Anionic surfactant find use especially in cleaning product like laundry detergents and shampoos. Non-inonic surfactants on the other hand are often used as wetting agents and in food industry. Both cationic and zwitterionic surfactants are more for special use as they are more expensive to produce.

Table 4.5 *Types of Surfactants and Their Uses*



Surfactant type	Example	Use
Anionic	Alkyl sulfates, soaps, Calsoft®, Texapon®	50 % of overall industrial production, laundry detergent, dishwashing liquids, shampoos
Cationic	Quaternary ammonium salts	Used together with nonionic surfactants but not with anionic, softeners in textiles, anti-static additives
Nonionic	Ethoxylated aliphatic alcohol, polyoxyethylene surfactants, Triton™ X-100, Span®, Tergitol™	45 % of overall industrial production, a wetting agent in coatings, food ingredient
Zwitterionic	Betaines, amphoacetates	Expensive, special use e.g. cosmetics

Surfactants Absorb at Interfaces

Because of their amphiphilic nature, surfactants absorb at the air-water or oil-water interface. At the interface, surfactants align themselves so that the hydrophobic part is in air (or oil) and hydrophilic part in water.

For simplicity, let's consider only the air-water interface. The cohesive forces between the water molecules are very strong making the surface tension of water high. As surfactants absorb they break these interactions. The intermolecular forces between surfactant and water molecule are much lower than between two water molecules and thus surface tension will decrease. When the surfactant concentration is high, they form micelles. The point at which micelles are formed is called critical micelle concentration.

The main purpose of the surfactants is to decrease the surface and interfacial tension and stabilize the interface. Without surfactants washing laundry would be difficult and many of the food products like mayonnaise and ice cream would not exist. Thus optimization of surfactants for different applications is highly important and surface and interfacial tension measurements have the key role in it.

In the bulk aqueous phase, surfactants form masses, such as micelles, where the hydrophobic tails form the core and the hydrophilic heads are immersed in the surrounding liquid. Other types of structures can also be formed, such as spherical micelles or lipid bilayers. The shape of the molecules depends on the balance in size between hydrophilic head and hydrophobic tail. A measure of this is the HLB, Hydrophilic-lipophilic balance. Higher HLB surfactants (>10) are hydrophilic (water loving) and form O/W (Oil-in-water) emulsions. Lipophilic surfactants possess low HLB values (1-10) and form W/O (water-in-oil) emulsions. Dish detergents, surfactants for emulsion polymerization, and the following example (SLS = Sodium Lauryl Sulfate) are high HLB surfactants.

The dynamics of surface active agent adsorption is of great importance for practical applications such as in emulsifying or coating processes as well as foaming, where bubbles or drops are rapidly generated and need to be stabilized.

As the interface is created, the adsorption is limited by the diffusion of the surfactant to the interface, which can result in the kinetics being limited. These energy barriers can be due to steric or electrostatic repulsions; steric repulsions form the basis of how dispersants function. Surface rheology of surfactant layers, are important to the stability of foams and emulsions.

Most surfactants' tails are fairly similar, consisting of a hydrocarbon chain, which can be branched, linear, or aromatic. Fluorosurfactants have fluorocarbon chains. Siloxane surfactants have siloxane chains. Recent advances in surfactant technology has seen the development of mixed chains or/and complex structures.

There are 4 types of surfactants with a brief review of each as follows. These classifications are based upon the composition of the polarity of the head group:

- Nonionic
- Anionic
- Cationic
- Amphoteric

A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic. Commonly encountered surfactants of each type are listed as follows:

Non-Ionic Surfactant

Many long chain alcohols exhibit some surfactant properties. As the name suggests they do not have any ions in their molecules, so they are uncharged. To produce nonionic detergents we react polyethene glycol with stearic acid. There are two main types of nonionic detergent polyoxyethylene and glycosidic.

Anionic Surfactant

Anionic surfactants contain anionic functional groups at their head, such as sulfonate, phosphate, sulfate and carboxylates. Alkyl sulfates include ammonium lauryl sulfate, sodium lauryl and the related alkyl-ether sulfates sodium laureth sulfate, also known as Sodium Lauryl Ether Sulfate (SLES), and sodium myreth sulfate. These are the most common surfactants and comprise the alkyl carboxylates (Soaps), such as sodium stearate. The stearates comprise >50% of the global usage of surfactants. Many of these find utilization in emulsion polymerization. Other anionic surfactants include Dioctyl Sodium SulfoSuccinate (DOSS), Per Fluoro Octane Sulfonate (PFOS), Linear Alkylbenzene Sulfonates (LABs) and perfluorobutanesulfonate, as well as alkyl-aryl ether phosphates. More specialized species include sodium lauroyl sarcosinate and carboxylate-based fluorosurfactants such as Perfluorononanoate, Perfluorooctanoate (PFOA or PFO).

Cationic Surfactant

Cationic surfactants are comprised of a positively charged head. Most of cationic surfactants find use as anti-microbials, anti-fungals, etc. in HI&I (Benzalkonium chloride (BAC), CetylPyridinium Chloride (CPC), Benzethonium chloride (BZT). The cationic nature of the surfactants is not typically consistent with the world of non-ionic and anionic charges, and they disrupt cell membranes of bacteria and viruses. Permanently charged quaternary ammonium cations include: Alkyltrimethylammonium salts: Cetyl Trimethylammonium Bromide (CTAB) and Cetyl Trimethylammonium Chloride (CTAC).

Zwitterionic Surfactants

Zwitterionic (amphoteric) surfactants have both cationic and anionic centers attached to the same molecule. The anionic part can be variable and include sulfonates, as in the sultaines CHAPS (3-[(3-Cholamidopropyl) dimethylammonio]-1-propanesulfonate). Betaines such as cocamidopropyl betaine have a carboxylate with the ammonium. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. Zwitterionic surfactants are often sensitive to pH and will behave as anionic or cationic based on pH. Fast dry (coacervation) latex traffic paints are based on this concept, with a drop in pH triggering the latex in the paint to coagulate.

Reducing Surface Tension

Water, for instance, has a very high natural surface tension (with air) which is what enables small insects to walk on its surface or a paper clip to float on it. If a few drops of surfactant were added to the water, a large decrease in the tension between water and air results, meaning that the insect or the paper clip would sink.

A similarly remarkable effect can be seen in the interaction between dirt (oil or fat) and water in cleaning processes. Introducing a surfactant, in the form of a detergent, into the process reduces interfacial tension between the water and soil, helping to release the dirt and keep it suspended in water so that it can be flushed or rinsed away.

That is exactly (but not only) what surfactants do every time you wash your face or hair, do the laundry, clean the dishes, mop the floors or wipe down the kitchen. In virtually every detergent or cleaning product is a smart surfactant designed specifically to make the task easier, more effective and more efficient.

Special Molecular Structure

The unique properties of surfactants (i.e., their ability to mobilise and mix naturally opposing or immiscible substances) are the result of their special molecular structure. Think of a surfactant molecule as a matchstick, with the thick end being the 'head' and the thin end being the 'tail'. This 'head' is water-soluble (hydrophilic) but oil--insoluble, whereas the 'tail' is water-insoluble (hydrophobic) but oil-soluble. When added to water as part of a detergent or cleaning formulation, surfactants form structures called micelles. These micelles are small spheres made of surfactant molecules where the tails attract and trap oil molecules while the heads of the micelle suspend them in water.

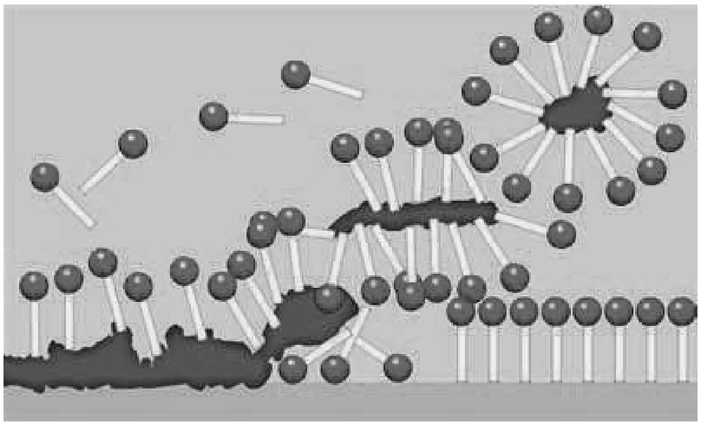


Fig. 4.17 *Molecular Structure of Surfactant*

Other Useful Properties

In addition to lowering surface and interfacial tension, and rendering soluble what is insoluble, surfactants also have a number of other useful properties including:

- Emulsifying or Dispersing Power
- Wetting

- Foaming
- Suspending/Stabilising Power

These properties are utilised in many everyday products - just imagine a day without surfactants: toothpaste would not foam while cleaning your teeth, nor rinse off properly after brushing; there would be no shaving foam at all and not only would face and sun cream look unappealing, there would be no way for them to be absorbed on the surface of the skin; and there would be no such thing as a relaxing foam bath.

But surfactants are not only vital for products found at home. Their unique characteristics are critical to a diverse range of commercial and industrial processes that are key to economic development, ranging from metal cleaning and textile processing to crop care and oil production. Using the right surfactant often makes products or processes more efficient, less energy, water or resource intensive, and hence more sustainable

Uses and Benefits

- Surfactants added to cleaning agents, like detergent, allow the detergent to mix into water, helping cleaning agents remove dirt from the surface being cleaned. Without surfactants, soaps wouldn't mix with the water, but would just roll off the water, making the cleaning process much more difficult.
- Surfactants also are used as an ingredient in lubricants, such as shaving cream, where they allow razors to easily remove stubble and help limit irritation.
- Surfactants added to car engine lubricants help keep particles from sticking to engine parts, allowing the parts to move easily and keep a car in proper running order.

Applications

The technical performance of surfactants plays a key role in enabling many applications, and their value chains, to become more sustainable. Smart surfactants can dramatically improve the overall sustainability of a value chain by promoting process efficiency and the use of fewer overall resources, whether energy, water or other materials, and often reducing levels of more hazardous components required.

Some examples where surfactants make a positive contribution to sustainability include:

- In household cleaning: surfactants have played a decisive role in making almost all household cleaning jobs easier while providing greater hygiene, appearance and protection of the surfaces cleaned and reducing the need for more hazardous chemicals
- In laundry detergents: smarter surfactants enable dirt and grime to be removed at lower washing temperatures - even in cold water - hence reducing energy and fossil fuel consumption used in the process.

- In insulation production: surfactants are key to the efficiency of manufacturing processes employed in the production of foam to make insulation boards and blocks that reduce the energy needed to heat and cool buildings.
- In industrial chemical processing: spraying surfactant solutions onto powdered chemicals, for example, the latter can be processed more effectively and more safely.
- In shampoo, liquid soaps and shower gels: surfactants are essential constituents of these formulations both for mobilising dirt but also allowing the foam to be easily rinsed off using the minimum amount of water.
- In crop protection: surfactants prevent spray solutions from rolling off the leaf surface, enable uniform dispersion of the active substance on the leaf and thus increase the effect of the agents used – the farmers can achieve the same protection using less chemicals.

Micelle

A micelle is an aggregate (or supramolecular assembly) of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic 'head' regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre. This phase is caused by the packing behavior of single-tail lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle.

This type of micelle is known as a normal-phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers, are also possible. The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions, such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellisation and forms part of the phase behaviour of many lipids according to their polymorphism.

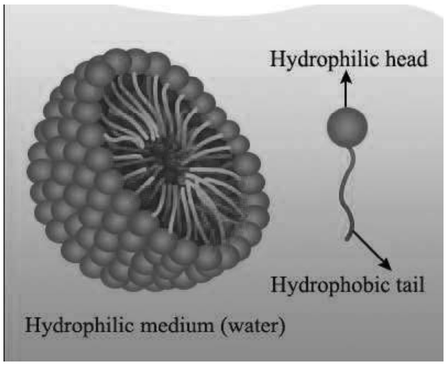


Fig. 4.18 *Micelle*

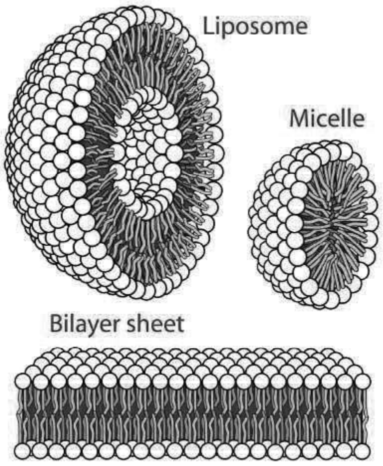


Fig. 4.19 *Cross-Section View of the Structures formed by Phospholipids in Aqueous Solutions*

The above Figure 4.19 illustrates the cross-section view of the structures that can be formed by phospholipids in aqueous solutions (unlike this illustration, micelles are usually formed by single-chain lipids, since it is tough to fit two chains into this shape).

Uses of Surfactants

- When surfactants are present above the Critical Micelle Concentration (CMC), they can act as emulsifiers that will allow a compound that is normally insoluble (in the solvent being used) to dissolve. This occurs because the insoluble species can be incorporated into the micelle core, which is itself solubilized in the bulk solvent by virtue of the head groups' favorable interactions with solvent species. The most common example of this phenomenon is detergents, which clean poorly soluble lipophilic material (such as oils and waxes) that cannot be removed by water alone. Detergents clean also by lowering the surface tension of water, making it easier to remove material from a surface. The emulsifying property of surfactants is also the basis for emulsion polymerization.
- Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. Bile salts formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (for example, lecithin) and lipid-soluble vitamins (A, D, E, and K) within the micelle by the small intestine.
- During the process of milk-clotting, proteases act on the soluble portion of caseins, ê-casein, thus originating an unstable micellar state that results in clot formation.
- Micelles can also be used for targeted drug delivery as gold nanoparticles

Detergents

Detergents are amphipathic molecules that contain both polar and hydrophobic groups. These molecules contain a polar group (head) at the end of a long hydrophobic carbon chain (tail). In contrast to purely polar or non-polar molecules, amphipathic molecules exhibit unique properties in water (Refer Figure 4.20). Their polar group forms hydrogen bonds with water molecules, while the hydrocarbon chains aggregate due to hydrophobic interactions. These properties allow detergents to be soluble in water. In aqueous solutions, they form organized spherical structures called micelles, each of which contain several detergent molecules. Because of their amphipathic nature, detergents are able to solubilize hydrophobic compounds in water. Incidentally, one of the methods used to determine the CMC relies on the ability of detergents to solubilize a hydrophobic dye. Detergents are also known as surfactants because they decrease the surface tension of water.

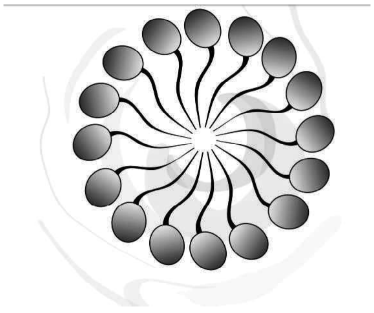


Fig. 4.20 *A Detergent-Micelle in Water*

Often we use the words 'soap' and 'detergent' interchangeably, but really they are quite different things. A detergent is a chemical substance you use to break up and remove grease and grime, while soap is simply one kind of detergent. Soap has a long history and was originally made from purely natural products like goat's fat and wood ash. Today, detergents are more likely to be a mixture of synthetic chemicals and additives cooked up in a huge chemical plant and, unlike traditional soap, they're generally liquids rather than solids. Detergents are used in everything from hair shampoo and clothes washing powder to shaving foam and stain removers. The most important ingredients in detergents are chemicals called surfactants—a word made from bits of the words surface active agents.

The Way Detergents Work

The cleverest part of a washing machine isn't the drum or the drive belt, the electric motor that spins it around or the electronic circuit that controls the program: it's the detergent (soap powder or liquid) you put in right at the start. Water alone can't clean clothes because it won't attach to molecules of grease and dirt. The surfactants it contains are made of molecules that have two different ends. One end is strongly attracted to water; the other is attracted to oily substances like grease.

When you wash your clothes in a washing machine the following steps occur:

- During the wash cycle, the surfactant (represented here by the orange blob) mixes with water.
- The grease-loving ends of the surfactant molecules start to attach themselves to the dirt on your jeans (shown by the brown blob on the leg). The tumbling motion beats your jeans about and breaks the dirt and grease into smaller, easier-to-remove pieces.

- During the rinse cycle, water molecules (blue blob) moving past attach themselves to the opposite, water-loving ends of the surfactant molecules.
- The water molecules pull the surfactant and dirt away from the jeans. During the final spin, the dirty water flushes away, leaving your jeans clean again!

Chemicals in Detergents

Surfactants aren't the only thing in detergents; look at the ingredients on a typical detergent bottle and you'll see lots of other chemicals too. In washing detergents, you'll find optical brighteners (which make your clothes gleam in sunlight). Biological detergents contain active chemicals called enzymes, which help to break up and remove food and other deposits. The main enzymes are proteases (which break up proteins), lipases (which break up fats), and amylases (which attack starch). Other ingredients include perfumes with names like 'limone', while household cleaning detergents contain abrasive substances, such as chalk to help scour away things like burned-on cooker grease and bath-tub grime.

4.3.1 Counter Ion Binding to Micelles

A counter ion is the ion that accompanies an ionic species in order to maintain electric neutrality. In table salt (NaCl, also known as Sodium Chloride) the sodium ion (positively charged) is the counter ion for the chloride ion (negatively charged) and vice versa. A counter ion will be more commonly referred to as an anion or a cation, depending on whether it is negatively or positively charged. Thus, the counter ion to an anion will be a cation, and vice versa.

Interfacial Chemistry of Counter Ion

Counter ions are the mobile ions in ion exchange polymers and colloids. Ion-exchange resins are polymers with a net negative or positive charge. Cation-exchange resins consist of an anionic polymer with counter cations, typically **Na^+ (Sodium).** The resin has a higher affinity for highly charged counter cations, for example by **Ca^{2+} (Calcium)** in the case of water softening. Correspondingly, anion-exchange resins are typically provided in the form of chloride **Cl^-,** which is a highly mobile counter anion. Polystyrene sulfonate (Refer Figure 4.21), a cation-exchange resin, is typically supplied with Na^+ as the counter ion.

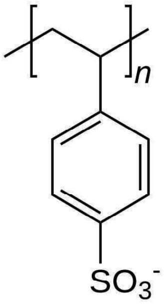


***Fig. 4.21** Structure of Polystyrene Sulfonate Supplied with Na^+ as the Counter Ion.*

The effects of counter ion specificity on the properties of sodium dodecyl sulfate micelles containing photochemically reactive solubilizates were studied by Laser flash photolysis and light scattering, potentiometric, spectroscopic and microelectrophoretic measurements. The counter ions investigated were an amphiphilic ion (cetyltrimethylammonium, CTA^+) and two divalent ions (cupric, Cu^{2+}, and methylviologen, MV^{2+}). Cu^{2+} and MV^{2+} showed lower effect than CTA^+ in promoting changes of micelle size and electrostatic potential at the micelle/solution interface. This can be attributed to the complex interplay between electrostatic and hydrophobic interactions, which determine the average location of counter ions, i.e., prevailing interfacial or intercalated binding to the micelle. Laser flash photolysis showed that Cu^{2+} enhanced the rate of decay of biphenyl triplet, while MV^{2+} did not show any effect. The differences between the quenching cations were attributed to the average location of MV^{2+} ions in the Stern layer further away from the micelle core than Cu^{2+}.

Counter ion binding of sodium and calcium to micelles, and mixed micellization have been investigated in the systems Sodium Dodecylsulfate (NaDS)/Sodium Decylsulfate (NaDeS) and NaDS/Sodium 4-Octylbenzenesulfonate (NaOBS) in order to accurately model the activity of the relevant species in solution. The Critical Micelle Concentration (CMC) and equilibrium micelle compositions of mixtures of these anionic surfactants, which is necessary for determining fractional counter ion binding measurements, is thermodynamically modeled by regular solution theory. The mixed micelle is ideal (the regular solution parameter $\beta(M)=0$) for the NaDS/NaOBS system, while the mixed micelle for NaDS/NaDeS has $\beta(M)=-1.05$ indicating a slight synergistic interaction. Counter ion binding of sodium to the micelle is influenced by the calcium ion concentration, and vice versa. However, the total degree of counter ion binding is essentially constant at approximately 0.65 charge negation at the micelle's surface. The counter ion binding coefficients can be quantitatively modelled using a simple equilibrium model relating concentrations of bound and unbound counter ions.

4.3.2 Thermodynamics of Micellization (Phase Separation and Mass Action Models)

Micelle or micellization is used in manufacturing and is actually the process that makes soapy water remove fats. Vitamins created through the micellization process are thought to be more easily and readily absorbed by the body. As mentioned earlier, the process of micellization is one of the most important characteristics of surfactant solution and hence it is essential to understand its mechanism (the driving force for micelle formation). This requires analysis of both the kinetic and the equilibrium aspects of the processes. The stability of micelles can be thought of generally in terms of thermodynamic and kinetic stability. Thermodynamic stability describes how the system acts as micelles are formed and reach equilibrium.

The surfactant's Critical Micelle Concentration (CMC) plays a factor in ***Gibbs free energy*** of micellization. The exact concentration of the surfactants that yield the aggregates being thermodynamically soluble is the CMC. The ***Krafft temperature*** determines the solubility of the surfactants which in turn is the temperature that CMC is achieved. There are many parameters that affect the CMC. The interaction between the hydrophilic heads and the hydrophobic tails play a part, as well as the concentration of salt within the solution and surfactants.

Surfactants: Surfactants are composed of a polar head group, i.e., hydrophilic and a nonpolar tail group, i.e., ***hydrophobic***. The head groups can be anionic, cationic, zwitterionic, or non-ionic. The tail group can be a ***hydrocarbon, fluorocarbon, or a siloxane***. Hydrophobic coagulation occurs when a positively charged solution is added with a sodium alkyl sulphate. The coagulation value is smaller when the alkyl chain length of the coagulator is longer. Hydrophobic coagulation occurs when a –ve Charged solution contains a cationic surfactant. The coulomb attraction between the head groups and surface competes with the hydrophobic attraction for the entire tail in a favourable manner.

Block Copolymer: Block copolymers also known as are '***Microphase separation molecules***' to form periodic nanostructures, Microphase separation is a situation similar to that of oil and water. Oil and water are immiscible - they phase separate. Due to incompatibility between the blocks, block copolymers undergo a similar phase separation. Because the blocks are covalently bonded to each other, they cannot demix macroscopically as water and oil. In '**Microphase Separation**' the blocks form nanometer-sized structures.

Driving Mechanism for Micellization

The driving mechanism for micellization is the transfer of hydrocarbon chains from water into the oil-like interior. This entropic effect is called the ***hydrophobic effect***. Compared to the increase of entropy of the surrounding water molecules, this hydrophobic interaction is relatively small. The water molecules are highly ordered around the hydrocarbon chain. The CMC decreases while the length of the alkyl chain increases when all the hydrocarbon chains are hidden inside micelles.

Ionic Micelles and Salt Concentration

The driving force for adsorption is the attraction between the surface and the surfactant head-group with low surfactant concentrations and the adsorption on hydrophilic surfaces. This means that the surfactant adsorbs at low surfactant concentrations with its head-group contacting the surface. Depending on the type of head-group and surface, the attraction will have a short-range contribution for both non-ionic and ionic surfactants. Ionic surfactants will also experience a generic electrostatic interaction. If the surfactants and the surface are oppositely charged then the interaction will be attractive to each other. If the surfactants and the surface are like charges then the interaction will be repulsive to each other. Aggregation is opposed due to the repulsion of the polar head groups as they come closer to each other. Hydration repulsion occurs because head groups have to be dehydrated as they come closer to each other. The head groups' thermal fluctuations become smaller as they come closer together because they are confined by neighbouring head groups. His causes their entropy to decrease and leads to a repulsion.

Gibbs Free Energy Of Micellization

In general, the Gibbs free energy of micellization can be approximated as:

$$\Delta G_{micellization} = RT \times \ln(CMC)$$

Where $\Delta \boldsymbol{G}_{\mathbf{micellization}}$ is the change in ***Gibbs free energy*** of micellization, ***R*** is the universal gas constant, ***T*** is the absolute temperature, and CMC is the Critical Micelle Concentration.

Non-Ionic Micelles: Two methods to extract the ***Gibbs free energy*** based on the value of CMC and n exist; Phillips method based on the law of mass action and the ***pseudo-phase separation model***. The law of mass action postulates that the micelle formation can be modelled as a chemical equilibrium process between the micelles M_n and its constituents, the surfactant monomers, ***S***:

$$n \cdot S \rightleftharpoons M_n .$$

Where ***n*** is the average number of surfactant monomers in solution that associate into a micelle, commonly denoted the aggregation number.

The equilibrium is characterized by an equilibrium constant defined by $K = [M_n]/[S]^n$, where $[M_n]$ and $[S]^n$ are the concentrations of micelles and free surfactant monomers, respectively. In combination with the law of conservation of mass, the system is fully specified by: $S_{tot} = [S] + nK[S]^n$ where S_{tot} is the total surfactant concentration. Phillips defined the CMC as the point corresponding to the maximum change in gradient in an ideal property-concentration (ϕ against S_{tot}) relationship $d^3\phi/\} \backslash dS^3_{tot} = 0$ By implicit differentiation of $S_{tot} = [S] + nK[S]^n$ three times with respect to S_{tot} and equating to zero it can be shown that the micellization constant is given by

$$K = \frac{n-2}{n^2(2n-1)}\left(CMC \cdot \frac{2n^2-n}{2n^2-2}\right)^{1-n}$$ for $n>2$. According to Phillips method the Gibbs free energy change of micellization is therefore given by:

$$\Delta G_{micellization} = -\frac{RT}{n}\ln\left(\frac{n-2}{n^2(2n-1)}\left(CMC \cdot \frac{2n^2-n}{2n^2-2}\right)^{1-n}\right)$$

The ***pseudo-phase separation model*** was originally derived on its own basis, but it has later been shown that it can be interpreted as an approximation to the ***mass-action model*** for large n., i.e., for micelles behaving in accordance with the law of mass-action, the ***pseudo-phase phase separation model*** is only an approximation and will only become asymptotically equal to the mass-action model as the micelle becomes a true macroscopic phase i.e. for ***n’!”***. However, the approximation that the aggregation number ***n*** is large is in most cases sufficient:

$$\Delta G_{micellization} \approx RT\ln(CMC)$$

Ionic Micelles: Ionic micelles are typically very affected by the salt concentration. In ionic micelles the monomers are typically fully ionized, but the high electric field strength at the surface of the micelles will cause adsorption of some proportion of the free counter-ions. In this case a chemical equilibrium process can be assumed between the charged micelles $M_n^{-(1-\beta)n}$ and its constituents, the bile salt monomers, S^- and bound counter-ions B^+:

$$n \cdot S^- + \beta \cdot n \cdot B^+ \rightleftharpoons M_n^{-(1-\beta)n}$$

Where ***n*** is the average aggregation number and β is the average degree of counter-ion binding to the micelle. In this case, the Gibbs free energy is given by:

$$\Delta G_{micellization} = -\frac{RT}{n}\ln\left(\frac{1}{([B^+]_{S_{tot}=CMC})^{\beta n}}\frac{n-2}{n^2(2n-1)}\left(CMC\cdot\frac{2n^2-n}{2n^2-2}\right)^{1-n}\right)$$

NOTES

Where $\Delta G_{\text{micellization}}$ is the Gibbs energy of micellization and $[B^+]_{Stot=CMC}$ is the free counter-ion concentration at CMC. For large n, i.e., in the limit when then the micelles becomes a true macroscopic phase, the Gibbs free energy is usually approximated by:

$$\Delta G_{micellization} \approx (1+\beta)RT\ln CMC$$

Dressed Micelle Model: Dressed micelle model is the ***total Gibbs energy*** is broken down into several components accounting for the hydrophobic tail, the ***electrostatic repulsion*** of the head groups, and the interfacial energy on the surface of the micelle.

$$\Delta G_{micellization} = \Delta G_{HP} + \Delta G_{EL} + \Delta G_{IF}$$

Where the components of the ***total Gibbs micellization energy*** are hydrophobic, electrostatic, and interfacial.

4.3.3 Micellar Solubilization

Micellar solubilization is the process of which is including the solubilizate (the component that undergoes solublization) into or onto micelles. Solublization may occur in a system consisting of a solvent, an association colloid (a colloid that forms micelles), and at least one other solubilizate.

Usage of the Term

Solubilization is distinct from dissolution because the resulting fluid is a colloidal dispersion involving an association colloid. This suspension is distinct from a true solution, and the amount of the solubilizate in the micellar system can be different (often higher) than the regular solubility of the solubilizate in the solvent. The term 'Solubilization' is sometimes used in a broader meaning as "to bring to a solution or (non-sedimenting) suspension" by any means, for example leaching by a reaction with an acid.

Application

Micellar solubilization is widely utilized, for example in laundry washing using detergents, in the pharmaceutical industry, for formulations of poorly soluble drugs in solution form, and in clean-up of oil spills using dispersants.

4.3.4 Microemulsion

Microemulsions are clear, thermodynamically stable isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) and/or other ingredients, and the 'Oil' may actually be a complex mixture of different hydrocarbons. In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ***ordinary emulsions***.

The three basic types of microemulsions are direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bicontinuous.

In ternary systems, such as microemulsions, where two ***immiscible phases*** (water and 'oil') are present with a surfactant, the surfactant molecules may form a monolayer at the interface between the oil and water, with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase.

Theory of Microemulsion

Various theories concerning microemulsion formation, stability and phase behaviour have been proposed over the years. For example, one explanation for their thermodynamic stability is that the oil/water dispersion is stabilized by the surfactant present and their formation involves the elastic properties of the surfactant film at the oil/water interface, which involves as parameters, the curvature and the rigidity of the film. These parameters may have an assumed or measured pressure and/or temperature dependence (and/or the salinity of the aqueous phase), which may be used to infer the region of stability of the microemulsion, or to delineate the region where three coexisting phases occur, for example. Calculations of the interfacial tension of the microemulsion with a coexisting oil or aqueous phase are also often of special focus and may sometimes be used to guide their formulation.

Uses of Microemulsion

Microemulsions have many commercially important uses:

- Water-in-oil microemulsions for some dry cleaning processes
- Floor polishers and cleaners
- Personal care products
- Pesticide formulations
- Cutting oils
- Drugs

Much of the work done on these systems have been motivated by their possible use to mobilize ***petroleum trapped*** in porous sandstone for enhanced oil recovery. A fundamental reason for the uses of these systems is that a microemulsion phase sometimes has an ultralow interfacial tension with a separate oil or aqueous phase, which may release or mobilize them from solid phases even in conditions of slow flow or low pressure gradients.

Microemulsions also have industrial applications, one of them being the synthesis of polymers. Microemulsion polymerization is a complex heterogeneous process where transport of monomers, free radicals and other species (such as, chain transfer agent, co-surfactant and inhibitors) between the aqueous and organic phases, takes place. Compared with other heterogeneous polymerization processes (suspension or emulsion) microemulsion polymerization is a more complicated system. Polymerization rate is controlled by monomer partitioning between the phases, particle nucleation, and adsorption and desorption of radicals. Particle stability is affected by the amount and type of surfactant and pH of dispersing medium. It is also used in the process of creating nanoparticles.

NOTES

The ***kinetics of microemulsion polymerization*** has much in common with emulsion polymerization kinetics, the most characteristic feature of, which is the compartmentalization, where the radicals growing inside the particles are separated from each other, thus suppressing termination to a high extent and, as a consequence, providing high rates of polymerization.

4.3.5 Reverse Micelles

They are water droplets that we obtain from the action of sulphates when it disperses in water. Also, surfactant atoms create with the polar part to the internal side ready to solubilize water and the polar part in contact with the natural dissolvable.

The differences between micelles and reverse micelles are preserved in the gas phase. Sharp peaks are detected for the reverse micelles while diffuse peaks are observed for regular micelles due to exchange of counter ions from the exposed head groups with the bulk solvent. The differences between micelles and reverse micelles are preserved in the gas phase. Comparison of tandem mass spectra at m/z 10,000 for regular micelles in 200 mM ammonium acetate (upper panel) and reverse micelles in H_2O (lower panel) made from the same surfactant (Cetyltrimethylammonium Bromide (CTAB)). At low m/z the bromide counter ions are exchanged from (CTAB-CTA) + in the regular micelle (b) while in reverse micelle they are retained (a). The product ions corresponding to stripped complexes, at m/z values >10,000, are formed by expulsion of the low mass (CTAB-CTA) + ions. The stripped complexs are labeled with the number of CTAB molecules (one peak labeled within each charge state cluster). Neighboring peaks within each cluster have the same charge but differ by the number of CTAB molecules. The stripped complexes reveal characteristic differences between the two micellar forms. Sharp peaks are detected for the reverse micelles while diffuse peaks are observed for regular micelles due to exchange of counter ions from the exposed head groups with the bulk solvent. The diagrams on the right show the rodlike structures which are believed to form in response to changes in concentration of the micellar solutions, similar process could occur during evaporation of the electrospray droplets.

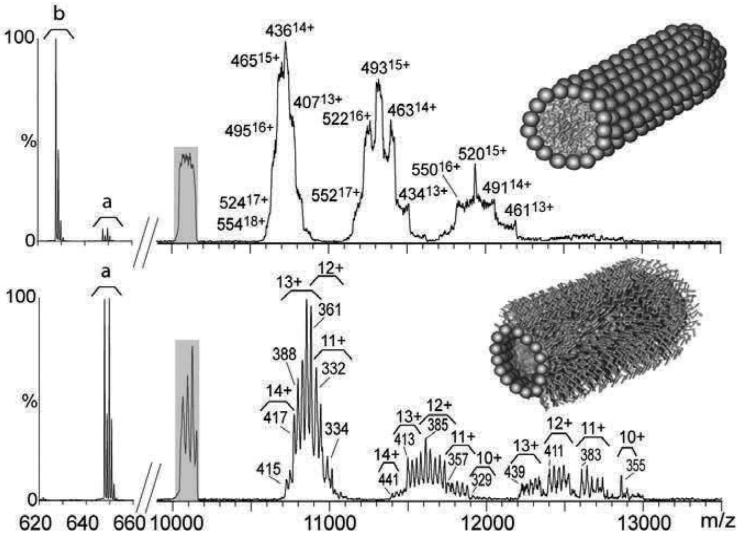


Fig. 4.22 The Differences Between Micelles and Reverse Micelles

Check Your Progress

12. Define the surfactant.
13. What is micelle?
14. What do you understand by detergent?
15. When counter ion binding of sodium and calcium to micelles?
16. Are micelles thermodynamically stable?
17. Define the term hydrophobic effect in micellization.
18. Give the definition of micellar solubilisation.
19. Define the microemulsions.
20. How are reverse micelles formed?

4.4 MACROMOLECULE

Polymerization, is a process in which relatively small molecules, called monomers, combine chemically to produce a very large chain like or network molecule, called a polymer. The monomer molecules may be all alike, or they may represent two, three, or more different compounds. Usually at least 100 monomer molecules must be combined to make a product that has certain unique physical properties, such as, elasticity, high tensile strength, or the ability to form fibres, that differentiate polymers from substances composed of smaller and simpler molecules; often, many thousands of monomer units are incorporated in a single molecule of a polymer. The formation of stable covalent chemical bonds between the monomers sets polymerization apart from other processes, such as crystallization, in which large numbers of molecules aggregate under the influence of weak intermolecular forces.

Two classes of polymerization usually are distinguished:

- Condensation Polymerization
- Addition Polymerization

In **condensation polymerization**, each step of the process is accompanied by the formation of a molecule of some simple compound, often water. In addition polymerization, monomers react to form a polymer without the formation of by-products.

Addition polymerization usually are carried out in the presence of catalysts, which in certain cases exert control over structural details that have important effects on the properties of the polymer.

NOTES

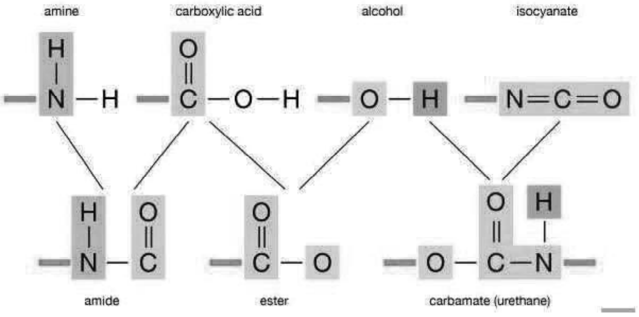


Fig. 4.23 *Functional Group: Monomers and Polymers*

Linear Polymers, which are composed of chainlike molecules, may be viscous liquids or solids with varying degrees of crystallinity; a number of them can be dissolved in certain liquids, and they soften or melt upon heating. Cross-linked polymers, in which the molecular structure is a network, are thermosetting resins (i.e., they form under the influence of heat but, once formed, do not melt or soften upon reheating) that do not dissolve in solvents. Both linear and cross-linked polymers can be made by either addition or condensation polymerization.

Polymerization - Addition Polymers

Polymers are very different from the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A polymer is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern. The small molecules which make up the polymer are called monomers. Polymers generally form either from an addition reaction or a condensation reaction.

Addition Polymers

An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond. Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.

$n\mathrm{CH_2{=}CH_2{=}(CH_2CH_2)}n$

The letter n stands for the number of monomers that are joined in repeated fashion to make the polymer and can have a value in the hundreds or even thousands.

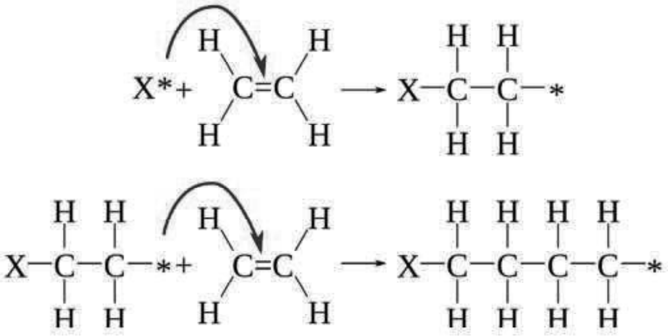


Fig. 4.24 *Polyethylene Synthesis*

The reactions above show the basic steps to form an addition polymer.

1. **Initiation:** A free radical initiator (X*) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: H–O–O–H→2H–O. This free radical attacks a carbon-carbon double bond. One of the pi electrons forms a single bond with the initiator while the other pi electron forms a new free radical on the carbon atom.
2. **Propagation:** The new free radical compound interacts with another alkane, continuing the process of chain growth (second step above).
3. **Termination:** It occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.

   Polyethylene can have different properties depending on the length of the polymer chains and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates.

   Several other kinds of unsaturated monomers can be polymerized and are components in common household products. Polypropylene is stiffer than polyethylene and is in plastic utensils and some other types of containers.

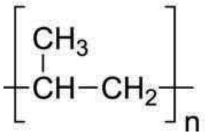


Fig. 4.25 Polypropylene Structure

Polystyrene is used in insulation and in molded items such as coffee cups.

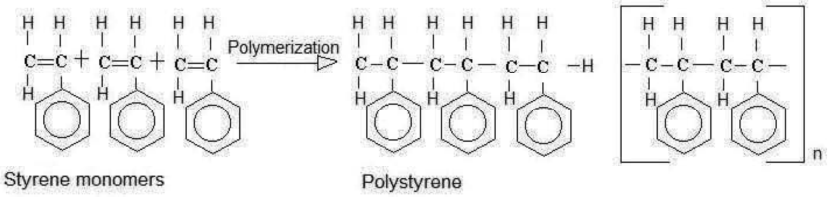


Fig. 4.26 Polystyrene Synthesis and Structure

Polyvinyl Chloride (PVC) is extensively used for plumbing pipes

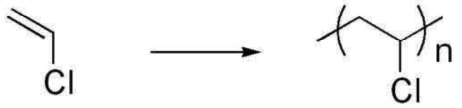


Fig. 4.27 Polyvinyl Chloride

Polyisoprene is a polymer of isoprene and is better known as rubber. It is produced naturally by rubber trees, but several variants have been developed which demonstrate improvements on the properties of natural rubber.

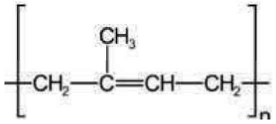
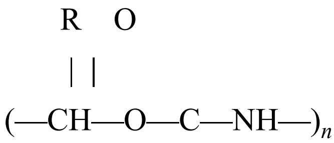


Fig. 4.28 *Polyisoprene*

Polymers are one of the most important products, which find an important place in every walk of modern civilisation. The term polymer (Greak word: *poly* + *meros*, means, many parts) denotes a molecule produced by the repetition of some simpler unit, called the mer or the monomer.

The term *macromolecule* (big molecule) is also often used to cover the large molecule of complex structure. A naturally occurring macromolecule is insulin, a protein hormone, which occurs in the pancreas, and is best known agent to lower blood sugar in diabetic patients. It has the repeating units with amide linkages, i.e.,



$(\text{—}\overset{\overset{R}{|}}{CH}\text{—O—}\overset{\overset{O}{|}}{C}\text{—NH—})_n$, where $n = 51$ and R has sixteen variations. The science of macromolecules is divided between biological and non-biological materials, each having vital importance in our daily life. Biological polymers, i.e., proteins, nucleic acids (DNA, RNA), starch, cellulose and enzymes are complex macro molecules form the very foundation of life and intelligence and provide much of the food for the existance of man. This chapter however, is concerned mainly with the chemistry of some polymers. These are primarily the synthetic materials used for plastics, fibres, and elastomers and a few naturally occurring polymers, such as rubber, wool and cellulose. The polymers are truly indispensible to mankind, as they are used to meet the basic needs-clothing, shelter, communication, and transportation, as well as to the conveniences of modern living.

The name of a polymer is usually derived from the name of the monomer (repeat unit) by prefixing the word poly to it. To illustrate the polymerization product of ethylene is known as polyethylene and that of sytrene is called polystyrene. The number of repeating units in the chain is called the Degree of Polymerization (DP) and specifies the length of the chain. Degree of polymerization is denoted by the letter n or P. The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the degree of polymerization, i.e.,

$$M_{\text{poly}} = n \times M_m$$

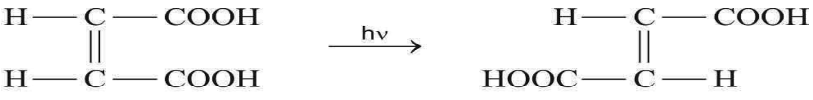
or

$$n\ \text{(Degree of polymerization)} = \frac{M_{\text{poly}}\ \text{(mol. wt. of polymer)}}{M_m\ \text{(mol. wt. of repeat unit)}}$$

The degree of polymerization may vary over a wide range, i.e., from a few units to 10,000 and even more. Polymers with high P are called high polymers and are mostly useful for plastics, rubbers or fibres, etc., while those with low P are known as oligomers.

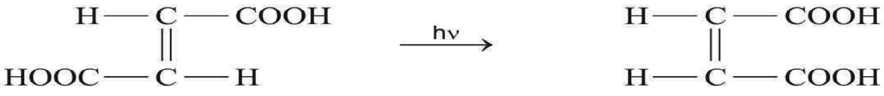
Classification of Polymers

A polymer may consist of monomers of identical or of different chemical structure. If it has identical units then it is known as homopolymer, whereas a polymer containing several types of monomeric units in its chain is known as copolymer, or mixed polymer. In some cases the repetition is linear and a chain is built up from its links. However, in cases the chains are branched or interconnected, to form three dimensional structures.



$$\begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array} \xrightarrow{h\nu} \begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array}$$

and



$$\begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array} \xrightarrow{h\nu} \begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array}$$

Copolymers may also be linear, branched or three-dimensional. The monomer residues, in co-polymer molecules may be arranged in the chain regularly or at random, according to the law of chance. Copolymers of the former group are called regular-copolymers and those of latter type, statistical or irregular copolymers.

Copolymers with long sequence of two monomers can have two arrangements of long chains:

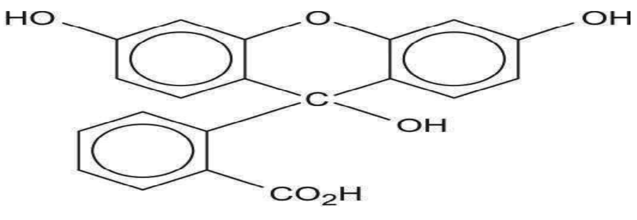
1. linear copolymers in which the units of each type form fairly continuous sequence (blocks) is known as block copolymers.
2. Branched copolymer, with monomer of one kind grafted into a backbone of the second monomer type is termed as graft copolymer.

According to the structure of main chain, all polymers are classified into homochain and heterochain polymers. Homochain polymers contain the chains composed of atoms of the same element, for example, carbon, sulphur phosphorus etc.

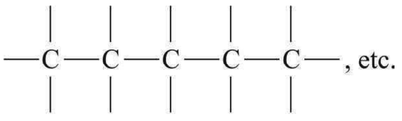
In heterochain polymers, the main chain is made up of atoms of different species, for example,

—A—A—A—A—B—B—B—B—A—A—A—A—B—B, etc.

Block polymer



Florescein (acid Form)



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-, \text{etc.}$$

Carbon-chain polymer

On the basis of chemical composition, the polymers can also be classified as:

1. **Organic Polymers:** Organic polymers include compounds containing carbon hydrogen, oxygen nitrogen, sulphur and halogen atoms. Oxygen, nitrogen or sulphur may also be present in the backbone chain.
2. **Elemento-Organic (Hetero-Organic) Polymers:** These include the following classes:
   - Compounds containing carbon atoms and hetero atoms (except for nitrogen, sulphur and oxygen atoms) in their chains.
   - Compounds with inorganic chains if they contain side groups with carbon atoms connected directly to the chain.

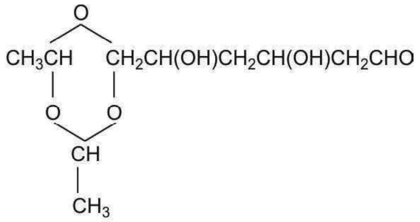
   (*iii*) Compounds having carbon atoms in the main chain and hetero-atoms (except for nitrogen, sulphur, oxygen and halogen atoms) in side groups connected directly to the carbon atoms of the chain. For example, polysiloxanes, polytitanoxanes, etc.
3. **Inorganic Polymers:** These include polymers containing no carbon atoms. Their are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains. Polysilanes, polygermanes, polysilicic acid, polyphosphates, polyarsenates, etc., are examples of inorganic polymers.

Polymerization Processes

The processes of polymerization were classified by the W H Carothers (1926) into two groups, i.e., *condensation* and *addition* polymerizations. In 1953, Flory amended, Carother's original distinction between addition and condensation polymerization. He laid special emphasis on the mechanisms by which the two types of polymerization, proceed. It was observed that condensation polymerization was preceded by the stepwise intermolecular condensation of reactive groups and the addition polymerization resulted from chain reactions involving some sort of active centres. Thus, the two classes of polymerzation are:

Condensation Polymerization

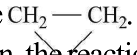
This is entirely analogous to condensation in low molecular weight compounds. For the formation of condensation polymer there is union between two polyfunctional molecules to produce the large polyfunctional molecule. The process involves the elimination of a small molecule, such as water, ammonia, etc. The reaction continues until almost all of the reagents is used up. Since there is an equilibrium between reactants and products, the rate of conversion can be controlled by the rate of removal of one of the products. A good example is, esterification, where water is eliminated between an acid and an alcohol.



(I)

Here, the rate of conversion can be controlled by the rate of removal of water.

Addition or Chain-Reaction Polymerization

This type of polymerization involves chain reactions. The chain carrier in such reactions, may be an ion or a reactive substance with one unpaired electron called a free radical. Chain polymerization is characteristic of compounds with multiple bonds, for example, ethylene $CH_2=CH_2$. isobutylene $(CH_3)_2$ $C=CH_2$ and vinyl chloride $CH_2=CHCl$, or of unstable rings containing heteroatoms, for example, ethylene oxide  $\underset{O}{CH_2 - CH_2}$. Depending upon the active centre, which may be a free radical or an ion, the reaction is one of radical or ionic polymerization, respectively. A free radical is produced by the decomposition of an initiator. The free radical then attacks to open the double bond of a vinyl monomer or ring or a cyclic compound and adds to it, with an electron remaining unpaired. Within a very short span of time (usually a few seconds or less) may more monomers add successively to form a long chain with active centers. Finally, chain termination results from saturation of the macro radical and may occur by the combination of free radicals, disproportionation of chain transfer.

With few exceptions, chain-reaction polymerization results in the formation of homochain polymers, where as step-reaction polymerization produces heterochain polymers. Polymerizations are classified without regard to loss of a small molecule (for example, polyurethanes are formed by step-reaction polymerization or type of interunit linkage (for example, phenol-formaldehyde resins results from stepwise polymerization even though they lack interunit functional groups). In case the differentiation is required on the basis of mechanism, the terms *step-reaction* and *chain-reaction* are used; but to avoid confusion, the common terms *condensation* and *addition* are permissible.

Initiators: Types and Initiator Efficiency

Initiator, is a source of any chemical species that reacts with a monomer (single molecule that can form chemical bonds) to form an intermediate compound that is capable of linking successively with a large number of other monomers into a polymeric compound.

The most commonly used initiators produce free radicals (reactive atoms or groups of atoms that contain odd numbers of electrons); examples of initiators include peroxides and aliphatic azo compounds used to polymerize vinyl chloride, methyl methacrylate, and other monomers.

Acid-forming systems such as boron trifluoride with traces of water react with a monomer to produce a positively charged (cationic) intermediate. Such initiation is used in the conversion of isobutylene to butyl rubber.

Reaction of metallic sodium and biphenyl produces an anionic initiator that causes formation of polymer chains with reactive sites at both ends; these may be further treated with a different monomer to yield block copolymers.

Polypropylene and high-density polyethylene are prepared by use of Ziegler catalysts, which are initiators composed of organometallic compounds and metallic halides, such as triethylaluminum and titanium tetrachloride.

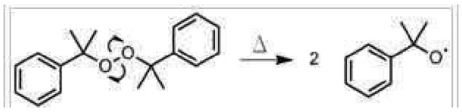
Initiation

Initiation is the first step of the polymerization process. During initiation, an active center is created from which a polymer chain is generated. Not all monomers are susceptible to all types of initiators. Radical initiation works best on the carbon–carbon double bond of vinyl monomers and the carbon–oxygen double bond in aldehydes and ketones. Initiation has two steps. In the first step, one or two radicals are created from the initiating molecules. In the second step, radicals are transferred from the initiator molecules to the monomer units present. Several choices are available for these initiators.

Types of Initiation and the Initiators

Thermal Decomposition

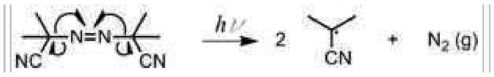
The initiator is heated until a bond is homolytically cleaved, producing two radicals. This method is used most often with organic peroxides or azo compounds



Thermal decomposition of dicumylperoxide

Photolysis

Radiation cleaves a bond homolytically, producing two radicals (Refer Figure 8.8). This method is used most often with metal iodides, metal alkyls, and azo compounds



Photolysis of azoisobutylnitrile (AIBN)

Photoinitiation can also occur by bi-molecular H abstraction when the radical is in its lowest triplet excited state.

An acceptable photoinitiator system should fulfill the following requirements:

- High absorptivity in the 300–400 nm range.
- Efficient generation of radicals capable of attacking the olefinic double bond of vinyl monomers.
- Adequate solubility in the binder system (prepolymer + monomer).
- Should not impart yellowing or unpleasant odors to the cured material.
- The photoinitiator and any byproducts resulting from its use should be non-toxic.

Redox Reactions

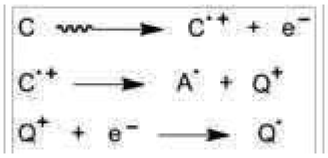
Reduction of hydrogen peroxide or an alkyl hydrogen peroxide by iron.Other reductants such as Cr^{2+}, V^{2+}, Ti^{3+}, CO^{2+}, and Cu^{+} can be employed in place of ferrous ion in many instances

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^{-} + HO^{\cdot}$$

Three steps involved in ionizing radiation: ejection, dissociation, and electron-capture

Ionizing Radiation

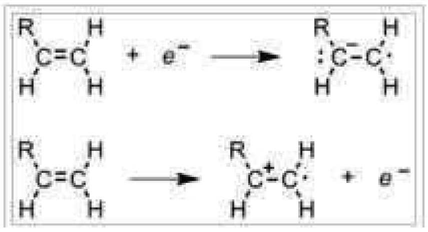
α-, β-, γ-, or x-rays cause ejection of an electron from the initiating species, followed by dissociation and electron capture to produce a radical.



(Top) Formation of radical anion at the cathode; (bottom) formation of radical cation at the anode

Electrochemical

Electrolysis of a solution containing both monomer and electrolyte. A monomer molecule will receive an electron at the cathode to become a radical anion, and a monomer molecule will give up an electron at the anode to form a radical cation. The radical ions then initiate free radical (and/or ionic) polymerization. This type of initiation of especially useful for coating metal surfaces with polymer films



Plasma

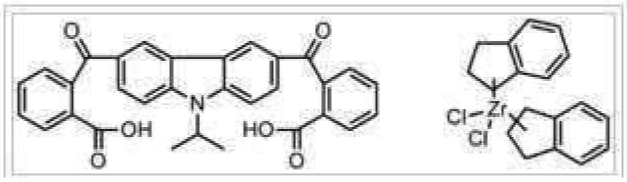
A gaseous monomer is placed in an electric discharge at low pressures under conditions where a plasma (ionized gaseous molecules) is created. In some cases, the system is heated and/or placed in a radiofrequency field to assist in creating the plasma.

Sonication

High-intensity ultrasound at frequencies beyond the range of human hearing (16 kHz) can be applied to a monomer. Initiation results from the effects of cavitation (the formation and collapse of cavities in the liquid). The collapse of the cavities generates very high local temperatures and pressures. This results in the formation of excited electronic states, which in turn lead to bond breakage and radical formation.

Ternary Initiators

A ternary initiator is the combination of several types of initiators into one initiating system. The types of initiators are chosen based on the properties they are known to induce in the polymers they produce. For example, poly(methyl methacrylate) has been synthesized by the ternary system benzoyl peroxide-3,6-bis o-carboxybenzoyl -N- isopropylcarbazole- di-η5- indenylzicronium dichloride.



Benzoyl peroxide-3,6-bis (o-carboxybenzoyl) -N-isopropylcarbazole- di-ç5- indenylzicronium dichloride

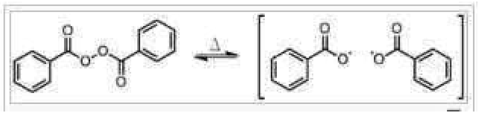
This type of initiating system contains a metallocene, an initiator, and a heteroaromatic diketo carboxylic acid. Metallocenes in combination with initiators accelerate polymerization of poly(methyl methacrylate) and produce a polymer with a narrower molecular weight distribution. The example shown here consists of indenylzirconium (a metallocene) and benzoyl peroxide (an initiator). Also, initiating systems containing heteroaromatic diketo carboxylic acids, such as 3,6-bis (o-carboxybenzoyl) -N- isopropylcarbazole in this example, are known to catalyze the decomposition of benzoyl peroxide. Initiating systems with this particular heteroaromatic diket carboxylic acid are also known to have effects on the microstructure of the polymer. The combination of all of these components—a metallocene, an initiator, and a heteroaromatic diketo carboxylic acid—yields a ternary initiating system that was shown to accelerate the polymerization and produce polymers with enhanced heat resistance and regular microstructure.

Initiator Efficiency

Due to side reactions and inefficient synthesis of the radical species, chain initiation is not 100%. The efficiency factor f is used to describe the effective radical concentration. The maximal value of f is 1, but typical values range from 0.3 to 0.8. The following is a list of reactions that decrease the efficiency of the initiator.

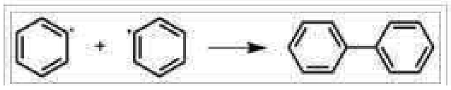
Primary Recombination

Two radicals recombine before initiating a chain (Refer Figure 8.13). This occurs within the solvent cage, meaning that no solvent has yet come between the new radicals. Primary recombination of BPO; brackets indicate reaction happening within the solvent cage is given below



Other Recombination Pathways

Two radical initiators recombine before initiating a chain, but not in the solvent cage. Recombination of phenyl radicals from the initiation of BPO outside the solvent cage is given below:



Side Reactions

One radical is produced instead of the three radicals that could be produced . The reaction of polymer chain R with other species in reaction is given below:

$$R\cdot + R'{-}O{-}O{-}R' \longrightarrow ROR' + R'O'$$

Polymeric materials possess a very wide range of physical properties, they are hard or soft or rubber-like, brittle or tough and malleable and non-malleable. These properties depends on the molecular structure of the polymer. The physical properties depend to a great extent on whether the polymer is (*i*) completely amorphous or (*ii*) partly crystalline. In an amorphous polymer the molecular chains are all tangled up in a disordered manner. The long chain polymers generally exist in the amorphous state this is because the long chains mostly exist in the random coiled configuration, the solid is thus clastic. However, due to the presence of some crystallinity the polymeric material is stiffer. Depending on the temperature of the amorphous polymer may be glassy or leathery.

Group OH Cl CN NO_2 H NH_2 CH_3

Most polymers are in the glassy state which is like that of a supercooled liquid. On raising the temperature there is a transition at the glass-transition temperature from the glassy to the leathery state. Below the glass-transition temperature of a polymeric substance can be raised by vulcanisation due to cross-linkages.

The mechanical properties of polymers are profoundly dependent on the stereo-regularity of their chains. Polymers of monomers like styrene have symmetric carbon atoms. There are two types of stereoregular vinyl polymers, isotactic and syndictactic depending on whether successive pseudoasymmetric carbon atoms have the same or opposite enantiomorphic configuration. Some polymers contain regions in which the chains are arranged in an orderly three dimensional array. These crystalline regions typically have dimensions of the order of 10 mm and they have an important influence on the physical properties of the polymer. The extent of crystallinity of the polymer is increased as it is stretched. This because on stretching the chains are drawn together thus reducing the random thermal motion.

4.4.1 Kinetics and Mechanism Polymerization

Radical, also called Free Radical, in chemistry, molecule that contains at least one unpaired electron. Most molecules contain even numbers of electrons, and the covalent chemical bonds holding the atoms together within a molecule normally consist of pairs of electrons jointly shared by the atoms linked by the bond. Most radicals may be considered to have arisen by cleavage of normal electron-pair bonds, every cleavage having produced two separate entities, each of which contains a single, unpaired electron from the broken bond (in addition to all the rest of the normal, paired electrons of the atoms).

Although free radicals contain unpaired electrons, they may be electrically neutral. Because of their odd electrons, free radicals are usually highly reactive. They combine with one another, or with single atoms that also carry free electrons, to give ordinary molecules, all of whose electrons are paired; or they react with intact molecules, abstracting parts of the molecules to complete their own electron pairs and generating new free radicals in the process. In all these reactions, each simple free radical, because of its single unpaired electron, is able to combine with one other radical or atom containing a single unpaired electron. Under special circumstances, diradicals can be formed with unpaired electrons on each of two atoms (giving an overall even number of electrons), and these diradicals have a combining power of two.

NOTES

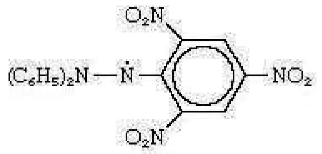
Certain free radicals are stabilized by their peculiar structures; they exist for appreciable lengths of time, given the right conditions. Most free radicals, however, including such simple ones as the methyl ($\cdot CH_3$) and ethyl ($\cdot C_2H_5$) radicals, are capable of only the most fleeting independent existence.

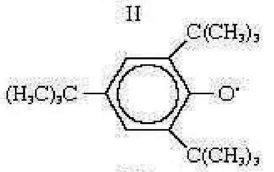
Stable Radicals

The first relatively stable free radical, triphenylmethyl (structure I), was discovered by Moses Gomberg in 1900. In this compound the central carbon is trivalent since it is combined with three substituents instead of four, and its unshared electron is represented by a dot. Free radicals of the triphenylmethyl type are stable only in certain organic solvents; they are rapidly destroyed by irreversible reactions in the presence of air, water, or strong acids.

In a manner analogous to the above, free radicals are formed by the breaking of the nitrogen–nitrogen bond in aromatic hydrazines of the general structure R_2N—NR_2, or of the central nitrogen–nitrogen bond in aromatic tetrazanes, R_2N—RN—NR—NR_2. Thus, the radical 1,1-diphenyl-2-picrylhydrazyl (structure II) exists as a stable violet solid.

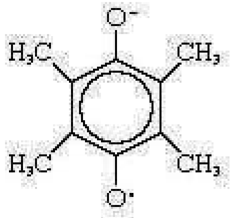
Similar examples of free radicals, in which, however, the odd electron is on oxygen, are also known, for example, the 2,4,6-tri-tert-butylphenoxy radical (structure III).


II


III

Still another type of stable radical ion, a metal ketyl, forms when a substance such as benzophenone, is treated with metallic sodium to give the coloured substance $(C_6H_5)2C$—O-. Similarly, sodium reacts with complex aromatic hydrocarbons such as naphthalene, converting them to highly coloured radical ions.

A final class of relatively stable organic free radicals are those containing the group > NO. An example is diphenylnitrogen oxide, $(C_6H_5)2NO$, which is obtained by the oxidation of diphenylhydroxylamine, $(C_6H_5)2NOH$.


IV

Certain structural features appear to be required for the existence of stable free radicals. One condition of particular importance is shown by the semiquinone radical ion IV. As depicted, the upper oxygen atom has a negative charge and the lower one an odd electron. This assignment is arbitrary, however, and the same molecule would be represented if the charge and the odd electron were interchanged. When such a situation is encountered, the actual average distribution of electrons within the molecule is presumed not to be that of either of the structures just described but to be intermediate between the two. This circumstance is called delocalization, or resonance; according to quantum mechanics, the resonance considerably increases the stability of the substance and, as in this case, the probability of its existence. Similar arguments account for the stability of the other free radicals discussed earlier.

Unstable Radicals

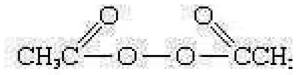
Simple free radicals such as methyl, $\cdot CH_3$, also exist and play key roles as transient intermediates in many chemical reactions. The existence of the methyl radical was first demonstrated by Friedrich A. Paneth and W. Hofeditz in 1929 by the following experiment. The vapours of tetramethyllead, $Pb(CH_3)4$, mixed with gaseous hydrogen, H2, were passed through a silica tube at low pressure. When a portion of the tube was heated to about 800° C, the tetramethyllead was decomposed and a mirror of metallic lead deposited on the internal surface of the tube. The gaseous products of the decomposition were found capable of causing the disappearance of a second lead mirror, deposited at a more distant cool point in the tube.

Since none of the recognized stable products of the decomposition was able similarly to dissolve a lead mirror, the inference was drawn that methyl radicals formed in the high-temperature decomposition reacted with lead at the cool mirror to regenerate tetramethyllead.

Methyl radicals obtained in this way proved to be highly reactive and short-lived. They not only reacted with lead and other metals but also disappeared rapidly and spontaneously, largely by dimerization to ethane, $H_3C—CH_3$. Techniques for producing reactive free radicals in the gas phase have been greatly extended by subsequent research. It has been found that various unstable species, such as ethyl, ($\cdot C_2H_5$), propyl, ($\cdot C_3H_7$), and hydroxyl, ($\cdot OH$), can be obtained by several methods including: (1) photochemical decomposition of a variety of organic and inorganic materials, (2) reaction between sodium vapour and an alkyl halide, and (3) discharge of electricity through a gas at low pressure. Atoms that arise from dissociation of a diatomic molecule (for example, the chlorine atom, $\cdot Cl$, from the dissociation of the chlorine molecule, C_{l2}) can also be obtained and have the properties of short-lived radicals of this type.

The existence of the various known unstable free radicals is most commonly demonstrated by the reactions that they undergo. Thus, ethyl radicals, formed from tetraethyllead, $Pb(C_2H_5)_4$, dissolve zinc and antimony mirrors. The resulting ethyl derivatives of zinc and antimony, $Zn(C_2H_5)_2$ and $Sb(C_2H_5)_3$, have been isolated and chemically identified. In a few instances, unstable radicals also have been identified spectroscopically. Here the important technique of flash photolysis, the use of a single, intense flash of light to produce a momentary high concentration of free radicals, is used.

Transient, unstable free radicals also may be produced in solution by several means. A number of molecules, of which organic peroxides are typical, possess such weak chemical bonds that they decompose irreversibly into free radicals on warming in solution. Diacetyl peroxide, for example, is considered to decompose, at least in large part, into carbon dioxide, CO_2, and methyl radicals. These, in turn, rapidly attack most organic solvents, often by abstracting hydrogen to given methane, CH_4, together with other products. Irradiation of solutions of many organic substances with ultraviolet light leads to the absorption of sufficient energy to disrupt chemical bonds and produce free radicals, and, in fact, most photochemical processes are at present thought to involve free-radical intermediates. The chemical changes that occur when solutions (and also gases) are exposed to high-energy radiation also appear to involve the transient formation of free radicals.



$$CH_3\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}CH_3$$

It is generally considered that free radicals are transient intermediates in many high-temperature reactions (such as combustion and the thermal cracking of hydrocarbons), in many photochemical processes, and in a number of other important reactions in organic chemistry, although the concentrations of the free radical intermediates are in general too low for direct detection. One class of free-radical reaction is of particular importance and is illustrated by the following example. Methane, CH_4, reacts with chlorine, Cl_2, by an overall process that gives chloromethane, CH_3Cl, and hydrogen chloride, HCl. The reaction is enormously accelerated by light and apparently involves the following steps:

$$\begin{aligned} Cl_2 &\longrightarrow 2Cl\cdot \\ Cl\cdot + CH_4 &\longrightarrow \cdot CH_3 + HCl \\ \cdot CH_3 + Cl_2 &\longrightarrow CH_3Cl + Cl\cdot \\ 2Cl\cdot &\longrightarrow Cl_2 \end{aligned} \qquad 1, 2, 3, 4$$

Chlorine atoms are produced in (1) and destroyed in (4), while the products that are actually isolated arise from (2) and (3). Since chlorine atoms consumed in (2) are regenerated in (3), a single atom of chlorine can lead to the production of many molecules of chloromethane. Such processes, in which an intermediate is continually regenerated, are known as chain reactions, and their study constitutes an important branch of chemical kinetics. Similar chains involving transient free radicals are involved in the halogenation of many other organic molecules, in many of the polymerization reactions that are employed in the manufacture of plastics and synthetic rubber, and in the reaction of molecular oxygen, O_2, with a great number of organic molecules.

Magnetic Properties of Free Radicals

The magnetic properties of free radicals provide a powerful tool for their detection and study. Molecules with even numbers of paired electrons are diamagnetic, .i.e., they are slightly repelled by a magnet. Free radicals, however, are paramagnetic (attracted by a magnet) because of the spin of the odd electron, the spins of the remaining paired electrons effectively canceling each other. The magnetic property of a substance most commonly studied is its magnetic susceptibility, effectively its behaviour in an inhomogeneous magnetic field, and the extent of paramagnetism of the substance is described in terms of its magnetic dipole moment. The magnitude of this dipole moment, which is the same for all free radicals containing single electrons, can be calculated, and the value obtained (1.73 Bohr magnetons) has been confirmed experimentally with free radicals in the solid state or at known concentrations in solution. Magnetic susceptibility measurements may be used to demonstrate the existence of free radicals and to measure the position of equilibrium between radicals and their dimers or disproportionation products. Diradicals, with even numbers of electrons, two of which, however, are not paired, are also paramagnetic, the oxygen molecule, O_2, being probably the simplest example of the kind.

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The electron paramagnetic-resonance spectra of free radicals provide another technique for their detection and study. According to quantum mechanics, the spin of the odd electron of a free radical, when placed in a magnetic field, may have two, and only two, orientations, one with and the other against the field. These two orientations differ slightly in energy by an amount proportional to the strength of the magnetic field, and the majority of the electrons have the orientation of lower energy. If a system containing free radicals is placed in a magnetic field and exposed to electromagnetic radiation (for example, in the region of very short radio waves), molecules with the lower energy orientation absorb radiation of a frequency corresponding to an energy just sufficient to flip the odd electron into its higher energy state. This phenomenon gives rise in the simplest case to a paramagnetic-resonance absorption spectrum consisting of a single sharp absorption line.

The technique is sensitive and will detect extremely small concentrations of free radicals, as little as one part in 107 having been reported detected. In many organic free radicals, interaction of the odd electron with the magnetic moments of the nuclei of different atoms in the molecule (most commonly with hydrogen nuclei) gives rise to a more complicated system of energy levels and an absorption spectrum consisting of a series of lines. The nature of the spectrum permits the identification of particular free radicals and also gives information about their electronic structure.

Mechanism of Free Radical Polymerization

Free radical polymerization consists of three fundamental steps, initiation, propagation, and termination. Initiation, involves the formation of radicals followed by the radical's reaction with a vinyl monomer, propagation is the rapid and progressive addition of monomers to the growing polymer chain without a change of the active center, and termination is the destruction of the growth active center, usually by combination or coupling of the radicals of two growing polymer chains or by disproportionation. In addition to these three processes, chain transfer might occur, which is the transfer of the growth active site from the active chain to a inactive (dormant) one, a monomer or a solvent molecule (transfer agent).

Initiation

This step involves the generation of active species. The free radicals can be produced in a number of ways, including thermal or photochemical decomposition of organic peroxides, hydroperoxides, azo or diazo compounds. Other methods of free radical generation are high-energy radiation and oxidation-reduction (redox) reactions.

The two most common initiators (I) are benzoyl peroxide (BPO) and 2,2'-azo-bis- isobutyrylnitrile (AIBN). Both molecules have a strong tendency to fall apart into two fragments with unpaired electrons, the so-called free radical initiators:

$$I \rightarrow 2\,R\cdot$$

Following its generation, the free radical then reacts with a vinyl monomer, that is, it adds to one of the electrons of the double bond of the vinyl monomer and the remaining electron becomes the new free radical:

$$R\cdot + M \rightarrow RM\cdot$$

Thus the process of chain initiation involves two steps; the first being the decomposition of the initiator (for example, BPO or AIBN) to yield a pair of free radicals $R\cdot$, and the second the addition of a monomer to the primary radical $R\cdot$ to yield the chain radical, which is called the initiation. It was found that the rate-limiting step is the initiation step, that is, the rate constant for initiator dissociation is much smaller than that for monomer addition.

Some of the monomers may also undergo other reactions such as combination with another radical to form inactive molecules.

The efficiency of the radicals with which they initiate chains can be estimated by comparing the number of initiators decomposed with the number of polymer chains formed, that is, only a fraction f of the initiator concentration does initiate a polymerization process. Based on observations, the rate of initiation is proportional to the concentration of initiators [I] and the efficiency *f*:

$$Ri = d[M\cdot] / dt = 2\, f kd\, [I]$$

where kd is the rate constant (velocity coefficient) of initiation.

Propagation

The growth of a polymer chain by successive addition of monomers during propagation can be represented as follows:

$$RM_1\cdot + M \rightarrow RM_2\cdot$$
$$RM_2\cdot + M \rightarrow RM_3\cdot$$

And in general:

$$RMx\cdot + M \rightarrow RMx{+}1\cdot$$

The general assumption is that the radical reactivity is independent of the chain length, this means, that all the propagation steps have the same rate constant $kp_1 = kp_2 = ... = kp$. Thus, the rate of polymerization equals the consumption of monomers in the propagation step. Since both a monomer and the growing polymer chain are involved in the reaction, the reaction rate is proportional to both concentrations.

$$Rp = -d[M] / dt = kp\, [M]\, [M^*]$$

where kp is the reaction constant or velocity coefficient of the process and

$$[M^*] = \sum RMx,$$

which is the sum of the concentration of all chain radicals.

Termination

The propagation step would theoretically continue until all monomers are consumed. However, pairs of radicals also have a tendency to react with each other and thus annihilate their activities. The termination can occur via combination or disproportionation. In the case of combination or coupling, two growing polymer chains react with each other forming a single nonreactive polymer chain:

$M_x\cdot + M_y\cdot \rightarrow M_{x+y}$

And in the case of disproportionation, a hydrogen atom is transferred from one radical to the other resulting in two polymers, one with a saturated end and the other with an unsaturated end and each with an initiator fragment.

$M_x\cdot + M_y\cdot \rightarrow M_x + M_y$

Usually, there is no need to distinguish between these two different types of termination reactions, that is, both reactions can be combined to one rate expression:

$Rt = -d[M\cdot] / dt = 2\ kt\ [M\cdot]^2$

Where the factor two occurs as a result of the disappearance of two radicals at each incidence of termination reaction.

The rate of radical polymerization reaction usually increases with rising temperature. The variation in temperature also effects the structure of the resulting products. To illustrate— the rise in temperature during the polymerization of butadiene causes ring dimer to form instead of chain molecules. That is why butadiene is always polymerized below 60ºC. The size and structure of the polymer chain depends upon the temperature. It has been established that low temperature favours formation of higher molecular mass polymer in most of the cases.

Raising the temperature increases the degree of branching of a polymer.

Effect of Pressure

Pressure changes also have a marked effect on the rate of a polymerization. If pressure is increased this would result in increase in the number of collisions between the active centres and the monomers. Hence, the rate of polymerization will considerably be increased. Further, the increase in pressure enable a lower temperature of polymerization and hence the production of polymers with higher molecular masses. For example, butadiene polymerization takes 45 hours at 7000 atm and 48ºC, and only 19 hours at the same pressure and 61ºC, but at 1 atm it takes hundred of days.

Effect of Catalyst

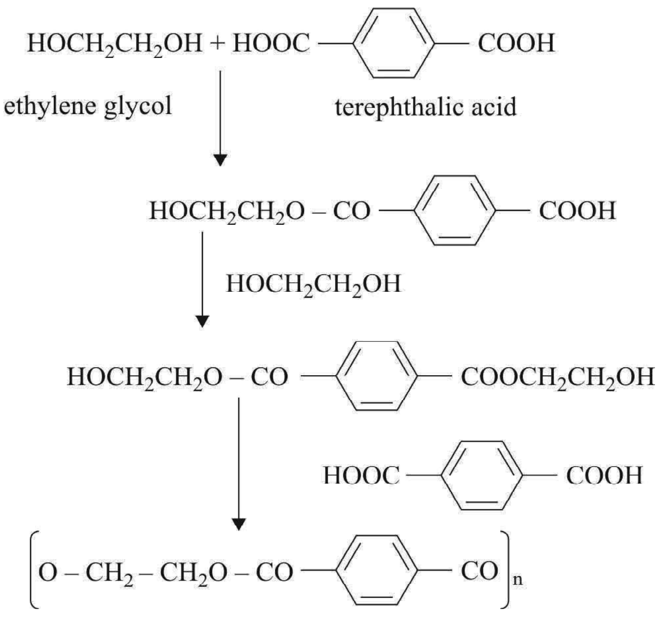
Catalyst plays a vital role in the chain polymerization. Ionic polymerizations always require a catalyst. In the presence of catalyst, the polymerization can be affected at low pressure. The use of elevated pressure for polymerization should always be considered in conjunction with the choice of a catalyst. To illustrate polyethylene, which could be produced formerly only at a pressure of 1000–2000 atm (high pressure polyethene), can now be obtained by the Ziegler method involving the use of triethyl aluminium and titanium chlorides as catalysts at a low pressure (low-pressure polyethene).

Cationic and Anionic Polymerization

Butene undergoes polymerization under the influence of various reagents but the product is not very satisfactory as a rubber substitute. Styrene is an aromatic compound which on polymerisation gives polystyrene. Ordinary glass has the weakness of being brittle. The development of clear transparent high polymers is certainly one of the may achievements in polymer chemistry. Methyl methacrylate readily polymerises yielding a clear transparent glass. This polymer, which is sold under trade names such as plexiglas and lucite may be made into sheets or various articles as desired. The injection molding process by which the polymer is forced under pressure into a mold is widely used with this polymer. Methyl methacrylate is used for transparent parts of airplanes.

Terephthalic acid combines with ethylene glycol which on condensation forms a polymer molecule known as dacron.

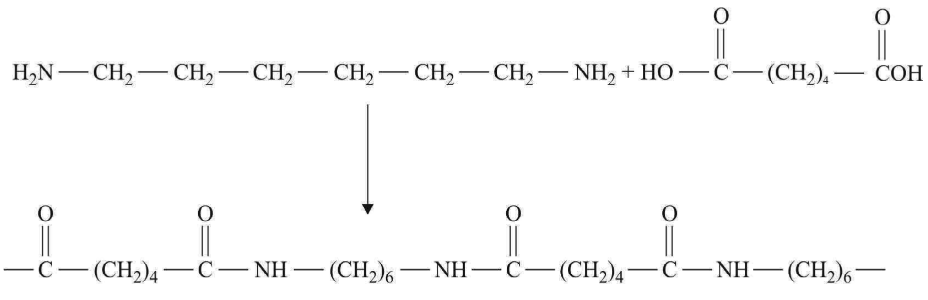
The reactions can be symbolized as under:



Dacron

The polymer is called polyethylene terephthalate and is sold by the trade name of dacron.

Nylon can be prepared by condensing hexamethylene diamine with adipic acid.



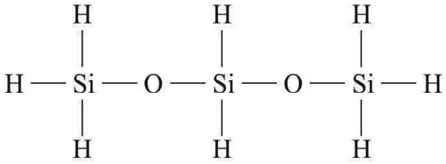
$$H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2+HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}OH$$

$$\downarrow$$

$$-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-$$

Nylon-66

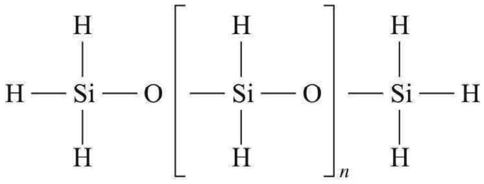
Organisilicon Polymers: Silicon is directly below carbon in the periodic table, but the chief interest in silicon has been with respect to natural silicates in silica and in glasses. The fact that silicon forms hydrides of the type $Si_n H_{2n+2}$. Silicon consists of very large groups silicon atoms joined together through an oxygen atom. The linkage –Si–O–Si–O–Si– seems to be very stable compounds in which the silicon-oxygen bond occurs and in which the remaining valences are filled by hydrogens are called siloxanes.



$$\mathrm{H-\underset{H}{\overset{H}{Si}}-O-\underset{H}{\overset{H}{Si}}-O-\underset{H}{\overset{H}{Si}}-H}$$

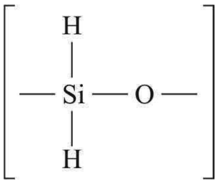
Siloxanes

Such molecules are quite large with many silicon atoms. These compounds are called polysiloxanes.



$$\mathrm{H-\underset{H}{\overset{H}{Si}}-O\left[-\underset{H}{\overset{H}{Si}}-O\right]_{n}-\underset{H}{\overset{H}{Si}}-H}$$

Polysiloxanes

The recurring unit in polysiloxane is  $\mathrm{\left[-\underset{H}{\overset{H}{Si}}-O-\right]}$ when the hydrogen atoms are replaced by alkyl groups a typical organosilicon polymer is obtained. Different organosilicon polymers are possible depending upon the choice of alkyl or aryl groups and on the extent of cross-linking between the chains.

Most of the organosilicon polymers are oils and remain liquid at very low temperatures and there is very small variation in viscosities with temperature and are used as lubricants. Those silicones with extensive cross linking are solids. One of the most important applications of organosilicones is as electrical insulating paste for use as spark plug terminals for aircraft. The silicones do not burn and can stand unusually high temperatures. Some organosilicones are used for making surfaces water repellant.

Ionic Polymerization

Chain reaction polymerization can occur by several mechanisms other than those involving free radicals as discussed earlier. The most important among these are the reactions in which the chain carriers are carbonium ions (cationic polymerization) or carbanions (anionic polymerization). Ionic polymerization proceeds in the presence of catalysts and is also called catalytic polymerisation. The reactivity of the ethenic monomers to polymerization by radicals, ions and complexing agents varies with the structure in a manner which can be correlated though not always quantitatively predicated. It can be seen that, for the vinyl monomer (CH_2=CH–X), cationic initiation is favoured when *X* is electron releasing and anionic when X

NOTES

is electron-withdrawing. This is because monomers with electron releasing groups attached to the double-bonded carbons are capable of forming stable carbonium ions, where as monomers with electron with-drawing substituents form stable carbanions. Ionic polymerizations tend to be very rapid even at low temperatures. The polymerization of isobutylene with $AlCl_3$ or BF_3 is carried out commercially at —100ºC and an estimate of the life-time of a growing chain of isobutylene in this case is about 10^{-6} sec, much shorter than the usual life time of a free-radical chain.

1. **Cationic or Carbonium Polymerization:** This involves the formation of a carbonium ion which is a polar compound with tricovalent carbon atom carrying a positive charge, R–CH–R. Typical catalysts for cationic polymerization are compounds with pronounced electron acceptor properties (Lewis acids), for example, $AlCl_3$, $AlBr_3$, $SnCl_4$, BF_3, H_2SO_4 and other strong acids. The cationic polymerization, involves the carbonium ion as the chain carrier. Carbonium ion ineracts with a monomer molecule, the reaction of chain growth being accompanied with the communication of positive charge along the chain. Consequently, the growing chain itself is a cation with a molecular mass increasing in the course of polymerization. For example, the polymerization of isobutylene in the presence of boron trifluoride catalyst can be represented as:

$$BF_3 + H_2O \rightleftharpoons H^+ (BF_3OH)^-$$

Catalyst-cocatalyst
complex

The catalyst-cocatalyst complex formed in step (I) donates a proton to an isobutylene molecule to give carbonium ion.

$$H^+ + (CH_3)_2\,C = CH_2 \longrightarrow (CH_3)_3C^+$$

(from complex)

$$(CH_3)_3\overset{+}{C} + (CH_3)_2C = CH_2 \dashrightarrow (CH_3)_3\,C — CH_2 — \overset{+}{C}(CH_3)_2$$

$$(CH_3)_3\,C — CH_2 — \overset{+}{C}(CH_3)_2 + (CH_3)_2\,C = CH_2 \dashrightarrow$$

$$(CH_3)_3\,C — CH_2C\,(CH_3)_2 —CH_2 — \overset{+}{C}\,(CH_3)_2$$

Thus, there is reformation of a carbonium ion at the end of each step by the 'head-to-tail' addition of monomer to ion.

Chain termination apparently occurs as a result of the mutual collision of the ends of growing ion to yield a polymer molecule with terminal unsaturation and the original complex

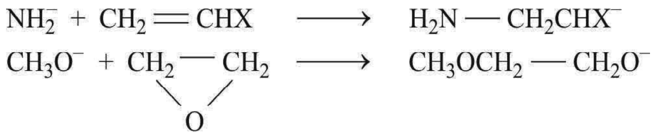
$$(CH_3)_3\;C — CH_2 — C\,(CH_3)_2 — CH_2 — \overset{+}{C}\,\underset{+}{(CH_3)_2} + (BF_3OH)^-$$

$$\underbrace{(CH_3)_3\,C-CH_2-C(CH_3)_2-CH_2-C(CH_3)=CH_2}_{\text{Polymer}} + \underbrace{H^+\,(BF_3OH)^-}_{\text{Catalyst-co-catalyst complex}}$$

NOTES

The third component present in low concentration which usually has pronounced effects on polymerization is called cocatalyst. The efficiency of the catalyst is dependent on the acid strength of the catalyst-cocatalyst complex. In cationic polymerization, the catalyst is not in the macromolecule.

2. **Anionic or Carbanion Polymerization:** Anionic polymerization involves the formation of a carbanion, a compound with a trivalent carbon atom carrying a negative charge. Catalyst for carbanion polymerization include, alkali metals, alkali metal amides, alkoxides, alkyls, aryls, hydroxides and cyanides. They are electron releasing groups. Polymerization occur by the carbanion mechanism in the case of monomers containing electronegative substituents at one of the carbon atoms connected by a double bond. The initiation of ionic chains involves the addition of a negative ion to the monomers, with the opening of a ring or bond and growth at one end

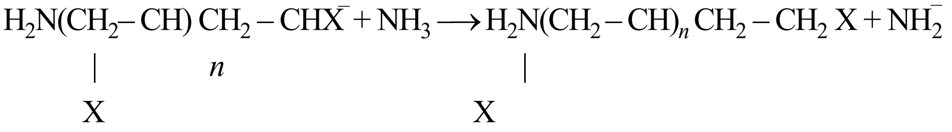


$$NH_2^- + CH_2{=}CHX \longrightarrow H_2N-CH_2CHX^-$$
$$CH_3O^- + \underset{\diagdown\ O\ \diagup}{CH_2-CH_2} \longrightarrow CH_3OCH_2-CH_2O^-$$

The more basic the ion (anion), the better it serves to initiate chains. Thus, $C_6H_5\,CH_2$- is powerful initiator than $\propto H_2^-$ which is stronger than OH^- in the anionic polymerization of styrene.

The chain growth reaction is always accompanied with a transfer of a negative charge along the chain, consequently, the growing chain is always an anion of growing size.

Chain termination occurs as a result of the collision of a growing ion with a molecule of the medium, such as an ammonia molecule:



$$H_2N(CH_2-\underset{\underset{X}{|}}{CH})_n\,CH_2-CHX^- + NH_3 \longrightarrow H_2N(CH_2-\underset{\underset{X}{|}}{CH})_n\,CH_2-CH_2\,X + NH_2^-$$

Thus, energy growing chain contains the $-NH_2$ group. The termination step is always unimolecular and usually be transfer.

It anionic polymerization, the end group of a growing molecule possesses high activity and great stability. Hence, the polymers obtained by anionic polymerization method retain active centres at the end of the chain, which are capable of initiation the polymerization of monomers. Such polymers are called living polymers. The polymer can be 'killed' by addition of a terminating agent, like water at the end of the reaction. Anionic polymerization has great advantages, since spontaneous chain termination does not occur.

4.4.2 Electrical Conducting and Fire Resistance Polymer

They can provide high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be perfectly adjusted using the methods of organic synthesis and by advanced dispersion techniques.

Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colourless but the oxidized forms were of deep blue colour.

The first highly-conductive organic compounds were the charge transfer complexes. There are evidences that the polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens. Organic Light-Emitting Diodes (OLEDs) are the significant application of conducting polymers.

Figure 4.28 illustrates the chemical structures of some conductive polymers. Starting from top left they are clockwise named as Polyacetylene, Polyphenylene Vinylene, Polypyrrole (X = NH) and Polythiophene (X = S), and Polypyrrole (X = NH) and Polyphenylene Sulfide (X = S).

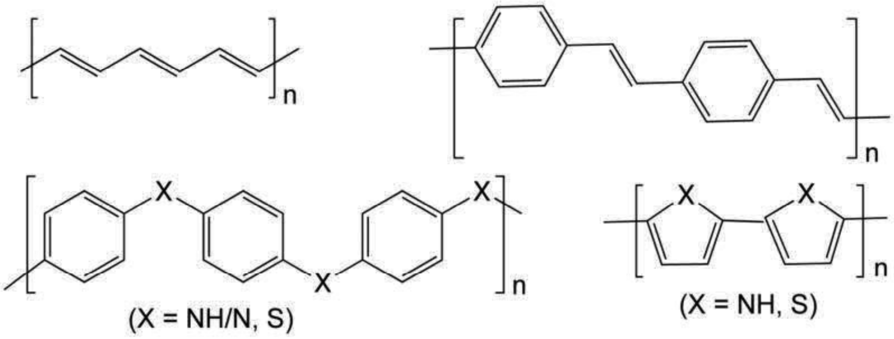


Fig. 4.28 *Chemical Structures of Some Conductive Polymers*

Types of Conductive Polymers

Linear backbone 'Polymer Blacks' typically includes polyacetylene, polypyrrole, polyindole and polyaniline, and their copolymers which form the main class of conductive polymers. Poly(P-Phenylene Vinylene) or PPV and its soluble derivatives have been developed as the prototypical electroluminescent semiconducting polymers. These days, poly(3-alkylthiophenes) are considered as the archetypical materials for solar cells and transistors.

Table 4.6 shows some organic conductive polymers according to their composition.

NOTES

Table 4.6 *Some Organic Conductive Polymers*

Main Chain Contains	Heteroatoms Present		
	No Heteroatom	**Nitrogen-Containing**	**Sulfur-Containing**
Aromatic Cycles	• Poly(Fluorene)s • *Poly*phenylenes • *Poly*pyrenes • *Poly*azulenes • *Poly*naphthalenes	The N is in the Aromatic Cycle: • **Poly(Pyrrole)s (PPY)** • *Poly*carbazoles • *Poly*indoles • *Poly*azepines The N is Outside the Aromatic Cycle: • **Polyanilines (PANI)**	The S is in the Aromatic Cycle: • **Poly(Thiophene)s (P)** • **Poly(3,4-Ethylenedioxythioph ne) (PEDOT)** The S is outside the Aromatic Cycle: • **Poly(P-Phenylene Sulfide) (PPS)**
Double Bonds	• **Poly(Acetylene)s (PAC)**		
Aromatic Cycles and Double Bonds	• **Poly(P-Phenylene Vinylene) (PPV)**		

Synthesis of Conductive Polymers

Conductive polymers are prepared using various methods. Most of the conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation as shown below:

$$n\ \mathrm{H} - [\mathrm{X}] - \mathrm{H} \rightarrow \mathrm{H} - [\mathrm{X}]_n - \mathrm{H} + 2(n-1)\ \mathrm{H}^+ + 2(n-1)\ \mathrm{e}^-$$

The low solubility of most polymers show unique behaviour. At times the solubilizing functional groups are added to some or all monomers to increase solubility. Some conductive polymers exhibit the formation of nanostructures and surfactant-stabilized conducting polymer dispersions in water, such as polyaniline nanofibers. In numerous situations, the molecular weight of conductive polymers are lower than conventional polymers, such as polyethylene. However, in some situations the molecular weight must not be high in order to achieve the desired properties.

There are two main methods used in the synthesis of conductive polymers, namely the chemical synthesis method and the electro (co)polymerization method. The chemical synthesis defines the connecting carbon-carbon bond of monomers by placing the simple monomers under various conditions, such as heating, pressing, light exposure and catalyst. The advantage is high yield. However, there are many impurities plausible in the end product. The electro (co)polymerization specifies that the three electrodes (reference electrode, counter electrode and working electrode) are inserted into solution including reactors or monomers. When the voltage is applied to electrodes then the redox reaction takes place to synthesize polymer. Electro (co)polymerization method can also be divided into 'Cyclic Voltammetry' and 'Potentiostatic' methods in which the cyclic voltage and constant voltage are applied. The advantage of electro (co)polymerization method is that it ensures high purity of products. But this method can only synthesize a few products at a time.

Applications of Conductive Polymers

Following are some applications of conductive polymers:

- Provide electromagnetic shielding of electronic circuits.
- Used as antistatic coating material to prevent electrical discharge exposure on photographic emulsions.
- Used as hole injecting electrodes for OLEDs (Organic Light Emitting Devices).
- Used in electroluminescent displays (mobile telephones).
- Used as emissive layer in full-colour video matrix displays.
- Capable for FETs (Field-Effect Transistors).
- Capable of absorbing microwaves, the stealth technique.

Polymer Electrolyte and Fire Retardant Polymer

Polymer electrolytes or gel-type polymer electrolytes are the alternatives to substitute liquid electrolytes in Dye-Sensitized Solar Cells (DSSCs). A polymer electrolyte is also referred to as a solid solvent that possesses ion transport properties similar to that of the common liquid ionic solution. It usually comprises a polymer matrix and electrolyte, wherein the electrolyte, such as a lithium salt dissolves in a polymer matrix. The polymer electrolytes are complexes of alkali metal salts (MX), with polymers as the host matrix.

Properties of Polymer Electrolyte

Following are the properties of polymer electrolyte:

- Adequate conductivity for practical purposes
- Low electronic conductivity
- Good mechanical properties
- High chemical, electrochemical and photochemical stability
- Ease of processing

Fundamentals of Polymer Electrolyte

Following are the fundamental types of polymer electrolyte:

1. **Solvent (Liquid) Free System:** This ionically conducting phase is formed by dissolving salts in polymer.
2. **Gel Electrolyte:** This is formed by dissolving salt in polar liquid and adding inactive polymeric material.

3. **Plasticized Electrolyte:** This is fundamentally a gel electrolyte but is typically associated with the addition of small amounts of a high dielectric constant solvent which enhances its conductivity.
4. **Ionic Rubber:** The ionic rubber is a liquid electrolyte which comprises of a low temperature molten salt mixture and then reduced to a rubbery condition by addition of a small amount of high M_w polymer.

Electrically Conducting Solution of a Salt in a Polymer Electrolyte

The most common example of a solid polymer electrolyte is a solution of a lithium salt in a poly(oxyethylene) matrix. The ionic conductivity is because of the mobility of lithium cations and their counter ions in an electric field. Both the terms solid polymer electrolyte and polymeric electrolyte are different and one should not be confused with the terms.

Fire Retardant Polymer

Fire safe polymers are particular type of polymers that are resistant to degradation at high temperatures. The fire resistant polymers are essentially required in the construction of small, enclosed spaces, such as skyscrapers, boats, and airplane cabins. In these tight spaces, ability to escape in the event of a fire is compromised, increasing fire risk. Fire safe polymers also have application as adhesives in aerospace materials, insulation for electronics, and in military materials, such as canvas tenting.

Some of the fire safe polymers naturally exhibit an intrinsic resistance to decomposition, while the other polymers are typically synthesized by incorporating fire resistant additives and fillers. Standard methods for testing polymer flammability is diverse in different countries.

Polymer Combustion

Traditional polymers decompose under heat and produce combustible products, thus, they are able to originate and easily propagate fire, as shown in Figure 4.28.

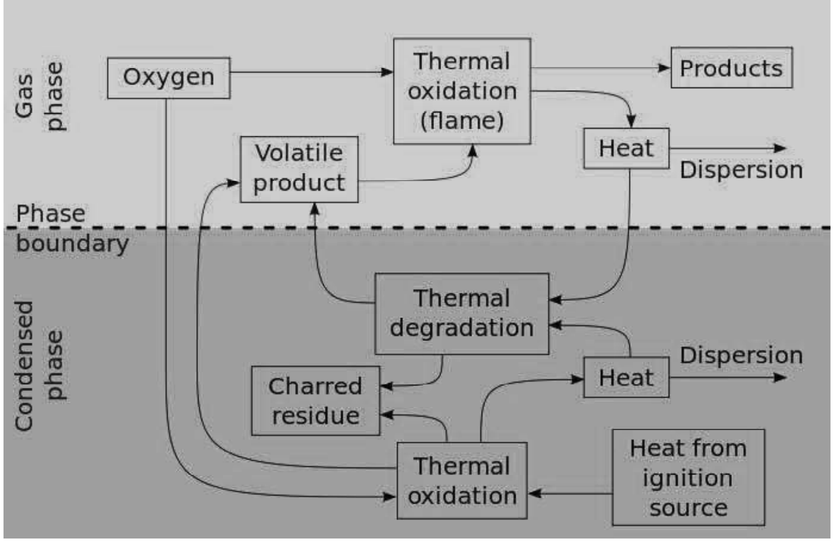


Fig. 4.28 General Scheme of Polymer Combustion

The process of combustion initiates when heating a polymer yields volatile products. If these products are sufficiently concentrated within the flammability limits and at a temperature above the ignition temperature, then combustion process continues. As long as the heat supplied to the polymer remains sufficient to sustain its thermal decomposition at a rate exceeding that required to feed the flame, combustion will continue.

Purpose and Methods of Fire-Retardant Systems

The purpose is to control heat below the critical level. To achieve this, an endothermic environment is created for producing non-combustible products, or the chemicals are added that would remove fire propagating radicals, such as H and OH, etc. These specific chemicals can be added into the polymer molecules either permanently or as additives and fillers.

Role of Oxygen: Oxygen catalyzes the pyrolysis of polymers at low concentration and initiates oxidation at high concentration. Transition concentrations are different for different polymers, for example polypropylene, between 5% and 15%. In addition, polymers exhibit a structural-dependent relationship with oxygen. Some structures are intrinsically more sensitive to decomposition upon reaction with oxygen. The amount of access that oxygen has to the surface of the polymer also plays a role in polymer combustion. Oxygen is capable to interact with the polymer before a flame has actually been ignited.

Role of Heating Rate: In most of the situations, results from a typical heating rate do not differ significantly from those obtained at higher heating rates, for example 10™/min for mechanical thermal degradation analysis. The extent of reaction can, however, be influenced by the heating rate. For example, some reactions may not occur with a low heating rate due to evaporation of the products.

Role of Pressure: Volatile products are removed more efficiently under low pressure, which means the stability of the polymer might have been compromised. Decreased pressure also slows down decomposition of high boiling products.

4.4.3 Molecular Mass and Its Determination

Since polymerization reactions of both synthetic and natural, can lead to high molecular weight compounds, the reaction chain is however broken by some termination process that usually occurs in a random manner with respect to the size, to which the polymer has already grown. It follows, therefore, that polymers possess a range of molecular weights and that any data for the size or weight of the molecules of polymer must represent some sort of average value. The molecular weights of polymers lend themselves to two types of averages, i.e., (*i*) number average molecular weights and (*ii*) weight average molecular weights.

Number average molecular weight: It is defined as the weight of the sample divided by the total number of moles n in the sample, i.e.,

$$M_n = \frac{\text{Weight}}{n}$$

If a method of molecular weight determination leads to the number of particles, or molecules; that are present, in a given weight of a sample, it will give the number average molecular weight. Let us consider a polymer as made up of fractions consisting of n_1 moles of molecular weight M_1, n_2 moles of molecular weight M_2 and so on, then M_n the number average molecular weight is given by the expression:

$$M_n = \frac{n_1 M_1 + n_2 M_2 + ...}{n_1 + n_2 ....} \qquad ...(1)$$

$$M_n = \frac{\sum_i n_1 M_i}{\sum_i n_i} \qquad ...(2)$$

On the other hand if in an experiment each particle makes a contribution to the measured result according to its molecular weight, we get *weight average molecular weight* of the polymer, M_w which is defined as,

$$M_w = \frac{\sum_i n_1 M_i^2}{\sum_i n_i M_i} \qquad ...(3)$$

Molecular weight of a polymer can be determined by relative or absolute methods. Many properties of polymers which depend upon molecular weight, such as –solubility, elasticity, absorption on solids, and their tear strength, can be corrected with an average molecular weight. Once correlated, the property can be used as a measure of molecular weight. The weight determination can be done by chemical or physical methods of functional group analysis, by measurement of the colligative properties, light scattering or ultra-centrifugation or by measurement of dilute solution viscosity. In all these methods, except the last, molecular weights can be calculated without reference to calibration by another method and therefore, are absolute methods. Dilute solution viscosity is not a direct measure of molecular weight. All molecular weight methods, except a few end group analysis methods, require solubility of the polymer and all involve extrapolation to infinite dilution of operation in a solvent in which ideal solution behaviour is attained. Some important methods used in practice for determining the molecular weight and size of macromolecules in dilute solutions are discussed below.

Degree of Polymerization

Some of the important methods employed for the determination of molecular weights of polymers are:

Osmometry

Osmometry can be used for determining molecular masses from 10^4 to 10^6. This is one of the most accurate methods, though due to its lengthy and tedious experimental procedure it cannot be frequently used for fast molecular weight determination. The method, involves the measurement of the osmotic pressure of solutions at several concentrations. The instrument used for the determination of molecular-weights by this method is called *osmometer*. In an osmometer, the solvent is separated from the solution by a semipermeable membrane. It then passes through the latter into the solution, until the level of the solution in the capillary stops rising. The osmotic pressure, at this stage, is equal to the weight of the hydrostatic column of the solution.

McMillan and Mayer showed that the osmotic pressure of non-electrolytes could be represented by a power series in the concentrations exactly like the virial equation for a non-ideal gas,

NOTES

$$\Pi = RT\left(\frac{C}{M_n} + BC^2 + DC^3 + ...\right)$$

where C is the concentration in mass per unit volume. In a fairly dilute solution of a polymer

$$\frac{\Pi}{C} = \frac{RT}{M_n} + RTBC$$

In low concentrations region a plot of $\frac{\Pi}{C}$ *vs* should give a straight line.

The capillary forces also raise the liquid in the capillary to some extent, to account for these forces a capillary having radius equal to that of osmometer capillary, is immersed in the liquid. This capillary is known as control capillary. The difference in the level of osmometer capillary and control capillary is the measure of osmotic pressure. The two more commonly used methods are:

1. **Static Method:** This method involves the measurement of the equilibrium difference of levels in the osmometer. The osmometer for this method are very simple in design, but equilibrium in such an osmometer is reached after a long time. The concentration of the solution near the membrane may increase as a result of absorption of polymer, at equilibrium. The shortcoming can be eliminated by proper production and storage of membranes. For cross linking polymers this method is usually not recommended.
2. **Dynamic Method:** This method consists of measuring the rate of penetration of solvent through the membrane, depending upon the pressure applied. The main advantage of this method is that the measurements take very less time as compared to the static method.

Choice of Membrane: A choice of suitable membrane plays an important role in osmometric measurements. The membrane should be permeable to the solvent and impermeable to the polymeric solute. It should satisfy the following two conditions:

- The membrane should not swell to any great extent in the solvent.
- It should have sufficient fine pores to allow the solvent molecules to pass through freely.

These days membranes are prepared from cellophane and specially treated films of denitrated cellulose nitrate. The untreated cellophane membranes have small pore radius and subsequently take long time to reach equilibrium. To increase the pore size, the cellophane is treated with ammonia solution or other reagents. For this reason only cellophane is generally used for measuring molecular weights of very low-molecular weight polymers. Denitrated cellulose nitrate membrancs give better and much more satisfactory results.

The polymer is first throughly freed from impurities by reprecipitation before determining the molecular-weight. A stock solution, usually 1 per cent is prepared from a purified polymer. From the stock solution, working solutions of various concentrations, varying from 0.075 per cent to 0.5 per cent are prepared by dilution. One fifth of the one per cent solution is left undiluted for exact determination of its concentration. In order to measure the osmotic pressure, a polymer solution and pure solvent are placed on the opposite sides of a semipermeable membrane. The membrane is so selected as to permit only solvent and not the polymer particles. To establish equilibrium, the pressure on the solution side must be greater. The osmotic pressure, can be measured at several concentrations either by waiting for equilibrium or by measuring and compensating for pressures automatically.

To calculate molecular weight of a polymer the osmotic pressure values obtained for the different solutions are divided by the corresponding concentrations and the resulting reduced osmotic pressures are plotted in π/C_n versus C. The straight line obtained in this way is extrapolated to zero concentration as shown in Figure 4.29. The resulting values A (intercept with the ordinate axis) is substituted in the equation given below and molecular weight is calculated.

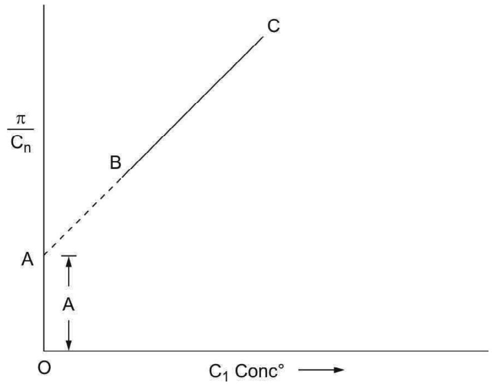


Fig. 4.29 *Variation of reduced osmotic pressure with concentration*

$$\left(\frac{\pi}{C_n}\right)_{C_n \to o} = \frac{RT}{M} \qquad ...(69)$$

or

$$M = \frac{RT}{\left(\frac{\pi}{C_n}\right)C_{n\to 0}} \qquad ...(70)$$

where, π = osmotic pressure (g/cm^2)$h\rho$

h = difference in liquid levels at equilibrium, cm

ρ = density of solvent, g/cm^3

C = concentration, g/cm^3

T = absolute temperature, K

M = molecular-weight, g/mole

R = gas constant, 8.48×10^4 g-cm/(mole) (K)

Viscometry

The first person to draw attention to the usefulness of solution viscosity as a measure of polymer molecular weight was Staudinger, who established the following relationship:

$$\eta_{sp} = KMC \qquad ...(71)$$

where, η_{sp} = specific viscosity of polymer solution

K = constant

M = molecular weight of a dissolved polymer

C = concentration of polymer in solution

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However, the above relation suffers from two serious drawbacks, first, the coefficient K does not give a constant value, but it depends on the molecular weight of a polymer and secondly, the equation represents the concentration dependence of specific viscosity incorrectly. According to the above equation, the reduced viscosity (ratio of the specific viscosity to the concentration) hsp/C, is independent of concentration.

$$\eta_{sp}/\mathrm{C} = KM \qquad ...(72)$$

But experimental data show that the η_{sp}/Cvs. C dependence is represented graphically by a straight line with a definite slope. Hence, it would be more accurate to relate molecular weight of a polymer to intrinsic (viscosity value that is independent of the solution concentration) and not to specific viscosity. Thus, Staudinger's equation can be modified by the following empirical relation,

$$[\eta] = KM^a \qquad ...(73)$$

where, $[\eta]$ = intrinsic viscosity of a solution, K and a are the constants characerizing the given polymer-solvent system.

Intrinsic viscosity is determined from the relative viscosity of the dissolved polymer solutions. Then the specific and reduced viscosities are calculated and a plot of η_{sp}/C*vs*. C is made. The extrapolation of this line to zero concentration, gives the value of $[\eta]$. K and a are calculated by plotting log $[\eta]$*vs*. log M, which represents a straight line having slope, a and intercept log K.

$$\log [\eta] = \log K + a \log M. \qquad ...(74)$$

Hence, K and a, can be determined graphically. Using the same solvent for which K and a, are determined, the viscosities can be calculated.

Owing to the simplicity of the equipment used (viscometer), this method can be very conveniently used in the laboratory.

Light Scattering

Light scattering accounts for many phenomena including the colours of the sky the rainbow, and of most white materials. A media may be transparent or turbid. The turbidity of a medium is due to scattering of light. The scattering of light occurs whenever a beam of light encounters matter. Similarly, when a polymer is dissolved in a solvent, the light scattered by the polymer far exceeds that scattered by the solvent, and is an absolute measure of molecular weight.

Debye gave a solution for the factor of internal interference $P(\theta)$ for the scattering particles of different shape. The Debye relationship is:

$$\frac{H'C}{K} = \frac{1}{MP(\theta)} + 2A_2C \qquad ...(75)$$

where H' is a lumped constant including geometric factors and also the change in refractive index with polymer concentration for the particular system being investigated. θ is the angle at which the intensity of light is measured and C is the concentration. A_2, second virial coefficient and $P(\theta)$ (function of molecular shape) are derived from data. The light intensity factor K is derived from the galvanometer reading I_g. The geometry and the scattering by solvent I_{gs} is compensated by

$$K = \frac{(I_g - I_{gs})\sin\theta}{1 + \cos^2\theta} \qquad ...(76)$$

since at $\theta = 0$, $P(\theta) = 1$, it is customary to extrapolate to $v = 0$ as well as $C = 0$. A plot of $\frac{H'C}{K}$ *vs* C constant θ and $\frac{1}{MP(\theta)}$ *vs*. $\sin^2(\theta/2)$ give intercept $1/M$. In Zimm plot, both can be done simultaneously where a net work is obtained. This method is more precise and makes it possible to calculate the values of molecular masses of polymers without assumption of the shape of macromolecules in a solution.

The presence of dust particles or gelled polymer particles cause a major practical problem in light scattering. A small concentration of these, obscures the scattering by ordinary polymer particles and result in $\bar{M}_w = \infty$. The removal of dust can be done by ultra centrifugation.

4.4.4 Chain Configuration of Macromolecules

The reactions by which complex macromolecules are formed are not completely understood. The process of building up polymers from simple repeating units (monomers) can proceed with many variations. As noted earlier, on the basis of mechanisms the two types of polymers are formed. Condensation polymers are usually formed by the step-wise intermolecular condensation of the reactive groups, addition polymers ordinarily result from chain reactions involving some sort of active centres.

Stepwise Polymerization

Most of the stepwise polymerizations are, stoichometrically, condensation polymerization. A monomer can be converted into polymer by any reaction that creates new bonds. Carother's defined this number of new-bonds as the functionality of a monomer in a given reaction. As the number of bonds formed depends upon the number of reactive functional groups, the *functionality* of a monomer can also be defined as the average number of reactive functional group per molecule. In a condensation reaction, the type of the product formed is determined by the functionality of the monomer. It should be obvious that a monofunctional monomer gives only a low-molecular-weight product. A functionality too can lead to linear structure. Polyfunctional monomer, with more than two functional groups per molecule, give branched or cross-linked (three-dimensional) polymers. The linear and the three-dimensional polymers differ widely in their properties.

The most important reaction which has been used for the preparation of condensation polymers is that addition and elimination at the carbonyl double bond of carboxylic acids and their derivatives. The generalized reaction is

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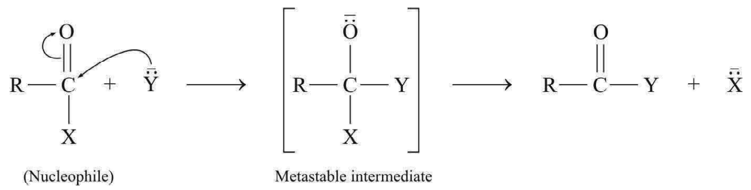
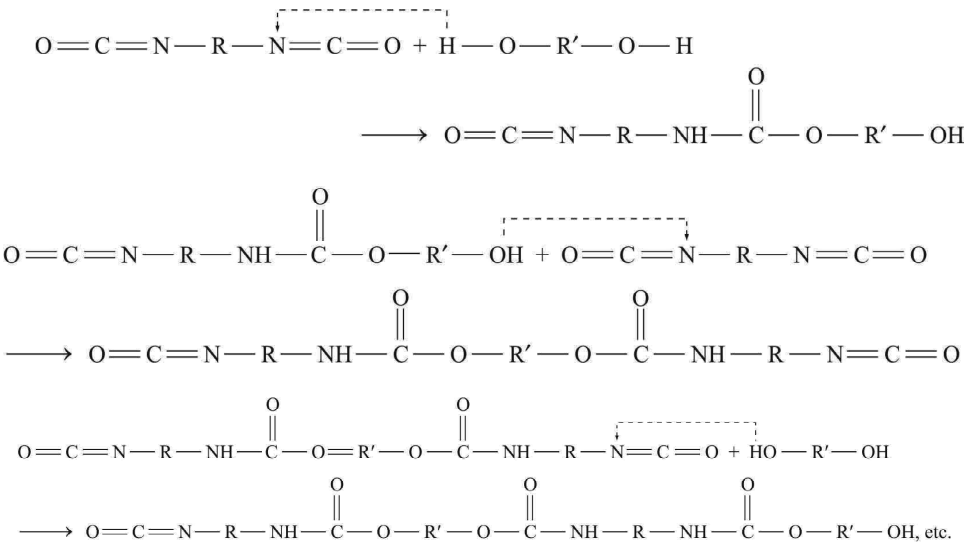


$$R{-}\overset{\overset{O}{\|}}{\underset{\underset{X}{|}}{C}} + \ddot{Y} \longrightarrow \left[R{-}\overset{\overset{\bar{\ddot{O}}}{|}}{\underset{\underset{X}{|}}{C}}{-}Y\right] \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}Y + \ddot{X}$$

where R may be alkyl or aryl group, *X* may be OH, OR′, NH_2. NHR, O—$\overset{\overset{O}{|}}{C}$—R, or Cl; and Y may be R′O–, R′OH, R′NH_2 or R′COO^-. The metastable intermediate can either return to the original state by Y or proceed to the final state by eliminating X. The formation of polymers, polyamides, nylon—66 poly (ethylene terephathalate), polyurethanes, polyureas, polysulphonamides, polyphenyl esters, etc. provides some typical examples of this reaction.

In simple terms, it can be stated that stepwise polymerization is the combination of several molecules by stepwise addition of the monomer molecules to one another as a result of migration of some mobile atom, usually a hydrogen atom, from one molecule to another. The formation of polyurethanes from di-isocyanates and dihydric alcohols is illustrated below:

A trihydric alcohol will give a cross-linked polymer.



$$O{=}C{=}N{-}R{-}N{=}C{=}O + H{-}O{-}R'{-}O{-}H$$

$$\longrightarrow O{=}C{=}N{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}OH$$

$$O{=}C{=}N{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}OH + O{=}C{=}N{-}R{-}N{=}C{=}O$$

$$\longrightarrow O{=}C{=}N{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}N{=}C{=}O$$

$$O{=}C{=}N{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{=}R'{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}N{=}C{=}O + HO{-}R'{-}OH$$

$$\longrightarrow O{=}C{=}N{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}OH, \text{etc.}$$

(A linear polymer)

Chain Polymerization

Chain polymerization is characteristic of unsaturated monomers. Ethenic polymerization is an economically important class whose kinetics typify chain polymerization. The terms 'vinyl', 'olefin' or 'addition' polymerization are often used, although they are more restrictive. Flory showed conclusively that chain polymerization proceeds by and requires the steps of interaction, propagation, and termination typical of chain reactions in low-molecular-weight species. The three stages which are essential to the formation of a high polymer can be represented as:

1. **Initiation:** This involves the creation of an 'active' centre, and can also be termed as activation of the monomer molecule, i.e.,

$$M \rightarrow M^*$$

(Excited monomer molecule or active centre)

2. **Propagation:** Propagation involves the addition of more monomer species to the chain end. This occurs usually very rapidly (mol. wt. 10^7 in one-tenth of a second) to final molecular weight value, as shown below.

$$\mathrm{M^* + M \rightarrow M_1^*}$$
$$\mathrm{M_1^* + M \rightarrow M_2^*}$$
$$\mathrm{M_2^* + M \rightarrow M_3^*}$$

....

....

....

$M_{n-1}^* + M \rightarrow M_n^*$ (Activated growing polymer molecule)

3. **Termination:** In this step there is disappearance of the 'active' centre

$M_n^* \rightarrow M_n$ (Inactivated polymer molecule)

The active centre in chain polymerization reactions may be a free radical or an ion, and the reaction is one of radical or ionic polymerization, respectively.

Radical Polymerization

The intermediates having an odd number of electrons (an unpaired electron) are known as free radicals. They can be generated in a number of ways, including thermal decomposition of peroxides or hydroperoxides; photolytic decomposition of covalently bonded compounds; dissociation of covalent bonds by high energy radiation (α-, β-, γ-rays); oxidation reduction reactions; and electrochemical interaction. However, the stability of the free radicals varies widely. Tertiary radicals are more stable and less reactive than secondary radicals, which are in turn more stable and less reactive than the primary ones. The benzyl radical is less reactive than phenyl radical, the allyl is quite stable and is quite unreactive.

1. **Initiation:** Once the primary free radicals (free radicals produced in the first stage) are produced by physical or chemical effects in the presence of a vinyl monomer (CH_2=CHX), the radical adds to the ethylenic double bond of an unexcited monomer molecule with the regeneration of another radical. If the radical formed by decomposition of initiator *R–R* is designated *R*.

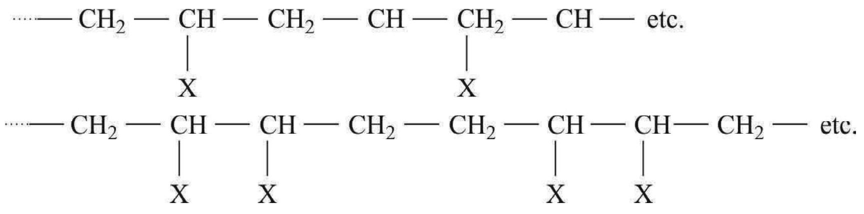
$$R - R \xrightarrow{\text{decomposition}} 2R \quad \text{(Primary free radical)}$$

$$\mathrm{CH_2{=}CHX} + R. \xrightarrow{\hspace{2em}} \mathrm{RCH_2CH.}—X \quad \text{(chain radical)}$$

The regeneration of the new radical is characteristic of chain reactions as this is capable of further interaction with the initial monomers. The efficiency with which radicals initiate can be estimated by comparing the amount of initiator decomposed with the number of polymer chains formed. Most initiator in vinyl polymerisations have 60–100 per cent efficiency. The low efficiency is mainly due to the recombination of the radical pairs before they move apart, this is known as the *cage-effect*.

2. **Propagation:** The chain radical formed in the initiation step is capable of adding successive monomers to from macroradicals. The chain propagation

reaction determines the rate of the polymerization, the molecular mass of polymer, the structure of the polymer chain, i.e., the mode of monomer addition ('head-to-head' or head-to-tail)*, the degree of branching, etc.



$$\cdots - CH_2 - \underset{X}{CH} - CH_2 - CH - \underset{X}{CH_2} - CH - \text{etc.}$$

$$\cdots - CH_2 - \underset{X}{CH} - \underset{X}{CH} - CH_2 - CH_2 - \underset{X}{CH} - \underset{X}{CH} - CH_2 - \text{etc.}$$

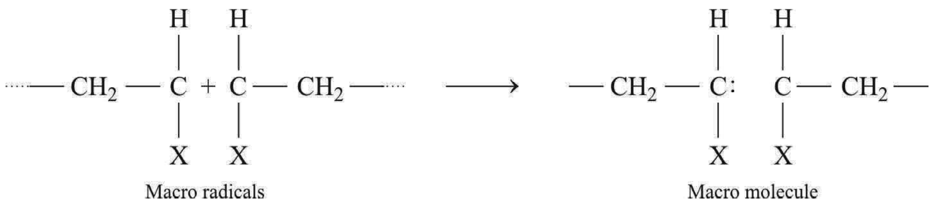
Addition according to the former scheme is called head-to-tail, configuration in which the substituents occur on alternate carbon, atoms, and that according to the latter scheme head-to-head or tail-to-tail In most polymerizations, monomers combine according to most favoured (steric factors) head-to-tail scheme.

The propagation step is given by following reaction:

$$R(CH_2–CHX)n\ CH_2–X + CH_2–CHX \rightarrow$$
$$R(CH_2–CHX)_{n+1}\ CH_2 – CHX$$
$$\text{Macro Radical}$$

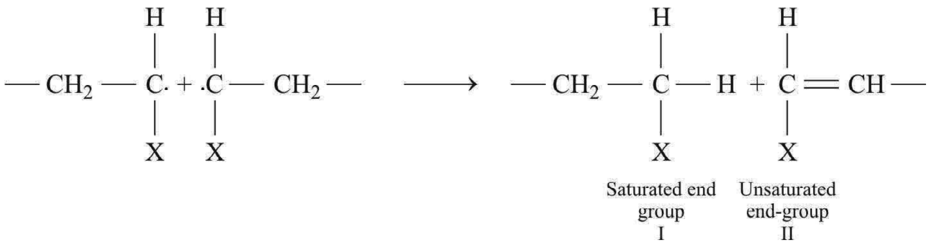
3. **Termination:** Propagation would continue until the supply of monomer is exhausted. The radicals also have the strong tendency to react in pairs to form a paired-electron convalent bond causing thereby loss of activity. In fee radical polymerzation, this tendency is compensated by the small concentration of radical species compared to monomers. Chain termination results from saturation (deactivation) of the macroradical and may occur in two ways:

(*i*) **Combination or Coupling:** Combination consists in the neutral saturation of two macroradicals or of a macroradical and a low molecular weight free radical:



$$\cdots - CH_2 - \underset{X}{\overset{H}{C}} + \underset{X}{\overset{H}{C}} - CH_2 - \cdots \longrightarrow - CH_2 - \underset{X}{\overset{H}{C}}: \ \underset{X}{\overset{H}{C}} - CH_2 -$$

(*ii*) **Disproportionation:** This involves the transfer of a hydrogen atom from one macroradical to another to form two macromolecules with one saturated and one unsaturated end group.



$$- CH_2 - \underset{X}{\overset{H}{C}}\cdot + \cdot\underset{X}{\overset{H}{C}} - CH_2 - \longrightarrow - CH_2 - \underset{X}{\overset{H}{C}} - H + \underset{X}{\overset{H}{C}} = CH -$$

Chemical substances capable of reacting with free radicals to terminate the reaction chain are called polymerization *inhibitors*, for example–

hydroquinone and trinitrobenzene. Chemical compounds which are only chain transfer agents and do not affect the rate of polymerization but determine the molecular mass of polymer are termed as polymerization regulators or modifiers.

Ionic Polymerization

Chain reaction polymerization can occur by several mechanisms other than those involving free radicals as discussed earlier. The most important among these are the reactions in which the chain carriers are carbonium ions (cationic polymerization) or carbanions (anionic polymerization). Ionic polymerization proceeds in the presence of catalysts and is also called catalytic polymerisation. The reactivity of the ethenic monomers to polymerization by radicals, ions and complexing agents varies with the structure in a manner which can be correlated though not always quantitatively predicated. It can be seen that, for the vinyl monomer (CH_2=CH–X), cationic initiation is favoured when *X* is electron releasing and anionic when X is electron-withdrawing. This is because monomers with electron releasing groups attached to the double-bonded carbons are capable of forming stable carbonium ions, where as monomers with electron with-drawing substituents form stable carbanions. Ionic polymerizations tend to be very rapid even at low temperatures. The polymerization of isobutylene with $AlCl_3$ or BF_3 is carried out commercially at —100ºC and an estimate of the life-time of a growing chain of isobutylene in this case is about 10^{-6} sec, much shorter than the usual life time of a free-radical chain.

1. **Cationic or Carbonium Polymerization:** This involves the formation of a carbonium ion which is a polar compound with tricovalent carbon atom carrying a positive charge, R–CH–R. Typical catalysts for cationic polymerization are compounds with pronounced electron acceptor properties (Lewis acids), for example, $AlCl_3$, $AlBr_3$, $SnCl_4$, BF_3, H_2SO_4 and other strong acids. The cationic polymerization, involves the carbonium ion as the chain carrier. Carbonium ion ineracts with a monomer molecule, the reaction of chain growth being accompanied with the communication of positive charge along the chain. Consequently, the growing chain itself is a cation with a molecular mass increasing in the course of polymerization. For example, the polymerization of isobutylene in the presence of boron trifluoride catalyst can be represented as:

$$BF_3 + H_2O \rightleftharpoons H^+ (BF_3OH)^-$$

Catalyst-cocatalyst
complex

The catalyst-cocatalyst complex formed in step (I) donates a proton to an isobutylene molecule to give carbonium ion.

$$H^+ + (CH_3)_2\,C = CH_2 \longrightarrow (CH_3)_3C^+$$

(from complex)

$$(CH_3)_3\overset{+}{C} + (CH_3)_2C = CH_2 \longrightarrow (CH_3)_3\,C — CH_2 — \overset{+}{C}(CH_3)_2$$

$$(CH_3)_3\,C — CH_2 — \overset{+}{C}(CH_3)_2 + (CH_3)_2\,C = CH_2 \dashrightarrow$$

NOTES

$$(CH_3)_3\,C — CH_2C\,(CH_3)_2 — CH_2 — \overset{+}{C}\,(CH_3)_2$$

Thus, there is reformation of a carbonium ion at the end of each step by the 'head-to-tail' addition of monomer to ion.

Chain termination apparently occurs as a result of the mutual collision of the ends of growing ion to yield a polymer molecule with terminal unsaturation and the original complex

$$(CH_3)_3\;C — CH_2 — C\,(CH_3)_2 — CH_2 — \overset{+}{C}\,(CH_3)_2 + (BF_3OH)^-$$

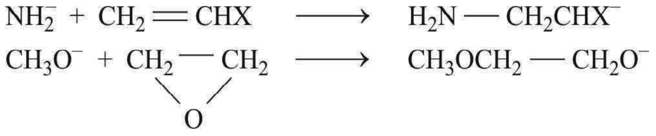
$$+$$

$$(CH_3)_3\,C — CH_2 — C(CH_3)_2 — CH_2 — C(CH_3) = CH_2 + H^+\,(BF_3OH)^-$$

Polymer $\xleftrightarrow{\text{Catalyst-co-catalyst complex}}$

The third component present in low concentration which usually has pronounced effects on polymerization is called cocatalyst. The efficiency of the catalyst is dependent on the acid strength of the catalyst-cocatalyst complex. In cationic polymerization, the catalyst is not in the macromolecule.

2. **Anionic or Carbanion Polymerization:** Anionic polymerization involves the formation of a carbanion, a compound with a trivalent carbon atom carrying a negative charge. Catalyst for carbanion polymerization include, alkali metals, alkali metal amides, alkoxides, alkyls, aryls, hydroxides and cyanides. They are electron releasing groups. Polymerization occur by the carbanion mechanism in the case of monomers containing electronegative substituents at one of the carbon atoms connected by a double bond. The initiation of ionic chains involves the addition of a negative ion to the monomers, with the opening of a ring or bond and growth at one end

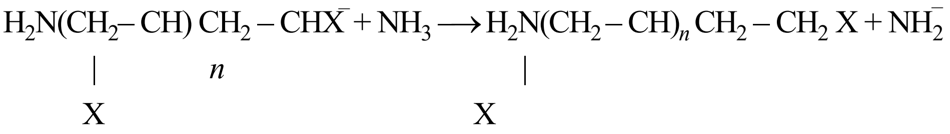


$$NH_2^- + CH_2 = CHX \longrightarrow H_2N — CH_2CHX^-$$

The more basic the ion (anion), the better it serves to initiate chains. Thus, $C_6H_5\,CH_2$- is powerful initiator than $\propto H_2^-$ which is stronger than OH^- in the anionic polymerization of styrene.

The chain growth reaction is always accompanied with a transfer of a negative charge along the chain, consequently, the growing chain is always an anion of growing size.

Chain termination occurs as a result of the collision of a growing ion with a molecule of the medium, such as an ammonia molecule:



$$H_2N(CH_2 – \underset{X}{CH})_n\, CH_2 – CHX^- + NH_3 \longrightarrow H_2N(CH_2 – \underset{X}{CH})_n\, CH_2 – CH_2\, X + NH_2^-$$

Thus, energy growing chain contains the $-NH_2$ group. The termination step is always unimolecular and usually be transfer.

It anionic polymerization, the end group of a growing molecule possesses high activity and great stability. Hence, the polymers obtained by anionic polymerization method retain active centres at the end of the chain, which are capable of initiation the polymerization of monomers. Such polymers are called living polymers. The polymer can be 'killed' by addition of a terminating agent, like water at the end of the reaction. Anionic polymerization has great advantages, since spontaneous chain termination does not occur.

Check Your Progress

21. What is polymerization?
22. What do you understand by organic polymer?
23. Give the properties of polymer electrolyte.

4.5 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The substance on which the adsorption takes place is known as the *adsorbent* and the substance which is adsorbed in known as *adsorbate*.
2. In chemisorption adsorption occurs by chemical force and a chemical bond is formed between the adsorbed molecule and the surface. Chemisorption is thus highly selective since only certain types of molecules will be adsorbed by a particular solid.
3. To show the variation of the amount of gas adsorbed per unit mass of the adsorbent with pressure at constant temperature, Freundlich suggested an empirical equation which is known as Freundlich's adsorption isotherm. The equation is

$$\frac{x}{m} = KP^{1/\mathrm{m}}$$

   where x is the mass of gas adsorbed, m the mass adsorbent, p is the equilibrium pressure and k and n are constants which depend on the nature of the adsorbate and adsorbent and on the temperature. This equation is applicable only at low pressures.
4. Temkin adsorption isotherm model contains a factor that explicitly taking into the account of adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than in logarithmic manner with the coverage.
5. The surface area of a solid object is a measure of the total area that the surface of the object occupies. The mathematical definition of surface area in the presence of curved surfaces is considerably more involved than the definition of arc length of one- dimensional curve, or of the surface area for

polyhedral, i.e., objects with flat polygonal faces, for which the surface area is the sum of the areas of its faces.

6. The units of surface tension are force per unit length or is the CGS system dyne per centimeter. It is because of surface tension that falling water droplets in vacuum and the mercury particles on a smooth surface acquire spherical shape (a sphere occupies a smallest area for the given volume).
7. This method is based on the fact that any liquid such as water which wets the walls of the glass capillary tube will rise in the tube when the tube is placed in the liquid. On the other hand, if a liquid, such as mercury which does not wet the walls of the capillary tube will not rise and show a depression in the level of the liquid in the capillary tube. The rise or falls of a liquid in a capillary tube is based on the surface tension.
8. The Gibbs adsorption isotherm for multi component systems is an equation used to relate the changes in concentration of a component in contact with a surface with changes in the surface tension, which results in a corresponding change in surface energy.
9. Relative Surface Excess quantities are more useful than arbitrary surface excess quantities. The Relative surface excess relates the adsorption at the interface to a solvent in the bulk phase. An advantage of using the relative surface excess quantities is that they don’t depend on the location of the dividing surface.
10. Contact angle is one of the common ways to measure the wettability of a surface or material. Wetting refers to the study of how a liquid deposited on a solid (or liquid) substrate spreads out or the ability of liquids to form boundary surfaces with solid states.
11. In this type, the catalyst is present in the same phase as the reactants. There can be gaseous or liquid phase.
12. Surfactant, also called surface-active agent, substance such as a detergent that, when added to a liquid, reduces its surface tension, thereby increasing its spreading and wetting properties. In the dyeing of textiles, surfactants help the dye penetrate the fabric evenly. They are used to disperse aqueous suspensions of insoluble dyes and perfumes. A term surfactant comes from the word surface active agent. They are amphiphilic molecules and are thus absorbed in the air-water interface.
13. A micelle is an aggregate (or supramolecular assembly) of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic ’head’ regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre.
14. Detergents are amphipathic molecules that contain both polar and hydrophobic groups. These molecules contain a polar group (head) at the end of a long hydrophobic carbon chain (tail).
15. Counter ion binding of sodium and calcium to micelles, and mixed micellization have been investigated in the systems Sodium Dodecylsulfate (NaDS)/Sodium Decylsulfate (NaDeS) and NaDS/Sodium 4-

Octylbenzenesulfonate (NaOBS) in order to accurately model the activity of the relevant species in solution. The Critical Micelle Concentration (CMC) and equilibrium micelle compositions of mixtures of these anionic surfactants, which is necessary for determining fractional counter ion binding measurements, is thermodynamically modeled by regular solution theory.

16. The stability of micelles can be thought of generally in terms of thermodynamic and kinetic stability. Thermodynamic stability describes how the system acts as micelles are formed and reach equilibrium.
17. The driving mechanism for micellization is the transfer of hydrocarbon chains from water into the oil-like interior. This entropic effect is called the hydrophobic effect.
18. Micellar solubilization is the process of which is including the solubilizate (the component that undergoes solublization) into or onto micelles. Solublization may occur in a system consisting of a solvent, an association colloid (a colloid that forms micelles), and at least one other solubilizate.
19. Microemulsions are clear, thermodynamically stable isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) and/or other ingredients, and the 'Oil' may actually be a complex mixture of different hydrocarbons.
20. They are water droplets that we obtain from the action of sulphates when it disperses in water. Also, surfactant atoms create with the polar part to the internal side ready to solubilize water and the polar part in contact with the natural dissolvable.
21. Polymerization, is a process in which relatively small molecules, called monomers, combine chemically to produce a very large chain like or network molecule, called a polymer.
22. Organic polymers include compounds containing carbon hydrogen, oxygen nitrogen, sulphur and halogen atoms. Oxygen, nitrogen or sulphur may also be present in the backbone chain.
23. **Properties of Polymer Electrolyte**

    Following are the properties of polymer electrolyte:

    - Adequate conductivity for practical purposes
    - Low electronic conductivity
    - Good mechanical properties
    - High chemical, electrochemical and photochemical stability
    - Ease of processing

4.6 SUMMARY

- When solids are allowed to remain in contact with a gas, a film of gas molecules accumulates on the surface. It was pointed out in the discussion of surface tension that the molecular forces at the surface of a liquid are unbalanced or unsaturated than in the bulk.

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- All solids adsorb gases to some measurable extent. The magnitude of adsorption of gases by solids depends on the nature of the solid and the gas being adsorbed, the state of subdivision (area) of the solid the temperature and the pressure of the gas.
- It is characterised by low heats of adsorption of the order of 5 to 10 kcal per mol of the gas. The process of adsorption is similar to the condensation of gas on liquid.
- Langmuir derived an equation from theoretical considerations for type I isotherms. He was the first to point out that in the chemical adsorption of a gas on a solid surface, a layer single molecule in thickness is formed.
- Solid surfaces can also adsorb solutes from the solution. An application of adsorption from solution is the use of activated charcoal for decolorising sugar solutions. Activated characoal can adsorb colouring impurities on its surface.
- A general definition of surface area was sought by Henri Lebesgue and Hermann Minkowski in the twentieth century. Their work defined geometric measure theory which studies various notions of surface area for irregular objects of any dimension.
- In chemistry, the surface area is considered significant in chemical kinetics. Increasing the surface area of a substance generally increases the rate of a chemical reaction. For example, iron in a fine powder will combust, while in solid blocks it is stable enough to use in structures.
- The absorption of vapours by porous solids to fill their capillary channels and the displacement of oil by gas or water in petroleum formations constitute specific examples of capillary effects.
- The surface tensions of all liquids decrease with increasing temperature and become zero at the critical temperature because at the critical temperature, there is no surface of separation between the liquid and the vapours.
- Surface excess is the difference between the amount of a component actually present in the system, and that which would be present in a reference system if the bulk concentration in the adjoining phases were maintained up to the arbitrary chosen but precisely determined in position dividing surface.
- The equation of the Gibbs Adsorption Isotherm can be derived from the particularization to the thermodynamics of the Euler theorem on homogeneous first-order forms.
- As per standard derivations, if Gibb's free energy values are negative then the adsorption process is spontaneous and if it is positive then the adsorption process is non-spontaneous.
- Liquids can interact with two main types of solid surfaces. Traditionally, solid surfaces have been divided into high-energy solids and low-energy types. The relative energy of a solid has to do with the bulk nature of the solid itself. Solids such as metals, glasses, and ceramics are known as 'hard solids' because the chemical bonds that hold them together (for example, covalent, ionic, or metallic) are very strong.

- Many of the small organic molecules used in the preparation of all kinds of chemical products, from pharmaceuticals to explosives and from perfumes to polymers, come from oil. Not only are chemicals constructed by catalytic oxidation, hydrogenation, chlorination, and long chain hydrocarbons squeezed out of the earth.
- The surface-active molecule must be partly hydrophilic (water-soluble) and partly lipophilic (soluble in lipids, or oils). It concentrates at the interfaces between bodies or droplets of water and those of oil, or lipids, to act as an emulsifying agent, or foaming agent.
- The main purpose of the surfactants is to decrease the surface and interfacial tension and stabilize the interface. Without surfactants washing laundry would be difficult and many of the food products like mayonnaise and ice cream would not exist. Thus optimization of surfactants for different applications is highly important and surface and interfacial tension measurements have the key role in it.
- Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. Bile salts formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (for example, lecithin) and lipid-soluble vitamins (A, D, E, and K) within the micelle by the small intestine.
- In condensation polymerization, each step of the process is accompanied by the formation of a molecule of some simple compound, often water. In addition polymerization, monomers react to form a polymer without the formation of by-products.
- Linear Polymers, which are composed of chainlike molecules, may be viscous liquids or solids with varying degrees of crystallinity; a number of them can be dissolved in certain liquids, and they soften or melt upon heating.
- Polyethylene can have different properties depending on the length of the polymer chains and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates.
- Polyisoprene is a polymer of isoprene and is better known as rubber. It is produced naturally by rubber trees, but several variants have been developed which demonstrate improvements on the properties of natural rubber.
- Copolymers may also be linear, branched or three-dimensional. The monomer residues, in co-polymer molecules may be arranged in the chain regularly or at random, according to the law of chance.
- Initiator, is a source of any chemical species that reacts with a monomer (single molecule that can form chemical bonds) to form an intermediate compound that is capable of linking successively with a large number of other monomers into a polymeric compound.
- A gaseous monomer is placed in an electric discharge at low pressures under conditions where a plasma (ionized gaseous molecules) is created. In some cases, the system is heated and/or placed in a radiofrequency field to assist in creating the plasma.

- Radical, also called Free Radical, in chemistry, molecule that contains at least one unpaired electron. Most molecules contain even numbers of electrons, and the covalent chemical bonds holding the atoms together within a molecule normally consist of pairs of electrons jointly shared by the atoms linked by the bond.
- Methyl radicals obtained in this way proved to be highly reactive and short-lived. They not only reacted with lead and other metals but also disappeared rapidly and spontaneously, largely by dimerization to ethane, H_3C¯CH_3. Techniques for producing reactive free radicals in the gas phase have been greatly extended by subsequent research.
- Free radical polymerization consists of three fundamental steps, initiation, propagation, and termination. Initiation, involves the formation of radicals followed by the radical's reaction with a vinyl monomer, propagation is the rapid and progressive addition of monomers to the growing polymer chain without a change of the active center, and termination is the destruction of the growth active center, usually by combination or coupling of the radicals of two growing polymer chains or by disproportionation.
- Polymer electrolytes or gel-type polymer electrolytes are the alternatives to substitute liquid electrolytes in Dye-Sensitized Solar Cells (DSSCs). A polymer electrolyte is also referred to as a solid solvent that possesses ion transport properties similar to that of the common liquid ionic solution.
- Molecular weight of a polymer can be determined by relative or absolute methods. Many properties of polymers which depend upon molecular weight, such as –solubility, elasticity, absorption on solids, and their tear strength, can be corrected with an average molecular weight.

4.7 KEY TERMS

- **The Tensiometric or Torsion Balance Method:** In this method, a platinum ring about 4 cm in circumference is immersed in the liquid to be tested from the end of the beam of a torsion balance and the force required to separate the ring from the surface of the liquid is then measured.
- **Heterogeneous Catalysis:** In this type, catalyst constitutes a separate phase from the reactions. The catalyst is generally solid and reactants are mostly gases and sometimes liquids.
- **Initiation:** A free radical initiator (X*) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: H–O–O–H→2H–O.
- **Inorganic Polymers:** These include polymers containing no carbon atoms. Their are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains. Polysilanes, polygermanes, polysilicic acid, polyphosphates, polyarsenates, etc., are examples of inorganic polymers.

- **Plasticized Electrolyte:** This is fundamentally a gel electrolyte but is typically associated with the addition of small amounts of a high dielectric constant solvent which enhances its conductivity.
- **Dynamic Method:** This method consists of measuring the rate of penetration of solvent through the membrane, depending upon the pressure applied. The main advantage of this method is that the measurements take very less time as compared to the static method.
- **Disproportionation:** This involves the transfer of a hydrogen atom from one macroradical to another to form two macromolecules with one saturated and one unsaturated end group.
- **Cationic or Carbonium Polymerization:** This involves the formation of a carbonium ion which is a polar compound with tricovalent carbon atom carrying a positive charge, R–CH–R.

4.8 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the surface chemistry.
2. What is absorption?
3. Define absorption isotherms.
4. Give the name of methods surface area determination.
5. Determine the pressure difference across curved surface (Laplace equation).
6. Define the vapour pressure of droplets.
7. What is Gibbs isotherms?
8. State the BET theory for vaporization of gasses.
9. What is wetting phenomenon?
10. Distinguish between homogeneous and heterogeneous catalysis.
11. Define the counter ion.
12. What is significance of thermodynamics of micellization?
13. Define the process of micellization.
14. What do you understand by dressed micelle model?
15. Give the applications of micellar solubilisation.
16. State the theory of microemulsion.
17. Define the reverse micelles.
18. Define the macromolecule.
19. What is initiators?
20. Differentiate between organic and inorganic polymer.
21. What do you understand by electrical conducting and fire resistance polymer?

Long-Answer Questions

1. What is phenomenon of absorption explain with various types of examples.
2. Elaborate on the methods for the determination of surface area.
3. Explain in detail about the Gibbs absorption isotherms with appropriate examples.
4. Describe the surface film on liquid with the help of examples.
5. Analyse the catalytic activity on surface area giving applications and type with examples.
6. Discuss in detail about the counter ion binding to micelles giving examples.
7. Analyse the thermodynamics of micellization (phase separation and mass action models) with Gibss free energy equation.
8. Elaborate on the micellar solubilisation.
9. What is microemulsion? Explain with examples and uses.
10. Differentiate the micelles and reverse micelles with help of graph.
11. What is polymerization? Explain with the kinetic and mechanism of polymerization
12. Analyse the methods degree of polymerization with the help of examples.
13. Illustrate the chain configuration of macromolecule with appropriate examples.

4.9 FURTHER READING

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UNIT 5 ELECTROCHEMISTRY

NOTES

Structure

5.0 INTRODUCTION

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte. A process of this kind is known generally as an electrode process. The Debye-Hückel Onsager equation explanation the interactions between the various ions, which are the principal cause of the discrepancies between the properties of dilute solutions of electrolytes and those of so-called ideal solutions.

Electrochemistry deals with the processes at the interface between an electron conductor and an ion conductor. By application of a potential, electronic surface charges aggregate at this interface inducing possibly electrochemical reactions, for example at a metal-water interface. Electrocapillarity or electrocapillary phenomena are the phenomena related to changes in the surface energy (or interfacial tension) of the Dropping Mercury Electrode (DME), or in principle, any electrode, as the electrode potential changes or the electrolytic solution composition and concentration change. The Lippmann equation, which relates the surface tension and surface charge density of the ideally polarizable interface to the potential drop across the interface, is of fundamental importance to our understanding1 of the electrochemical double layer.

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Gouy-Chapman theory is an electrostatic model of the spatial distribution of ions adsorbed, but not immobilized, by a charged particle surface reacting with an aqueous electrolyte solution. In electrochemistry, the Butler–Volmer equation also known as Erdey-Grúz–Volmer equation, is one of the most fundamental relationships in electrochemical kinetics. It describes how the electrical current through an electrode depends on the voltage difference between the electrode and the bulk electrolyte for a simple, unimolecular redox reaction, considering that both a cathodic and an anodic reaction occur on the same electrode.

A semiconductor material has an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator, such as glass. Its resistivity falls as its temperature rises; metals behave in the opposite way. An electro catalyst is a catalyst that participates in electrochemical reactions. Electro catalysts are a specific form of catalysts that function at electrode surfaces or, most commonly, may be the electrode surface itself.

The Standard Hydrogen Electrode (SHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. Bioelectrochemistry is a branch of electrochemistry and biophysical chemistry concerned with electrophysiological topics like cell electron-proton transport, cell membrane potentials and electrode reactions of redox enzymes. In electrophysiology, the threshold potential is the critical level to which a membrane potential must be de

polarized to initiate an action potential. In neuroscience, threshold potentials are necessary to regulate and propagate signaling in both the central nervous system (CNS) and the Peripheral Nervous System (PNS). The time dependent form of the Nernst–Planck equation is a conservation of mass equation used to describe the motion of a charged chemical species in a fluid medium. The Hodgkin–Huxley model, or conductance-based model, is a mathematical model that describes how action potentials in neurons are initiated and propagated. Core-conductor model: In the core-conductor model we approximate an axon or a segment of a dendrite as a uniform cylinder. Electrocardiography is a commonly used, noninvasive procedure for recording electrical changes in the heart. Polarography is a type of voltammetry where the working electrode is a Dropping Mercury Electrode (DME) or a Static Mercury Drop Electrode (SMDE), which are useful for their wide cathodic ranges and renewable surfaces. Ilkovic equation is a relation used in polarography relating the diffusion current (i_d) and the concentration of the depolarizer (c), which is the substance reduced or oxidized at the dropping mercury electrode. In a given supporting electrolyte, the half-wave potential is unique for each element and its different valence states and chemical forms. Observation of a current peak at a specific half-wave potential therefore identifies the chemical species producing the current.

Corrosion is a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide, carbonate or sulphide.

In this unit, you will study about the electrochemistry of solution, Debye-Hückel Onsager equation, thermodynamics of electrified interface equation, derivation of electrocapillary, Lippmann equation (surface excess), and method of determination surface of electrified interfaces, Gouy-Chapman model, Graham Devanathan-Mottwatts, Tobin Bockris, Devanathan models, Butler-Volmer Equation and approximation of the equation, quantum aspects of charge transfer at electrode solution interface, semiconductors, electrocatalysis, hydrogen electrode, bioelectrochemistry, threshold membrane phenomena, Nernst–Planck and Hodges - Huxley equation, core conductor models, electrocardiography, palarography theory, Llkovic equation, half wave potential and its significance, introduction to corrosion, homogeneous theory, forms of corrosion, corrosion monitoring and prevention methods.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain the electrochemistry of solution
- Discuss about the Debye-Hückel Onsager equation
- Understand the thermodynamics of electrified interface equation
- Comprehend the derivation of electrocapillary
- State the Lippmann equation (surface excess)
- Know about the method of determination surface of electrified interfaces
- Interpret the Gouy-Chapman model
- Analyse the Graham Devanathan-Mottwatts, Tobin Bockris, Devanathan models
- Elaborate on the Butler-Volmer Equation and approximation of the equation
- Determine the quantum aspects of charge transfer at electrode solution interface
- Know about the semiconductors
- Understand the electrocatalysis
- Explain the hydrogen electrode
- Discuss about the bioelectrochemistry
- Know about the threshold membrane phenomena
- Analyse the Nernst–Planck and Hodges - Huxley equation
- Comprehend the core conductor models
- Interpret the electrocardiography and palarography theory
- State the Llkovic equation
- Determine the half wave potential and its significance
- Introduced to corrosion
- Analyse the forms of corrosion and prevention methods

5.2 ELECTROCHEMISTRY OF SOLUTIONS

NOTES

In chemistry, the transport number is also termed as 'Ion transport number' or the 'Transference number'. It is the fraction of the total electrical current carried in an electrolyte by a given ionic species '***i***' and is denoted by,

$$t_i = \frac{I_i}{I_{tot}}$$

Differences in transport number arise from differences in electrical mobility, for example, in a solution of sodium chloride, less than half of the current is carried by the positively charged sodium ions (cations) and more than half is carried by the negatively charged chloride ions (anions) because the chloride ions are capable to move faster, i.e., chloride ions have higher mobility than sodium ions. The sum of the transport numbers for all of the ions in solution always equals unity.

The concept and measurement of transport number were introduced by Johann Wilhelm Hittorf in the year 1853. When the ions in a solution have different ion transport numbers then this gives liquid junction potential.

At zero concentration, the limiting ion transport numbers may be expressed in terms of the limiting molar conductivities of the cation (λ_0^+), anion (λ_0^-), and electrolyte (Λ_0), represented by the equations:

$$t_+ = v^+ \cdot \frac{\lambda_0^+}{\Lambda_0}$$

And,

$$t_- = v^- \cdot \frac{\lambda_0^-}{\Lambda_0}$$

Where v^+ are the numbers of cations and anions, respectively per formula unit of electrolyte. In practice the molar ionic conductivities are calculated from the measured ion transport numbers and the total molar conductivity. For the cation $\lambda_0^+ = t_+ \cdot \frac{\Lambda_0}{v^+}$, and similarly for the anion.

The friction of the total current carried in a solution by a given ion. Ions may carry drastically different portions of the total current if their mobilities are different.

Example 5.1: In a solution of sodium chloride, less than half of-the current is carried by the positively charged sodium cations and more than half is carried by the negatively charged chloride anions because the chloride ions are able to move faster (they have a larger ionic mobility).

The transport of the anion and the cation adds up to unity. As a matter of fact, the case when the ions move equally and the transport number of both ions is equal to 0.5 is a rarity. The Hifforf method is an experimental technique for the determination of the transport nilmbers. Also called 'transference number'.

For the simplest case of a solution of a single salt of univalent ions, the transport numbers are defined as the mobility of the ion divided by the sum of mobilities of the two ions. If there are more than one solutes present (for example, An acidified sodium chloride solution or a mixture of sodium chloride and potassium bromide), every ion will have its own transport number with the sum of them being Unity. In these cases, the concentrations of the ions must also be taken into account into the calculation of the transport numbers, and in the case of polyvalent ions, the charges of the ions must also be accounted for.

$$\boxed{t_+ + t_- = 1}$$

Ionic Mobilities

A quantitative measure of an ion's ability to move under the influence of a potential difference in solution: It is the speed of movement under the influence. of unit potential difference.

While the mobility is defined in terms electromigration, it also affects the speed of diffusion.

Transference Numbers

We have seen that the different types of ions move with different speeds under the same potential gradient. It, therefore, follows that the cations and the anions carry different amounts of electricity during the electrolysis. This current carried by individual ions depend upon its velocity, and the total current is constituted by the movement of cations and anions.

'*The fraction of the current carried by a given ionic species in the solution is called the transport number of Hittorf's number or transference number of the ion and designated by the symbols* t_+ and t_-'. In the simplest case of a single electrolyte yielding two ions, denoted by the suffixes + and –, the symbols for transport number are t_+ and t_- respectively.

According the Kohlrausch law, the current carried by an ion is proportional to its ionic conductance. The speed of an ion in a solution at any concentration is proportional to the conductance of the ion at that concentration. Thus, we have

$$\text{Current carried by the cation } \mu \ \lambda_0^+$$

$$\text{Current carried by the anion } \mu \ \lambda_0^-$$

$$\text{Total current} \quad \propto \left(\lambda_0^+ + \lambda_0^-\right)$$

$$\therefore \text{ Transport number of cation, } t_+ = \frac{\lambda_0^+}{\lambda_0^+ + \lambda_0^-} \text{ and}$$

$$\text{Transport number of an anion, } t_- = \frac{\lambda_0^-}{\lambda_0^+ + \lambda_0^-}$$

The transport number of the ions can be measured by finding the change in concentration round the electrodes. To illustrate this, let us consider the electrolysis cell shown in Fig. 5.1. Further, let the solutions be divided into three compartments by means of imaginary partitions *ab* and *cd.* In the diagram, ⊖ represents anion and Å represents cation. Before electrolysis, the position of the ions is shown by the line I, where every anion is associated with a cation.

NOTES

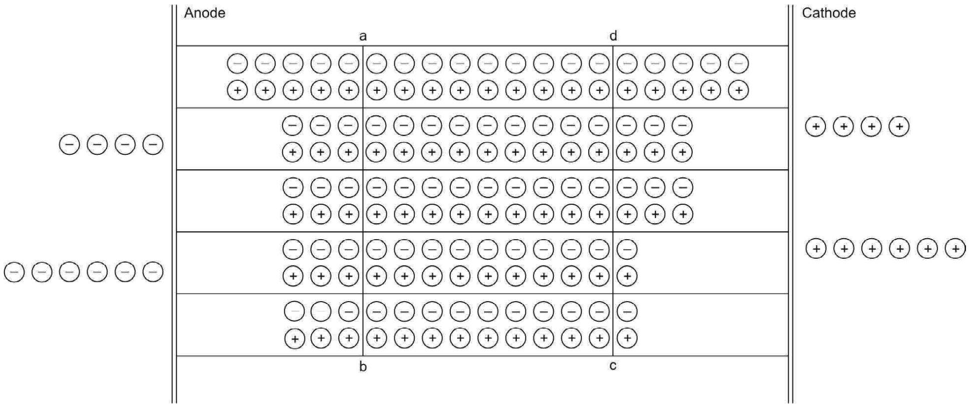


Fig. 5.1: *Migration of Ions*

Case I: Let the cation and the anion move with the same speed and say two anions have crossed the partition towards the anode; then two cations will have crossed in the opposite direction towards the cathode. This is shown in line II. As a result of this, excess ions in the two compartments near the anode and the cathode are discharged as shown in line III. The concentration of both the anode compartment and the cathode compartment has decreased to the same extent, i.e., by two ionpairs.

Case II: Let the anion moves with twice the speed of the cation and further let two cations reach the cathode. Then four anions will cross to the anode compartment. The state now is as in *IV.* The excess ions near the anode and the cathode compartment are discharged. The state of the solution is as shown in *V*. The fall in the amount of electrolyte near the anode will be (5 – 3) = 2 and that near the cathode will be (5 – l) = 4. But, the concentration in the middle part of the cell is uncharged by the passage of the current in both the cases.

These fall in concentration near the two electrodes are proportional to the speed of the ions leaving that compartment, i.e.,

$$\frac{\text{Fall near the anode}}{\text{Fall near the cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} \qquad ...(1)$$

Let t is the fraction of the current carried by the anion; then the fraction $1 - t$ must be carried by the cation. Since the amounts of electricity carried are proportional to the speed of the ions, we have:

$$\frac{\text{Loss at anode}}{\text{Loss at cathode}} = \frac{1-t}{t}$$

If u is the speed of the anion and n is the speed of the cation, then we have:

$$\frac{t_-}{t_+} = \frac{t}{1-t} = \frac{\text{Loss at cathode}}{\text{Loss at anode}} = \frac{u}{\nu} \qquad ...(2)$$

Electrolytic Conductance

Electrolytes are also conductors of electricity. The electrical conductance of an electrolyte is due to the ions it contains. The greater the concentration of ions, the higher will be the conductance. To compare the conductivity of different solutions, the size of the electrodes and the distance between the electrodes must be standardized. It has been found that the resistance offered by a solution is directly proportional to the distance between the electrodes and inversely proportional to the cross-sectional area of the solution between the electrodes. The resistance R is thus, given by:

$$R = \rho\left(\frac{l}{a}\right) \qquad ...(3)$$

where, l is the distance between the electrodes, a is the area of cross-section and r is the constant of proportionality known as the specific resistance or resistivity.

In equation (14.7) if

$$l = 1 \text{ cm}$$

and $$a = 1 \text{ sq cm},$$

then $$\rho = R$$

Hence, the specific resistance is the resistance in ohms of a solution kept between electrodes 1 cm apart and area between electrodes being one square centimetre.

The reciprocal of resistance is defined as conductance, if we denote this by L, then

$$L = \frac{1}{R} \qquad ...(4)$$

It is measured in ohm^{-1} or mho. The reciprocal of specific resistance is defined as specific conductance. It is given by k (Kappa), i.e.,

$$k = \frac{1}{\rho} = \left(\frac{l}{a}\right) \times \frac{1}{R} \qquad ...(5)$$

It is the conductance of a solution between electrodes, 1 cm^2 is area and 1 cm apart. Specific conductance is measured in units of $\text{ohm}^{-1}\ \text{cm}^{-1}$ and is a property of conducting medium.

Equivalent and Molar Conductance

In dealing with solutions of electrolytes we define a quantity known as equivalent conductance (Λ). It represents the conducting power of all ions produced by one gram equivalent of electrolyte in solution. The equivalent conductance of an electrolyte may be defined as the conductance of a volume of solution containing one gram equivalent of dissolved substance, the solution being placed between two parallel electrodes, 1 cm apart, and large enough to contain between them all of the solution. Let *vcc* be the volume of solution containing 1 g equivalent of an electrolyte and let κ be the specific conductance of the solution. The equivalence conductance L (lambda) will then be:

$$\Lambda = \kappa v \qquad ...(6)$$

If C is the concentration of a solution in gram equivalent per litre, the volume v of the solution containing one gram equivalent will be $\frac{1000}{C}$.

The equation (6) then becomes:

$$\text{Equivalent conductivity,} \quad \Lambda = \frac{1000\ \kappa}{C} \qquad ...(7)$$

NOTES

Units of equivalent conductance

Since Λ is given by

$$\Lambda = \kappa v$$

and

$$\kappa = \left(\frac{l}{a}\right) \cdot \frac{1}{R}$$

$$\Lambda = \left(\frac{l}{a}\right) \frac{1}{R} . v$$

$$\Lambda = \frac{(\text{cm}) \times 1 \times (\text{cm})^3}{(\text{cm})^2 \times \text{ohm} \times \text{equiv}}$$

$$\Lambda = \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}.$$

Therefore, units of equivalent conductance are $\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$.

Molecular conductance (μ) is defined as the conductance of a volume of solution containing one mole of solute, the solution being placed between the two electrodes 1 cm apart and large enough to contain in between them all the solution. It is equal to the specific conductance multiplied by that volume of solution in cc which contains one gram molecule of the electrolyte.

If C is the concentration in moles per litre then

$$\mu = \kappa v \qquad ...(8)$$

or

$$\mu = \frac{1000}{C} \times \kappa$$

The units of molar conductance are $\text{ohm}^{-1}\ \text{cm}^{-2}\ \text{mol}^{-1}$.

For an electrolyte containing two univalent ions, Λ and μ are identical.

5.2.1 Debye-Hückel-Onsager Equation

The Debye-Hückel theory was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes. It was further modified by Lars Onsager in 1927 with the following postulates.

- The solute is completely dissociated, it is a strong electrolyte.
- Ions are spherical and are not polarized by the surrounding electric field.
- The solvent plays no role other than providing a medium of constant relative permittivity (dielectric constant).
- It was assumed that the electric field causes the charge cloud to be distorted away from spherical symmetry.
- There is no electrostriction.
- Individual ions surrounding a 'central' ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach.

The last assumption means that each cation is surrounded by a spherically symmetric cloud of other ions. The cloud has a net negative charge. Similarly each anion is surrounded by a cloud with net positive charge.

Considering the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to derive a theoretical expression to account for the empirical relation known as 'Kohlrausch's Law', for the molar conductivity, Λ_m.

$$\Lambda_m = \Lambda_m^0 - K\sqrt{c}$$

Here Λ_m^0 is known as the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. Limiting here means 'at the limit of the infinite dilution'. Onsager's expression is,

$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{c}$$

Where A and B are constants that depend only on known quantities, such as temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. This is known as the Debye-Hückel-Onsager equation. Figure 5.2 illustrates the graph for strong and weak electrolyte.

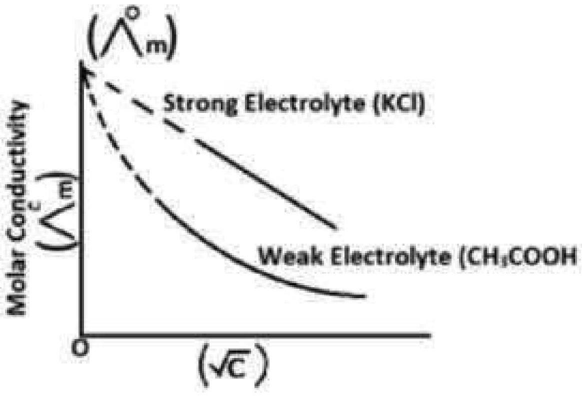


Fig. 5.2 *Graph for Strong and Weak Electrolyte*

Equivalent Conductivity (Λ): The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity. It is denoted by Λ.

Strong and Weak Electrolytes

Electrolytes are chemicals that break into ions in water. Aqueous solutions containing electrolytes conduct electricity. Strong electrolytes include the strong acids, strong bases, and salts. These chemicals completely dissociate into ions in aqueous solution.

Weak electrolytes only partially break into ions in water. Weak electrolytes include weak acids, weak bases, and a variety of other compounds. Most compounds that contain nitrogen are weak electrolytes.

Nonelectrolytes do not break into ions in water. Common examples include most carbon compounds, such as sugars, fats, and alcohols.

The equivalent conductivity Λ of an electrolyte solution is related to the mobilities of the constituent ions as

$$\Lambda = F\,(U_+ + U_-) \qquad \text{...(9)}$$

$$U_+ = \left[U_+^0 - \frac{X}{300}\left(\frac{Z_X e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT}\right) U_+^0\right]$$

$$U_- = \left[U_-^0 - \frac{x}{300}\left(\frac{Z_- e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT}\right) U_-^0\right]$$

Substituting the values of U_+ and U_- in Equation (1), we get

$$\Lambda = F\left[U_+^0 = \frac{X}{300}\left(\frac{Z_X e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT} U_+^0\right)\right] + \left[U_-^0 = \frac{X}{300}\left(\frac{Z_{-1} e_0}{6\pi\eta} + \frac{300 e_0^2 \omega}{6 \in KT} U_-^0\right)\right] \text{...(10)}$$

Where F - Faraday

X - Distance traveled by the ion

e_0 - Charge of the electric cloud

η - Viscosity of the liquid

Z_0 - Charge of the ion

$\in$ - correction factor

K - Boltamann constant

T - Absolute Temp

Λ - Equivalent conductivity

ω - Dielectric constant of the medium

For a symmetrical electrolyte, $Z = Z_+ = Z_-$

Therefore, the Equation (10) reduces to,

$$\Lambda = \left[\left(FU_+^0 - \frac{FXZe_0}{300 \times 6\pi\eta} - \frac{FXZe_0 300 e_0^2 \omega}{300 \times 6 \in KT}\right)\right.$$

$$\left. + FU_-^0\left(\frac{FXZe_0}{300 \times 6\pi\eta} - \frac{FXZe_0 300 e_0^2 \omega}{300 \times 6 \in KT} U_-^0\right)\right]$$

$$\Lambda = F\left(U_+^0 - U_-^0\right) - \frac{ZFXZe_0}{300 \times 6\pi\eta} - \frac{FXe_0^2 \omega}{6 \in KT}\left(U_+^0 - U_-^0\right)$$

$$\Lambda = F\left(U_+^0 - U_-^0\right) - \frac{FXZe_0}{900\pi\eta} - \frac{Xe_0^2 \omega}{6 \in KT}\left(U_+^0 - U_-^0\right)$$

But, $\Lambda^0 = F\left(U_+^0 + U_-^0\right)$

$$\Lambda = \Lambda^0 - \left[\frac{FXZe_0}{900\pi\eta} + \frac{xX_0^2 \omega}{6 \in KT} \Lambda^0\right] \qquad \text{...(11)}$$

Replacing X by the familiar expression,

$$X = \left(\frac{8\pi z^2 e_0^2 C}{\in KT}\right)^{1/2}\left(\frac{NA}{1000}\right)^{1/2}$$

NOTES

Then Equation (3) becomes,

$$\Lambda = \Lambda^0 - \left[\frac{FZe_0}{900\pi\eta}\left(\frac{8\pi z^2 e_0^2 C}{\in KT}\right)^{1/2}\left(\frac{NA}{1000}\right)^{1/2} + \frac{e_0^2\omega}{6 \in KT}\left(\frac{8\pi z^2 e_0^2 C}{\in KT}\right)^{1/2}\left(\frac{NA}{1000}\right)^{1/2}\Lambda^0\right] \quad ...(12)$$

Equation (11) is the Debye-Hückel-Onsagar equation for a symmetrical electrolyte.

Validity and Extension of the Theory and Activity of Ions in Solution

The verification of the Debye-Hückel-Onsager equation is more difficult for electrolytes of unsymmetrical valence types (different Z^+ and Z^- values) since determination of the value of ω can be done only on knowing the mobility's of the individual ions at infinite dilution and also the transference numbers of the ions. For $CaCl_2$ and $LaCl_3$ dilute solutions, the results are in close agreement with the requirements of the theoretical equation at concentrations λ against square root of the concentration up to 4×10^{-5} equivalents per liter. The higher the valence type of the electrolyte, the lower is the limit of concentration at which the Onsager equation is applicable. It has been observed for aqueous solutions of various electrolytes that there is good agreement between the experimental slopes and theoretically calculated values.

The validity for Onsager theory is also provided by conductance measurements of a number of electrolytes made at 0^0C and 100^0C. At both temperatures, the observed slope of the plot of agrees with the calculated result within the limits of experimental error.

Thus the Onsager equation represents the dependence of the concentration of the equivalent conductance electrolytes. The shapes of the curves indicate that in sufficiently dilute solutions the slopes would be very close to the theoretical Onsager values.

The effect of concentration on equivalent conductance can be studied from the plots of Λ^0 values versus square root of the concentration of the electrolyte.

It has been found that different types of plots are obtained depending on the nature of the electrolyte.

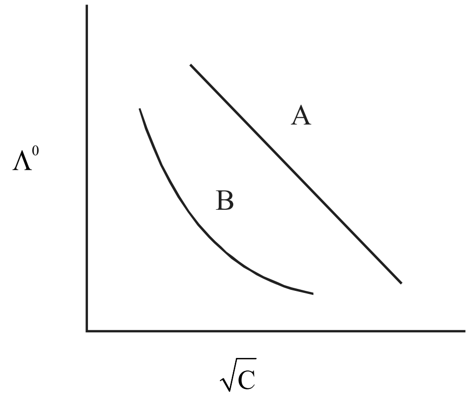


Fig. 5.3 *Concentration of Different Electrolyte*

Validity for Non-Aqueous Solvents

For methyl alcohol solutions, chlorides and thiocyanates of the alkali metals, the experimental values closely agree with the theoretical values. But nitrate solutions, tetra alkyl ammonium salts and salts of higher valence types show appreciable deviations. The discrepancies are more prominent when the dielectric constant of the medium is low. The conductance of KI in a number of solvents was determined and the slopes of the plots of λ against square root of C was found out. At higher dielectric constants, there is close agreement between the experimental and calculated slopes. But at lower dielectric constants, greater discrepancies are observed. The deviation from theoretical Onsager behaviour for non-aqueous solutions occurs because many strong electrolytes which are completely dissociated in water behave as weak, incompletely dissociated electrolytes in solvents of low dielectric constant.

Activity Coefficients of different electrolytes

The activity coefficients of different electrolytes can be determined based on measurements of vapor pressure, freezing point, solubility or electromotive force. The results obtained by the various methods are in good agreement with each other and hence they may be regarded as reliable.

The activity coefficients deviate appreciably from unity. The values always decrease at first as the concentration is increased, but they generally pass through a minimum and then increase again. The activity coefficients often exceed unity at high concentrations so that the mean activity of the electrolyte is actually greater than the concentration. The deviations from ideal behaviour at high concentrations are in the opposite direction to those which occur at low concentrations.

(a) The electrolytes of the same valence type have almost identical activity coefficients in dilute solutions.

(b) The deviation from ideal behaviour at a given concentration is greater if the product of the valences of the ions constituting the electrolyte is higher.

Debye-Hückel Limiting Law

Coulombic interactions between ions in solution are relatively strong, long-range forces compared to the other types of intermolecular force in solution. They are thus an important contributor to the non-ideality of ionic solutions, and in the Debye-Hückel theory of such solutions, they are taken to dominate the non-ideality to such an extent that all other contributions may be neglected.

NOTES

The theory is based around the simple fact that oppositely charged ions attract one another, while the like charged ions repel each other. Hence, the motion of ions in solution is not entirely random, but there is a slight tendency for ions of opposite charge to encounter each other more frequently than ions of the same charge.

The 'Debye-Hückel Limiting Law' is applicable only at very low concentrations of solute. This law enables calculation of the mean activity coefficient from basic properties of the solution. The name 'Limiting Law' is applied because in the limit of arbitrarily low molalities, i.e., as the concentration of the solute gets closer and closer to zero, all solutions are expected to behave in a manner consistent with the expression.

To test the Debye-Hückel model of ion-ion interactions it is necessary to relate the theoretical individual activity coefficient f_i to the mean activity coefficient f_{+-} which is experimentally accessible. For an electrolyte, this gives $v+$ positive and v - negative ions.

$$f_{\pm} = \left[f_{+}^{v^{+}} f_{-}^{v^{-}} \right]^{1/v}$$

Where f_+ and f_- are the activity coefficients of the positive and negative ions and $v = v_+ + v_-$. Taking logarithms and introducing the Debye-Hückel expression for f_+ and f_-,

$$Inf_{\underline{\pm}} = 1/v(v + Inf_{+} + v\_Inf_{-})\ \frac{Ne^2 x}{v(4\pi\varepsilon_0)2\varepsilon RT}(v + Z_{+}^{2} v\_Z_{-}^{2})$$

Since the solution as a whole is electronetural,

$$v_{+}\, Z_{+} = v_{-}\, Z_{-}$$

$$\begin{aligned}(v_{+} Z_{+}^{2} v_{-} Z_{-}^{2}) &= v_{-} Z_{-} Z_{+} + v_{+} Z_{+} Z_{-} \\ &= Z_{+} Z_{-} (v_{+} + v_{-}) \\ &= Z_{+} Z_{-} v\end{aligned}$$

$$B = \left[\frac{8000\pi e^2 N}{(4\pi\varepsilon_0) \in KT} \right]^{1/2} \frac{Z_{-}\big)\overline{e^2 X}}{\varepsilon_0\big)\overline{2 \in RT}}$$

Where $X = BI^2$

$I =$ Ionic strength,

$$Inf_{\underline{\pm}} = \frac{N(Z_{+} Z_{-}) e^2 B I^{1/2}}{(4\pi\varepsilon_0) 2 \in RT}$$

$$A = \frac{1}{2.303} \times \frac{Ne^2 B}{(4\pi\varepsilon_0) 2 \in RT}$$

NOTES

The equations predicts that the logarithm of activity coefficient must decrease linearly with the square root of ionic strength or in the case of uni-valent electrolytes with $C^{1/2}$ (since $Z_+ = Z_- = I$ and $I = C$). Also, the slope of the line should not depend on the particular electrolyte but only on its valence type. It is found that the experimental plots of log $f_\pm$ vs. $I^{1/2}$, are indeed linear and the plots are grouped according to the valence type of the electrolyte, provided the electrolyte concentrations are very low (Refer Figure 5.4). It follows at limiting low concentrations, is called the Debye - Hückel limiting law. However, at the higher concentrations deviations have been found from the limiting law.

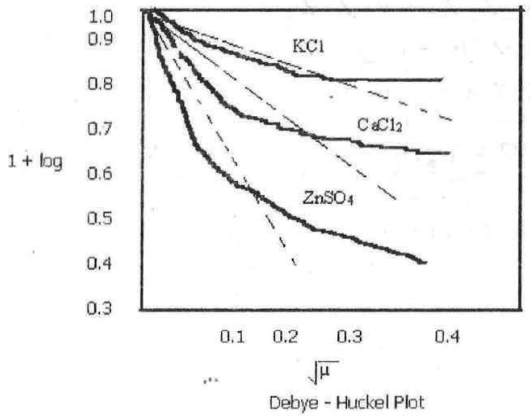


Fig. 5.4 *Debye-Hückel Plot*

5.2.2 Thermodynamics of Electrified Interface Equation

Electrochemistry deals with the processes at the interface between an electron conductor and an ion conductor. By application of a potential, electronic surface charges aggregate at this interface inducing possibly electrochemical reactions, for example at a metal-water interface. The sluggish kinetics for example of an ion conducting liquid, such as water and the shere size of the diffuse double layer however often hamper a straight forward fully explicit description. A 'Thermodynamic System' is a part of the physical world constituted by a significantly large number of particles (i.e., atoms, molecules or ions). A 'Homogeneous Thermodynamic System' is defined as the one whose intensive thermodynamic properties are constant in space.

If a portion of a thermodynamic system behaves in this way throughout all its volume, it is called a 'Phase', i.e. the term 'Phase' is used for a region that is chemically and structurally homogeneous. According to a more general definition, a phase is a region of ***(spatially)*** constant or continuously changing physical (intensive thermodynamic) and chemical properties.

A ***heterogeneous system*** can involve more than one phase, and the passage through the interface among two phases leads to a discontinuous variation of one or more intensive functions, such as concentrations, density, electric potential, etc. The plane ideally marking the boundary between two phases is called the interface. Although interfaces are always dealt with from a ***thermodynamic*** point of view, if attention is actually focused on only one of the two phases, the plane between the phase and the environment is called the ***surface*** of the phase. The region between two phases where the properties vary between those in the bulk is the '***interfacial or interface region'***. It is sometimes regarded as a distinct – though not autonomous – phase and is called the ***interphase***. The primary objectives of all thermodynamic treatments are to describe systems involving interfaces in terms of experimentally observable quantities and to derive equations (functions) that enable one to relate the thermodynamic properties of a system under one set of conditions to those valid for another set of conditions. An interface or a surface does not exist in isolation. It is the interface region in a ***two-phase system*** and valid thermodynamic conclusions can only be drawn by considering the system, namely, the interface and the two regions adjacent to the interface, as a whole. Provided that the radius of curvature is sufficiently large, the ***interface/interphase*** may be regarded as plane and its energy then differs from that of a bulk phase by a term expressing the contribution of changes of energy due to a change of the area of contact. Edge effects can be eliminated by considering a section of an interface in a larger system. There is no clear boundary between the interfacial region and the bulk of the phases so that the thickness of the interphase depends on the model chosen to describe this region. The words interface and surface are often used synonymously, although interface is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly, e.g. the solid/gas interface. Nevertheless, solid surfaces are usually not perfectly flat but are somewhat rough. The geometric area, as represented by the product of the length and breadth of a rectangle enclosing part of a surface, is not the same as the actual surface area which takes into account the areas of the hills and valleys within the rectangle. If the surface is very rough, the geometric area may be considerably smaller than the actual area. The properties of a portion of surface are dependent on orientation, and if there are many portions of different orientation, correct summation over the whole surface may be a difficult task. Such a surface is unlikely to be in a state of equilibrium and caution should be exercised when considering systems containing such surfaces. Consideration will be restricted here to systems in which the difference between geometric and actual areas is not of major importance. Generally, the thickness of the interface or local values of physical quantities (parameters) cannot be measured. That is the reason why integrated quantities (which are accessible experimentally, or can be calculated from experimental data) are used for the thermodynamic characterization of interfaces. Usually, these quantities are given by the expression

$$\Psi^{s} = \int_{\alpha\alpha}^{\beta\beta} \Xi(z)\,\mathrm{d}z$$

Or by

$$\Psi^{s} = \int_{\alpha\alpha}^{\beta\beta} \xi(z)\,\mathrm{d}V\,,$$

Where z is the coordinate perpendicular to the plane of the interface, Ψ^{s} is the integrated quantity, $\alpha\alpha$ and $\beta\beta$ are the two adjacent phases, dV represents the volume element, $\Xi(z)$ is the local value (related to the area) and **$\xi(z)$** is the volume density of any extensive physical quantity in the interfacial region.

In heterogeneous systems, mobile electric charges may accumulate at the interfaces between the constituent phases, thus a thermodynamic approach requires us also to be able to characterize the state of the system containing electrified interfaces.

5.2.3 Derivation of Electrocapillary

Electrocapillarity or ***electrocapillary*** phenomena are the phenomena related to changes in the surface energy (or interfacial tension) of the Dropping Mercury Electrode (DME), or in principle, any electrode, as the electrode potential changes or the electrolytic solution composition and concentration change. The term ***electrocapillary*** is used to describe the change in **Mercury (Hg)** electrode potential as a function of the change in the surface or interfacial tension of the Hg determined by the capillary rise method. The phenomena are the historic main contributions for understanding and validating the models of the structure of the electrical double layer. The phenomena are related to the ***electrokinetic phenomena*** and consequently to the ***colloid chemistry***.

Interfacial Tension

The interfacial (surface) tension, St, (dyne cm$^{”1}$), can be calculated by applying the equation of capillary rise method (when the contact angle è ’! 0):

$$St = \frac{h \cdot r \cdot g \cdot d}{2}$$

Where:

- h (cm) is the height of Hg column above the Hg meniscus in the capillary
- r (cm) is the radius of capillary
- g is the acceleration due to gravity
- d (g cm$^{”3}$) is the Hg density

The circuit contains Hg electrode as the ideally polarizable electrode and a reference electrode as the non-polarizable electrode. Thus, when an external voltage is applied, only **EM/S** of **Hg/solution** fluid interface is changed.

Electrocapillary Equation

At electrochemical equilibrium, the interfacial tension **γ** depends on the thermodynamic parameters and the electrical potential:

$$\gamma = f(\Delta)\left(\Delta\varphi^{\alpha\beta}\right) \text{ at } T, p, \mu_i = \text{const.}$$

The electrocapillarity equation is therefore

$$\mathrm{d}\gamma = -\sum_i \Gamma_i^{\alpha} \cdot \mathrm{d}\mu_i^{\alpha} - \sum_i \Gamma_i^{\beta} \cdot \mathrm{d}\mu_i^{\beta} + q \cdot \mathrm{d}E$$

Where **q** = charge density at the interface, **Γ** = interface concentration of the species **i** and **E** the measurable electrical potential.

Lippmann Equation(Surface Excess)

This equation contains the principle of ***electrowetting,*** and more specifically Electro Wetting On Dielectrics (EWOD), a technique aimed at activating and transporting liquid droplets on a solid substrate. This technique was pioneered by Berge in the 1990s who combined the Lippmann law with the Young law to obtain the now-called Lippmann–Young law

$$\cos\theta = \cos\theta_0 + \frac{C}{2\gamma_{\mathrm{LG}}}V^2$$

Where ***C*** is the capacitance of the dielectric layer separating the bottom electrode from the liquid.

The studies of electrocapillary phenomena, focusing at how the interfacial charge influences the surface tension. A complete description of electrocapillarity is given in courses in electrochemistry.

The repulsion between charges of the same sign in the interfacial double layer should make an increase in the surface area easier, for example it should decrease the interfacial tension **σ**. It is well known from electrostatics that the work $\mathbf{W}_{\mathbf{q}}$ required to supply a charge **q** to a spherical surface of radius **r** at a potential difference of **φ=q/4πεε0r** is given by

$$W_q = \frac{q^2}{8\pi\varepsilon\varepsilon_0 r} = 2\pi\varepsilon\varepsilon_0 r\varphi^2$$

One may expect that the specific (per unit area) work of charging is exactly the value of the work ***'Already Accumulated'*** by the interface that is needed to ease the increase in the interfacial area. In other words, the specific work of charging is equal to the potential energy lowering:

$$\sigma_0 - \sigma(\varphi) = \frac{W_q}{4\pi r^2} = \frac{q^2}{32\pi^2\varepsilon\varepsilon_0 r^3} = \frac{\varepsilon\varepsilon_0\varphi^2}{2r}$$

Differentiation of the above equation with respect to **φ** yields the **Lippmann equation**, which is the main relationship of electrocapillarity:

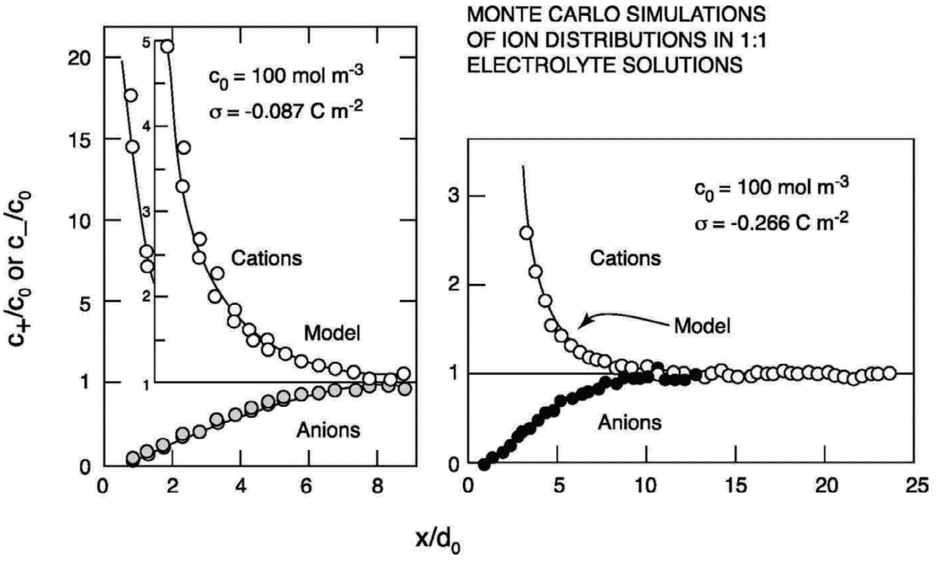
$$-\frac{\mathrm{d}\sigma}{\mathrm{d}\varphi} = \frac{\varepsilon\varepsilon_0\varphi}{r} = -\frac{q}{4\pi r^2} = \rho_s,$$

Where $\boldsymbol{\rho}_{\mathbf{s}}$ is the surface charge density.

5.2.4 Gouy-Chapman model

Louis Georges Gouy in 1910 and ***David Leonard Chapman*** in 1913 both observed that capacitance was not a constant and that it depended on the applied potential and the ionic concentration. The 'Gouy–Chapman Model' made significant improvements by introducing a diffuse model of the DL. In this model, the charge distribution of ions as a function of distance from the metal surface allows Maxwell–Boltzmann statistics to be applied. Thus the electric potential decreases exponentially away from the surface of the fluid bulk.

Gouy-Chapman theory is an electrostatic model of the spatial distribution of ions adsorbed, but not immobilized, by a charged particle surface reacting with an aqueous electrolyte solution. These ions are relatively free to move about while reacting with surface charge either by accumulation (positive adsorption) or depletion (negative adsorption) in the interfacial region. The fundamental question answered by Gouy-Chapman theory is how this '**Diffuse Swarm'** of adsorbed ions with given valence and radius will distribute itself near a particle of given charge and radius solely under the influence of coulomb forces between the ions and between them and the particle surface.



Gouy-Chapman Theory Model

5.3 BUTLER-VOLMER EQUATION AND APPROXIMATION OF THE EQUATION

The **Butler–Volmer equation** is named after John Alfred Valentine Butler and Max Volmer. Also sometimes known as **Erdey-Grúz–Volmer** equation, it is one of the most fundamental relationships in electrochemical kinetics. It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode,

$$j = j_0 \cdot \left\{ \exp\left[\frac{\alpha_a zF}{RT}(E - E_{eq})\right] - \exp\left[-\frac{\alpha_c zF}{RT}(E - E_{eq})\right] \right\}$$

Or in a more compact form:

$$j = j_0 \cdot \left\{ \exp\left[\frac{\alpha_a zF\eta}{RT}\right] - \exp\left[-\frac{\alpha_c zF\eta}{RT}\right] \right\}$$

Where:

j = Electrode current density, A/m^2 (defined as $j = I/S$)
j_0 = Exchange current density, A/m^2
E = Electrode potential, V
E_{eq} = Equilibrium potential, V

T = Absolute temperature, K

z = Number of electrons involved in the electrode reaction

F = Faraday constant

R = Universal gas constant

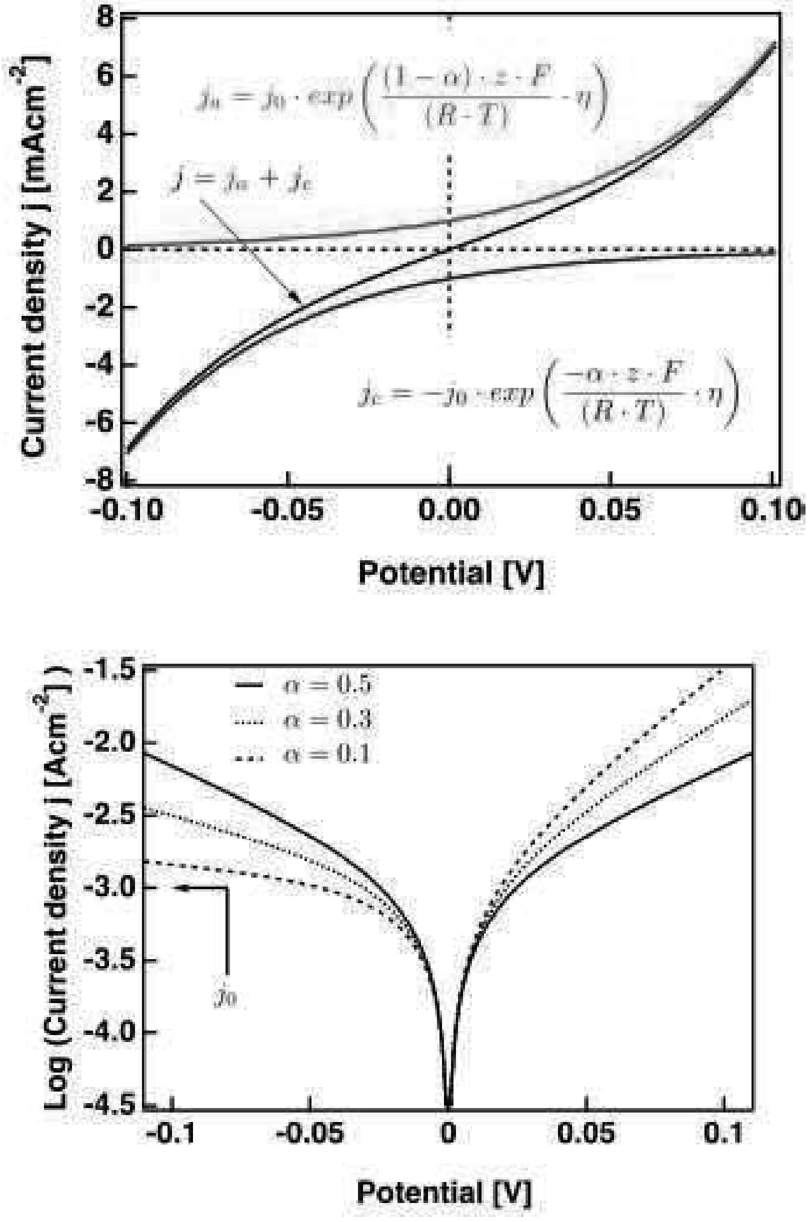
α_c = Cathodic charge transfer coefficient, dimensionless

α_a = Anodic charge transfer coefficient, dimensionless

η = Activation over-potential or over-voltage (defined as $\eta = E - E_{eq}$).

Thus, the over-voltage may be defined as $\eta = E - E_{eq}$ where E_{eq} is the expected (equilibrium) electrode potential and E is the actual electrode potential. It has been experimentally observed that at low currents, the current is exponentially related to the over-potential or over-voltage.

The Figure displays plots valid for $\alpha_a = 1 - \alpha_c$.



Displays Plots Valid for $\alpha_a = 1 - \alpha_c$

NOTES

In Figure, the first graph displays the current density as function of the over-voltage or over-potential ?. The anodic and cathodic current densities are shown as j_a and j_c, respectively for $\alpha = \alpha_a = \alpha_c = 0.5$ and j_0=1mAcm^{-2}, which is close to values for platinum and palladium. The second graph displays the logarithmic plot for different values of α (Tafel Plot).

The Butler–Volmer equation has been widely used to analyze the electron transfer for electrochemical simulation. Though it has been approximately used for numerous applications, but the Butler–Volmer equation is specifically approximated for finding the activation over-potential or over-voltage. Some parameters are essential in Butler–Volmer equation, such as exchange current density and symmetry factor which may not be known parameters. For approximation of Butler–Volmer equation, there are some approximation equations, such as Tafel, linear low polarization, and hyperbolic sine approximation. However, all these equations can be appropriate and applicable only in a specific range of current density or definite condition.

For very fast reactions, K° ~ infinity. The equation then becomes merely a statement of the Nernst equation. Another way of obtaining the Nernst equation is to consider equilibrium conditions (I = 0). Therefore, the Butler–Volmer theory fulfils one requirement for a successful kinetic theory, i.e., it collapses to the Nernst equation at equilibrium or if the reaction is reversible.

Check Your Progress

1. Define the transport number.
2. What is ionic mobilities?
3. State the Kohlrausch law.
4. Define the equivalent conductivity.
5. What is thermodynamics of electrified interface?
6. What is the phenomenon of electrocapillary?
7. State the Gouy-Chapman theory.
8. State the Butler-Volmer equation.

5.4 QUANTUM ASPECTS OF CHARGE TRANSFER AT ELECTRODE SOLUTION INTERFACE

Charge transfer is the transfer of electrons that occurs when an electron relocates from an atom or molecule to a different such entity.

Electrode reactions are characterized by charge transfer across the interface. The charge can be carried by electrons or by ions. It is shown here that when both mass and charge cross the interface, the charge must be carried by the ionic species, not by the electrons, as a result of the very large difference in the time scale for electron and ion transfer. A prime example of charge transfer by ions is metal deposition.

It is proposed that ion transfer occurs by migration of the ions across the interface, under the influence of the high electrostatic field in the double layer. The rate constants observed for metal deposition are comparable to those for outer-sphere charge transfer. These unexpectedly high rate constants for metal deposition are explained by a model in which removal of the solvation shell and reduction of the effective charge on the metal ion occur in many small steps, and a make-before-break mechanism exists, which lowers the total ***Gibbs energy*** of the system as it moves along the reaction coordinate from the initial to the final state.

Quantization of Charge Transfer

Electric charge is the transfer of electrons from one material to another. So negative charge means that there is an excess of electrons while positive charge is a deficiency of electrons. Quantization of charge means that when we say something has a given charge, we mean that that is how many times the charge of a single electron it has. Because all charges are associated with a whole electron, this is possible.

The fact that all observable charges are always some integral multiple of elementary charge $\mathbf{e = 1.6 \times 10^{-19}\ C}$ is known as quantization of electric charge. Thus $\mathbf{q = \pm ne}$, where n = 1, 2, 3, ….. $\mathbf{e = 1.6 \times 10^{-19}}$ C is the magnitude of the lowest possible charge which is carried by an electron and proton.

Tunneling

Tunneling is a quantum mechanical phenomenon when a particle is able to penetrate through a potential energy barrier that is higher in energy than the particle's kinetic energy. This amazing property of microscopic particles play important roles in explaining several physical phenomena including radioactive decay. Additionally, the principle of tunneling leads to the development of Scanning Tunneling Microscope (STM) which had a profound impact on chemical, biological and material science research.

Quantum tunnelling or tunneling (US) is the quantum mechanical phenomenon where a wavefunction can propagate through a potential barrier.

The transmission through the barrier can be finite and depends exponentially on the barrier height and barrier width. The wave function may disappear on one side and reappear on the other side. The wave function and its first derivative are continuous. In steady-state, the probability flux in the forward direction is spatially uniform. No particle or wave is lost. Tunneling occurs with barriers of thickness around 1–3 nm and smaller.

Quantum tunneling plays an essential role in physical phenomena, such as nuclear fusion. It has applications in the tunnel diode, quantum computing, and in the scanning tunneling microscope. The effect was predicted in the early 20th century. Its acceptance as a general physical phenomenon came mid-century.

Quantum tunneling is projected to create physical limits to the size of the transistors used in microelectronics, due to electrons being able to tunnel past transistors that are too small.

Tunneling may be explained in terms of the ***Heisenberg uncertainty principle*** in that a quantum object can be known as a wave or as a particle in general. In other words, the ***uncertainty*** in the exact location of light particles allows these particles to break rules of classical mechanics and move in space without passing over the potential energy barrier. Quantum tunnelling may be one of the mechanisms of proton decay.

NOTES

5.5 SEMICONDUCTORS

This text focuses on the semiconductors and their properties. Most widely used semiconductors are Silicon (Si), Germanium (Ge), Selenium (Se) etc., that exists as simple semiconductors and compound semiconductors such as Gallium Arsenide (GaAs), Indium Phosphate (InP), Gallium Nitride (GaN) etc. Semiconductors based on the purity of the materials are classified as

- Intrinsic Semiconductors
- Extrinsic semiconductors

Intrinsic Semiconductors

Semiconductors that exists in pure form without any impurities added are called as intrinsic semiconductors. Consider the semiconductor Silicon, Si with atomic number 14. It has 14 number of protons and 14 number of electrons. The first shell occupies 2 electrons, the second shell occupies 8 electrons and the third shell which could accommodate 18 electrons has only 4 valence electrons. Similarly, germanium with an atomic number of 32 as shown in Figure 5.5a has 4 shells with an outermost shell consisting of 4 valence electrons. These atoms exist in the crystalline structure with bonding as shown in Figure 5.5b. One atom of silicon shares the bonding with 4 other atoms thereby filling the 3rd shell of an atom with all 8 electrons creating a stable composition of silicon crystal. This type of bonding is known as covalent bonding.

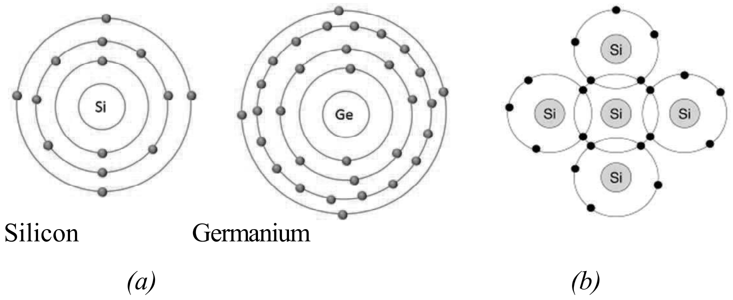


Fig. 5.5 *(a)Atomic Structure of Silicon and Germanium, (b) Crystalline Structure of Silicon*

Intrinsic semiconductors behave as perfect insulators under normal room temperatures. Silicon and germanium that consists of 4 valence electrons in their outermost shells are also known as **tetravalent atoms**. Similarly, atoms with three valence electrons are known as **trivalent atoms** and atoms with five valence electrons are known as **pentavalent atoms**.

Conduction in Intrinsic Semiconductors

When an external energy is supplied to the intrinsic semiconductor crystal, the electrons absorb the energy supplied and gain enough energy to break the covalent bond and are set free to move as free electrons in the crystal. Such free electrons move randomly inside the crystal until they lose their energy and finds a bonding pair of an electron with some other atom. When the electron leaves a covalent bond due to external energy, they leave behind a vacant space known as holes. Electrons are negatively charged and the vacant hole spaces wanting for electrons to occupy the space are considered as positively charged. When the free electrons leave the covalent bonding due to external energy, they form an electron-hole pair.

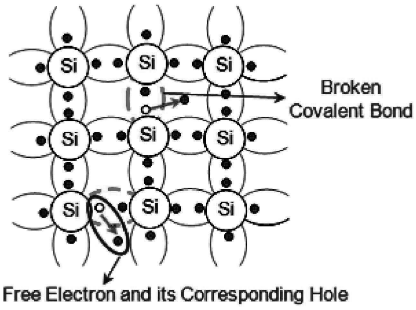


Fig. 5.6 *Conduction Inside Intrinsic Semiconductors*

Electron Current and Hole Current

Current constituted by electrons inside the semiconductor crystal are called an **electron current**. Since electrons are negatively charged, when a potential is applied across the semiconductor crystal, the electrons are attracted towards the positive terminal of the battery.

Current constituted by holes inside a semiconductor crystal are known as **hole current**. Though the holes (vacant spaces) do not move, consequent movement of electrons creates an illusion such that holes move, but in the opposite direction as that of the electron. Electron movement occurs towards the positive polarity of the battery and the hole movement is illusioned to appear as though holes move towards negative terminal of the battery. The movement of holes, i.e., the movement towards a negative terminal (from the positive terminal) is considered as the conventional current movement and hence the hole movement is considered as conventional current flow and the electron movement is considered as the electron flow. The electron and hole current is depicted in Figure 5.7

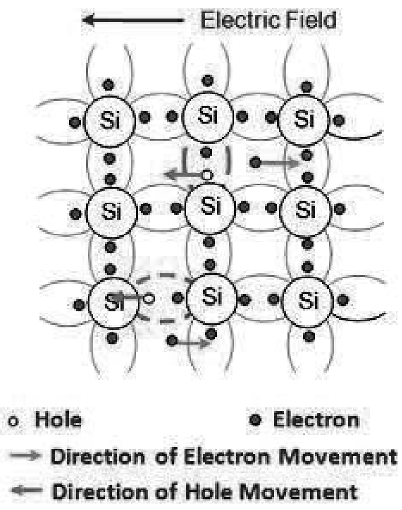


Fig. 5.7 *Electron and Hole Current*

The hole current is known as the conventional current is opposite to the direction of the electron movement and flows from the positive terminal of the battery to the negative terminal of the battery. The electron current and hole current occur due to two process, they are

- Drift and
- Diffusion.

Drift Current

The current flow that takes place due to the application of the external potential through a battery results in drifting of the electrons, thereby resulting in drift current. When an external energy is applied to the semiconductor crystal, the electrons gain energy and starts to drift across the crystal and tends move towards the battery terminal (positive terminal). Such currents are said to be drift current caused due to drifting of electrons.

Diffusion Current

Diffusion current occurs due to the movement of electrons through diffusion when they move from higher concentration area to a lower concentration area of the semiconductor crystal without applying any external force or energy.

Extrinsic Semiconductors

An extrinsic semiconductor is one that has been doped, i.e., during manufacture of the semiconductor crystal a trace element or chemical called a doping agent has been incorporated chemically into the crystal, for the purpose of giving it different electrical properties than the pure semiconductor crystal, which is called an intrinsic semiconductor. In an extrinsic semiconductor, these foreign dopant atoms in the crystal lattice provide the charge carriers which carry electric current through the crystal. The doping agents used are of two types, resulting in two types of extrinsic semiconductor. An electron donor dopant is an atom which, when incorporated in the crystal, releases a mobile conduction electron into the crystal lattice. An extrinsic semiconductor which has been doped with electron donor atoms is called an *n*-type semiconductor, because the majority of charge carriers in the crystal are negative electrons. An electron acceptor dopant is an atom which accepts an electron from the lattice, creating a vacancy where an electron should be called a hole which can move through the crystal like a positively charged particle. An extrinsic semiconductor which has been doped with electron acceptor atoms is called a *p*-type semiconductor, because the majority of charge carriers in the crystal are positive holes.

Doping is the key to the extraordinarily wide range of electrical behaviour that semiconductors can exhibit, and extrinsic semiconductors are specifically used to make semiconductor electronic devices, such as diodes, transistors, integrated circuits, semiconductor lasers, LEDs, and photovoltaic cells. Sophisticated semiconductor fabrication processes like photolithography can implant different dopant elements in different regions of the same semiconductor crystal wafer, creating semiconductor devices on the wafer's surface. For example a common type of transistor, the *n-p-n* bipolar transistor, consists of an extrinsic semiconductor crystal with two regions of *n*-type semiconductor, separated by a region of *p*-type semiconductor with metal contacts attached to each part.

Intrinsic semiconductors are the purest form of semiconductors. Their conductivity of electricity is limited. They have an equal number of electrons and holes. To make semiconductors practically relevant with better conduction of current, it is important to enhance the conduction capability of semiconductors. One such technique to enhance the conductivity is by the process of **doping**. Doping is a process of adding impurities to the intrinsic semiconductors, such that the conductivity of the semiconductors is improved. The impurity that is added to the semiconductor is called as a dopant. The doped semiconductors are called as extrinsic semiconductors. The type of impurities added may enhance the number of electrons or they may enhance the number of holes. Hence, depending on the type of impurities, the extrinsic semiconductors can be classified as

- *n*-type semiconductors
- *p*-type semiconductors.

When an intrinsic semiconductor is added with an impurity with pentavalent atoms, *n*-type semiconductors are formed. When an intrinsic semiconductor is added with a trivalent impurity atom, *p*-type semiconductors are formed. Pentavalent impurity atoms are also known as donor atoms and trivalent atoms are known as acceptor atoms. Atoms that donate atoms to the host atoms are called donor atoms and the atoms that accept an electron from the host atoms are called acceptor atoms.

n-Type Semiconductor

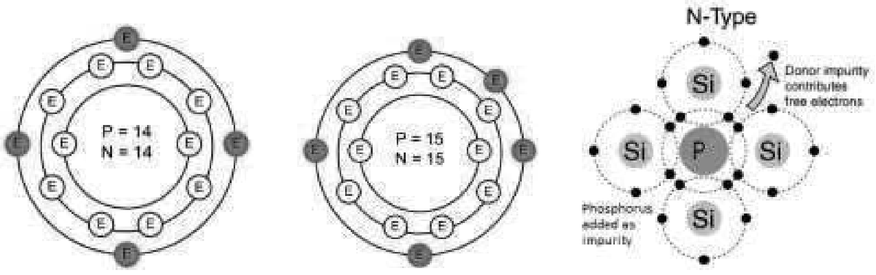


Fig. 5.8 *n-Type Semiconductor*

When a pentavalent impurity atom from group V of the periodic table such as Phosphorus (P) or Arsenic (As) is added to the intrinsic silicon atom, *n*-type semiconductors are formed.

When the *n*-type impurity atom (donor atoms) is added with the intrinsic silicon atom, the four valence electrons out of five valence electrons in the impurity atom forms a covalent bond with the four silicon atoms as shown in Figure 5.8. The remaining one valence electrons from the impurity atoms remain as free electron inside the mixture crystal. Similarly, when 1 of phosphorus can generated free electrons of the order of number of free electrons. Number of free electrons required are controlled by the amount of pentavalent impurity added to the intrinsic silicon atom.

NOTES

The conductivity of *n*-type semiconductors

The mobility of electrons is approximately three times that of the mobility of holes. When more free electrons are added to the intrinsic semiconductor, the average energy level of the semiconductor increases. This makes the electrons move easier from the valence band to the conduction band even with an application of the small amount of an external potential. In addition, the Fermi level, which marks the energy level of electrons is closer to the conduction band as shown in Figure 5.9. In *n*-type semiconductors since the electrons are more than the number of holes, electrons are known as majority carriers and the holes are known as minority carriers. The current constituted by majority carriers (electrons) are predominant and the current constituted by minority carriers (holes) are negligent.

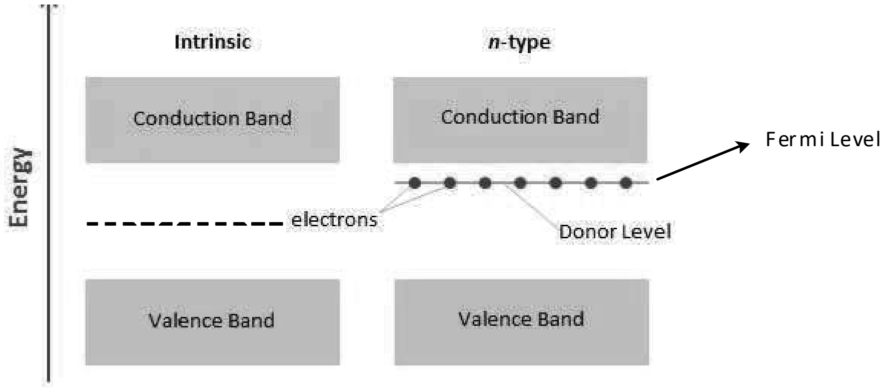


Fig. 5.9 *n-Type Semiconductor Band Diagram*

p-Type Semiconductors

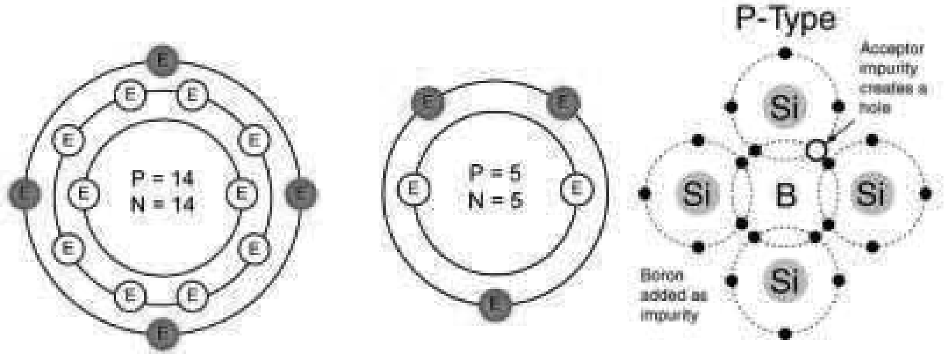


Fig. 5.10 *p-Type Semiconductor*

When a trivalent impurity atom from group III of the periodic table such as Boron (B) or Gallium (Ga) is added to the intrinsic silicon atom, *p*-type semiconductors are formed.

When the p-type impurity atom (acceptor atoms) is added with the intrinsic silicon atom, the three valence electrons of the acceptor atoms form a covalent bond with the three silicon atoms leaving behind one silicon atom form an electron-hole pair as shown in Figure 5.10. The one hole generated due to nonavailability of an electron to fill from the impurity atom forms one electron-hole pair. Similarly, when 1 of Boron can generated electron-hole pairs of the order of numba er of holes. Number of holes required are controlled by the amount of trivalent impurity added to the intrinsic silicon atom.

The conductivity of *p*-type semiconductors

When more holes are added to the intrinsic semiconductor, the average energy level of the semiconductor decreases. Hence, a larger magnitude of external energy needs to be applied to make the electrons conduct. In other words to make the electrons move from the valence band to conduction band. However, it is easier to make the electrons conduct in the reverse direction by applying a negative potential. The Fermi level, which marks the energy level of electrons is closer to the valence band as shown in Figure 5.11. In *p*-type semiconductors since the holes are more than the number of electrons, holes are known as majority carriers in *p*-type semiconductors and the electrons are known as minority carriers. The current constituted by majority carriers (holes) are predominant and the current constituted by minority carriers (electrons) are negligent.

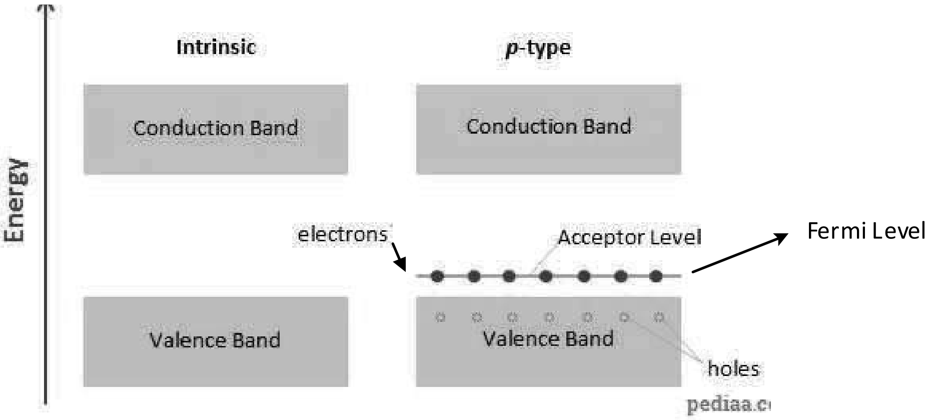


Fig. 5.11 *p-Type Semiconductor Band Diagram*

p-n Junction Diode

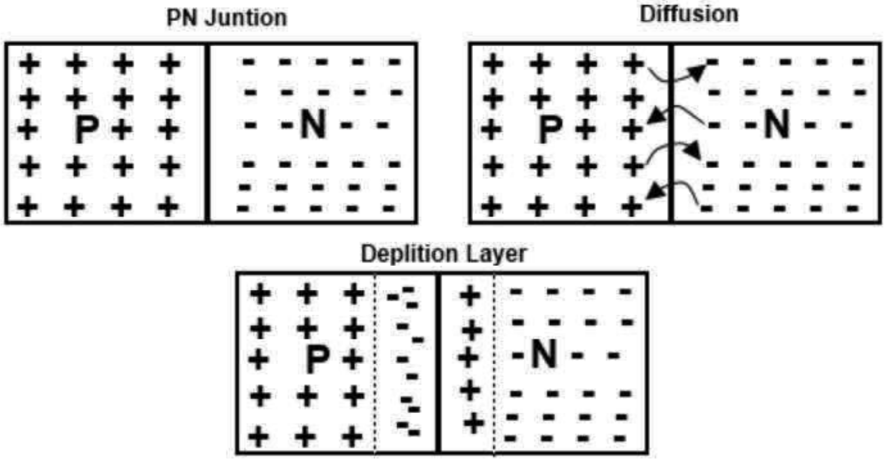


Fig. 5.12 *p-n Diffusion*

When a *p*-type semiconductor and *n*-type semiconductor are joined together, diffusion takes place. Since the *p*-type material is highly concentrated with holes leading to an overall high positive charge material and *n*-type a negatively charged material due to the concentration of electrons, when joined together, they together generate a high potential on the *p*-type side and now potential on the *n*-type side. This leads to the process of diffusion making the electrons to move towards the *p*-side. As electrons move towards the *p*-type crossing the junction, they leave behind holes. The electrons spend enough energy to cross over the junction after which they occupy a hole position nearer to the junction. Thus, holes are formed on the *n*-type side of the junction and electrons on the *p*-type junction. Any electron that wants to cross over the junction further must have enough energy to overcome the holes and the junction together. Thus, creates a region of depletion of charges with positive charges on *n*-type and negative charges on *p*-type. The buildup of the depletion region continues until the electrons cannot diffuse further. Once the diffusion stops, the potential difference created by the process of electron diffusion results in approximately 0.7 volts for silicon semiconductors and 0.3 volts for germanium semiconductors. This potential difference created by the process of diffusion is also known as barrier potential. The electrons that require moving to the *p*-type material further must overcome the barrier potential of 0.7V for silicon material. The electrons alone do not possess such amount of energy to cross the barrier potential and hence on the application of an external voltage equal to the barrier potential is required to make the electrons move to the other side of the *p*-*n* junction.

The barrier potential depends on various factors as follows:

- Type of semiconductor
- Type of impurity
- External atmospheric temperature and
- The concentration of intrinsic semiconductor

5.6 ELECTROCATALYSIS

An electrocatalyst is a catalyst that participates in electrochemical reactions. Electrocatalysts are a specific form of catalysts that function at electrode surfaces or, most commonly, may be the electrode surface itself. An electrocatalyst can be heterogeneous such as a platinized electrode. Homogeneous electrocatalysts, which are soluble, assist in transferring electrons between the electrode and reactants, and/or facilitate an intermediate chemical transformation described by an overall half reaction.

Electrocatalysis can be defined as the heterogeneous catalysis of electrochemical reactions, which occur at the electrode–electrolyte interface and where the electrode plays both the role of electron donor/acceptor and of catalyst.

Electrocatalysis facilitates conversion between electrical and chemical energy in fuel cells and electrolysis devices. Rational design of the electrocatalytic interface, including selection of electrode and electrolyte compositions and their optimal structure, requires establishing composition–structure–function relationships. Electronic structure calculations, most typically performed within the framework of Density Functional Theory (DFT), help to develop these relationships by determining how elementary reaction energetics are impacted by electrocatalysis composition and structure. Though DFT methods can explain and predict catalytic behavior at the most fundamental level, they are challenged by difficulties in representing the length and time scales associated with processes at the dynamic electrode–electrolyte interface.

Electrocatalysis is concerned with electrochemical reactions at the interface between an electrolyte and an electrode. Electrocatalysts can be heterogeneous such as bulk platinum electrodes or homogeneous like an enzyme or a coordination complex. Electrocatalytic processes are technologically rather relevant as they occur for example in fuel cells or electrolyzers. Even in electrochemical energy storage in batteries, electrocatalytic processes occur, in particular in metal–air batteries.

Electrocatalytic processes are of an immense technological relevance in the context of our future sustainable energy technology. For example, decades of intense research have not been sufficient to reduce the substantial overpotential associated with the Oxygen Reduction Reaction (ORR), one of the crucial reactions in fuel cells and metal–air batteries.

Electrocatalysis, from a general chemist's point of view, is usually described as increase in reaction rate on increasing potential that is electric field. Yet an electrochemist, inconsiderate of this typical explanation, defines electrocatalysis as an introduction of new material on electrode surface to alter the electrochemical reaction rate providing new reaction pathways under same potential or electric field without inhibiting electron transfer rate. Even if electron transfer between surface material and reactant can proceed without specific interaction, the surface adsorption of intermediate species is the key step in electrocatalysis as it provides alternate energy pathways.

Electrolysis of Water

Electrolysis of water is the process of using electricity to decompose water into oxygen and hydrogen gas by the process of electrolysis. Hydrogen gas released in this way can be used as hydrogen fuel, or remixed with the oxygen to create oxyhydrogen gas, which is used in welding and other applications.

The Standard Hydrogen Electrode (SHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. Its absolute electrode potential is estimated to be 4.44 ± 0.02 V at 25 °C, but to form a basis for comparison with all other electroreactions, hydrogen's standard electrode potential (E°) is declared to be zero volts at any temperature.Potentials of any other electrodes are compared with that of the standard hydrogen electrode at the same temperature.

Hydrogen electrode is based on the redox half cell:

$$2\,H^+ (aq) + 2\,e^- \rightarrow H_2 (g)$$

This redox reaction occurs at a platinized platinum electrode. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced form and oxidised form is maintained at unity. That implies that the pressure of hydrogen gas is 1 bar (100 kPa) and the activity coefficient of hydrogen ions in the solution is unity. The activity of hydrogen ions is their effective concentration, which is equal to the formal concentration times the activity coefficient. These unit-less activity coefficients are close to 1.00 for very dilute water solutions, but usually lower for more concentrated solutions. The Nernst equation should be written as:

$$E = \frac{RT}{F} \ln \frac{a_{\mathrm{H}^+}}{\sqrt{p_{\mathrm{H}_2}/p^0}}$$

$$E = -\frac{2.303RT}{F}\mathrm{pH} - \frac{RT}{2F} \ln \frac{p_{\mathrm{H}_2}}{p^0}$$

Where:

a_{H+} is the activity of the hydrogen ions, $a_{H+} = f_{H+} C_{H+} / C^0$

P_{H2} is the partial pressure of the hydrogen gas, in pascals, Pa

R is the universal gas constant

T is the temperature, in kelvins

F is the Faraday constant (the charge per mole of electrons), equal to 9.6485309×10^4 C mol$^{”1}$

P^0 is the standard pressure, 10^5 Pa

Sometimes called water splitting, electrolysis requires a minimum potential difference of 1.23 volts.

Check Your Progress

9. Define the electrode reaction.
10. Give the names of semiconductor which are most widely used.
11. Define the tunnelling.
12. Define electrocatalyst.
13. How will you define electrocatalysis?
14. Which gas is released in the process of electrolysis of water?
15. What is the other name of the process of electrolysis of water?

5.7 HYDROGEN ELECTRODE

Standard Hydrogen Electrode

The Standard Hydrogen Electrode (abbreviated as SHE), also called Normal Hydrogen Electrode (NHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. Its absolute electrode potential is estimated to be $4.44. \pm 0.02V$ at 25°C, but to form a basis for comparison with all other electrode reactions, Hydrogen's Standard Electrode Potential (E^0) is declared to be zero at all temperatures. Potentials of any other electrodes are compared with that of the standard hydrogen electrode at the same temperature.

Hydrogen electrode is based on the redox half cell,

$$2H^+ (aq) + 2e^- \rightarrow H_2(g)$$

This redox reaction occurs at platinized platinum electrode.

The Nernst equation should be written as,

$$E = \frac{RT}{F} In \frac{a_{H^+}}{(pH_2 / p^0)^{1/2}}$$

Or

$$E = \frac{2.303RT}{F} pH - \frac{RT}{2F} In\, pH_2 / p^0$$

Where:

(i) a_{H^+} is the activity of the hydrogen ions, $a_{H^+} = f_H^+ C_H^+ / C^0$

(ii) pH_2 is the partial pressure of the hydrogen gas, in Pascals, *Pa*

(iii) *R* is the universal gas constant

(iv) *T* is the temperature, in Kelvins

(v) *F* is the Faraday constant (the charge per a mole of electrons), equal to 9.6485 C mol^{-1}

(vi) p^0 is the standard pressure 10^5 in Pa

Construction

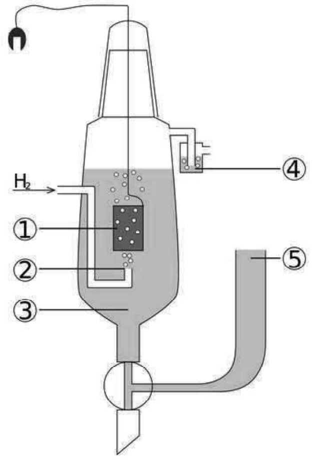


Fig. 5.13 *The Scheme of the Standard Hydrogen Electrode*

In the above Figure 4.4 the detailed description is given as,

(i) Platinized platinum electrode

(ii) Hydrogen blow

(iii) Solution of the acid with activity of $H^+ = 1$ mol kg^{-1}

(iv) Hydroseal for prevention of the oxygen interference

(v) Reservoir through which the second half-element of the Galvanic cell should be attached. This creates an ionically conductive path to the working electrode of interest.

The choice of platinum for the hydrogen electrode is due to several factors:

(i) Inertness of platinum (it does not corrode)

(ii) The capability of platinum to catalyze the reaction of proton reduction

(iii) A high intrinsic exchange current density for proton reduction on platinum (see the data in the table for comparison of platinum with other materials)

(iv) Excellent reproducibility of the potential (bias of less than $10\mu V$ when two well-made hydrogen electrodes are compared with one another.

The surface of platinum is platinized (i.e., covered with platinum black) because of:

(i) Necessity to employ electrode with large true surface area. The greater the electrode true area, the faster electrode kinetics.

(ii) Necessity to use electrode material which can adsorb hydrogen at its interface. Platinization improves electrode kinetics.

Nevertheless, other metals can be used for building electrodes with a similar function, for example, palladium-hydrogen electrode.

Because of the high adsorption activity of the platinized platinum electrode, it's very important to protect electrode surface and solution from the presence of organic substances as well as from oxygen of atmosphere. Inorganic ions that can reduce to a lower valency state at the electrode also have to be avoided (For example, Fe^{3+}, CrO_4^{2-}).

Cations that can reduce and deposit on the platinum can be source of interference, such as silver, mercury, copper, lead, cadmium and thallium. Substances that can inactivate ('poison') the catalytic sites include arsenic, sulfides and other sulfur compounds, colloidal substances, alkaloids, and material found in living systems.

5.8 BIOELECTROCHEMISTRY

Bioelectrochemistry is a branch of electrochemistry and biophysical chemistry concerned with electrophysiological topics like cell electron-proton transport, cell membrane potentials and electrode reactions of redox enzymes.

History of Bioelectrochemistry

The beginnings of bioelectrochemistry, as well as those of electrochemistry, are closely related to physiology through the works of Luigi Galvani and then Alessandro Volta. The first modern work in this field is considered that of the German physiologist Julius Bernstein (1902) concerning the source of biopotentials due to different ion concentration through the cell's membrane. The domain of bioelectrochemistry has grown considerably over the past century, maintaining the close connections to various medical and biological and engineering disciplines like electrophysiology, biomedical engineering, and enzyme kinetics. The achievements in this field have been awarded several Nobel prizes for Physiology or Medicine. Among prominent electrochemists who have contributed to this field one could mention John Bockris.

5.8.1 Threshold Membrane Phenomena

In electrophysiology, the threshold potential is the critical level to which a membrane potential must be depolarized to initiate an action potential. In neuroscience, threshold potentials are necessary to regulate and propagate signaling in both the Central Nervous System (CNS) and the Peripheral Nervous System (PNS).

Most often, the threshold potential is a membrane potential value between –50 and –55 mV, but can vary based upon several factors. A neuron's resting membrane potential (–70 mV) can be altered to either increase or decrease likelihood of reaching threshold via sodium and potassium ions. An influx of sodium into the cell through open, voltage-gated sodium channels can depolarize the membrane past threshold and thus excite it while an efflux of potassium or influx of chloride can hyperpolarize the cell and thus inhibit threshold from being reached.

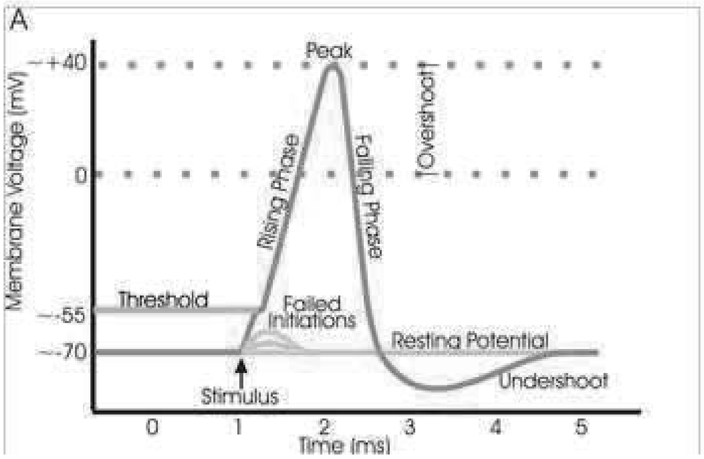


Fig. 5.17 *Schematic Action Potential*

Invention of Threshold potential

Initial experiments revolved around the concept that any electrical change that is brought about in neurons must occur through the action of ions. The German physical chemist Walther Nernst applied this concept in experiments to discover nervous excitability, and concluded that the local excitatory process through a semi-permeable membrane depends upon the ionic concentration. Also, ion concentration was shown to be the limiting factor in excitation. If the proper concentration of ions was attained, excitation would certainly occur. This was the basis for discovering the threshold value.

Along with reconstructing the action potential in the 1950s, Alan Lloyd Hodgkin and Andrew Huxley were also able to experimentally determine the mechanism behind the threshold for excitation. It is known as the Hodgkin–Huxley model. Through use of voltage clamp techniques on a squid giant axon, they discovered that excitable tissues generally exhibit the phenomenon that a certain membrane potential must be reached in order to fire an action potential. Since the experiment yielded results through the observation of ionic conductance changes, Hodgkin and Huxley used these terms to discuss the threshold potential. They initially suggested that there must be a discontinuity in the conductance of either sodium or potassium, but in reality both conductances tended to vary smoothly along with the membrane potential.

They soon discovered that at threshold potential, the inward and outward currents, of sodium and potassium ions respectively, were exactly equal and opposite. As opposed to the resting membrane potential, the threshold potential's conditions exhibited a balance of currents that were unstable. Instability refers to the fact that any further depolarization activates even more voltage-gated sodium channels, and the incoming sodium depolarizing current overcomes the delayed outward current of potassium. At resting level, on the other hand, the potassium and sodium currents are equal and opposite in a stable manner, where a sudden, continuous flow of ions should not result. The basis is that at a certain level of depolarization, when the currents are equal and opposite in an unstable manner, any further entry of positive charge generates an action potential. This specific value of depolarization (in mV) is otherwise known as the threshold potential.

Physiological function and characteristics of Threshold Potential

The threshold value controls whether or not the incoming stimuli are sufficient to generate an action potential. It relies on a balance of incoming inhibitory and excitatory stimuli. The potentials generated by the stimuli are additive, and they may reach threshold depending on their frequency and amplitude. Normal functioning of the central nervous system entails a summation of synaptic inputs made largely onto a neuron's dendritic tree. These local graded potentials, which are primarily associated with external stimuli, reach the axonal initial segment and build until they manage to reach the threshold value. The larger the stimulus, the greater the depolarization, or attempt to reach threshold. The task of depolarization requires several key steps that rely on anatomical factors of the cell. The ion conductances involved depend on the membrane potential and also the time after the membrane potential changes.

Resting membrane potential

The phospholipid bilayer of the cell membrane is, in itself, highly impermeable to ions. The complete structure of the cell membrane includes many proteins that are embedded in or completely cross the lipid bilayer. Some of those proteins allow for the highly specific passage of ions, ion channels. Leak potassium channels allow potassium to flow through the membrane in response to the disparity in concentrations of potassium inside (high concentration) and outside the cell (low). The loss of positive(+) charges of the potassium(K^+) ions from the inside of the cell results in a negative potential there compared to the extracellular surface of the membrane. A much smaller 'Leak' of sodium(Na^+) into the cell results in the actual resting potential, about –70 mV, being less negative than the calculated potential for K^+ alone, the equilibrium potential, about –90 mV.The sodium-potassium ATPase is an active transporter within the membrane that pumps potassium (2 ions) back into the cell and sodium (3 ions) out of the cell, maintaining the concentrations of both ions as well as preserving the voltage polarization.

Depolarization

However, once a stimulus activates the voltage-gated sodium channels to open, positive sodium ions flood into the cell and the voltage increases. This process can also be initiated by ligand or neurotransmitter binding to a ligand-gated channel. More sodium is outside the cell relative to the inside, and the positive charge within the cell propels the outflow of potassium ions through delayed-rectifier voltage-gated potassium channels. Since the potassium channels within the cell membrane are delayed, any further entrance of sodium activates more and more voltage-gated sodium channels. Depolarization above threshold results in an increase in the conductance of Na sufficient for inward sodium movement to swamp outward potassium movement immediately. If the influx of sodium ions fails to reach threshold, then sodium conductance does not increase a sufficient amount to override the resting potassium conductance. In that case, subthreshold membrane potential oscillations are observed in some type of neurons. If successful, the sudden influx of positive charge depolarizes the membrane, and potassium is delayed in re-establishing, or hyperpolarizing, the cell. Sodium influx depolarizes the cell in attempt to establish its own equilibrium potential (about +52 mV) to make the inside of the cell more positive relative to the outside.

Variations

The value of threshold can vary according to numerous factors. Changes in the ion conductances of sodium or potassium can lead to either a raised or lowered value of threshold. Additionally, the diameter of the axon, density of voltage activated sodium channels, and properties of sodium channels within the axon all affect the threshold value. Typically in the axon or dendrite, there are small depolarizing or hyperpolarizing signals resulting from a prior stimulus. The passive spread of these signals depend on the passive electrical properties of the cell. The signals can only continue along the neuron to cause an action potential further down if they are strong enough to make it past the cell's membrane resistance and capacitance. For example, a neuron with a large diameter has more ionic channels in its membrane than a smaller cell, resulting in a lower resistance to the flow of ionic current. The current spreads quicker in a cell with less resistance, and is more likely to reach the threshold at other portions of the neuron.

The threshold potential has also been shown experimentally to adapt to slow changes in input characteristics by regulating sodium channel density as well as inactivating these sodium channels overall. Hyperpolarization by the delayed-rectifier potassium channels causes a relative refractory period that makes it much more difficult to reach threshold. The delayed-rectifier potassium channels are responsible for the late outward phase of the action potential, where they open at a different voltage stimulus compared to the quickly activated sodium channels. They rectify, or repair, the balance of ions across the membrane by opening and letting potassium flow down its concentration gradient from inside to outside the cell. They close slowly as well, resulting in an outward flow of positive charge that exceeds the balance necessary. It results in excess negativity in the cell, requiring an extremely large stimulus and resulting depolarization to cause a response.

Tracking techniques

Threshold tracking techniques test nerve excitability, and depend on the properties of axonal membranes and sites of stimulation. They are extremely sensitive to the membrane potential and changes in this potential. These tests can measure and compare a control threshold (or resting threshold) to a threshold produced by a change in the environment, by a preceding single impulse, an impulse train, or a subthreshold current. Measuring changes in threshold can indicate changes in membrane potential, axonal properties, and/or the integrity of the myelin sheath.

Threshold tracking allows for the strength of a test stimulus to be adjusted by a computer in order to activate a defined fraction of the maximal nerve or muscle potential. A threshold tracking experiment consists of a 1-ms stimulus being applied to a nerve in regular intervals. The action potential is recorded downstream from the triggering impulse. The stimulus is automatically decreased in steps of a set percentage until the response falls below the target (generation of an action potential). Thereafter, the stimulus is stepped up or down depending on whether the previous response was lesser or greater than the target response until a resting (or control) threshold has been established. Nerve excitability can then be changed by altering the nerve environment or applying additional currents. Since the value of a single threshold current provides little valuable information because it varies within and between subjects, pairs of threshold measurements, comparing the control threshold to thresholds produced by refractoriness, supernormality, strength-duration time constant or 'Threshold Electrotonus' are more useful in scientific and clinical study.

Tracking threshold has advantages over other electrophysiological techniques, like the constant stimulus method. This technique can track threshold changes within a dynamic range of 200% and in general give more insight into axonal properties than other tests. Also, this technique allows for changes in threshold to be given a quantitative value, which when mathematically converted into a percentage, can be used to compare single fiber and multifiber preparations, different neuronal sites, and nerve excitability in different species.

Threshold Electrotonus

A specific threshold tracking technique is threshold electrotonus, which uses the threshold tracking set-up to produce long-lasting subthreshold depolarizing or hyperpolarizing currents within a membrane. Changes in cell excitability can be observed and recorded by creating these long-lasting currents. Threshold decrease is evident during extensive depolarization, and threshold increase is evident with extensive hyperpolarization. With hyperpolarization, there is an increase in the resistance of the internodal membrane due to closure of potassium channels, and the resulting plot 'Fans Out'. Depolarization produces has the opposite effect, activating potassium channels, producing a plot that 'Fans In'.

The most important factor determining threshold electrotonus is membrane potential, so threshold electrotonus can also be used as an index of membrane potential. Furthermore, it can be used to identify characteristics of significant medical conditions through comparing the effects of those conditions on threshold potential with the effects viewed experimentally. For example, ischemia and depolarization cause the same 'Fanning In' effect of the electrotonus waveforms. This observation leads to the conclusion that ischemia may result from over-activation of potassium channels.

Clinical significance

The role of the threshold potential has been implicated in a clinical context, namely in the functioning of the nervous system itself as well as in the cardiovascular system.

Febrile seizures

A febrile seizure, or 'Fever Fit', is a convulsion associated with a significant rise in body temperature, occurring most commonly in early childhood. Repeated episodes of childhood febrile seizures are associated with an increased risk of temporal lobe epilepsy in adulthood.

With patch clamp recording, an analogous state was replicated in vitro in rat cortical neurons after induction of febrile body temperatures; a notable decrease in threshold potential was observed. The mechanism for this decrease possibly involves suppression of inhibition mediated by the GABAB receptor with excessive heat exposure.

ALS and diabetes

Abnormalities in neuronal excitability have been noted in amyotrophic lateral sclerosis and diabetes patients. While the mechanism ultimately responsible for the variance differs between the two conditions, tests through a response to ischemia indicate a similar resistance, ironically, to ischemia and resulting paresthesias. As ischemia occurs through inhibition of the sodium-potassium pump, abnormalities in the threshold potential are hence implicated.

Arrythmia

Since the 1940s, the concept of diastolic depolarization, or 'Pacemaker Potential', has become established; this mechanism is a characteristic distinctive of cardiac tissue. When the threshold is reached and the resulting action potential fires, a heartbeat results from the interactions; however, when this heartbeat occurs at an irregular time, a potentially serious condition known as arrythmia may result.

Use of medications

A variety of drugs can present prolongation of the QT interval as a side effect. Prolongation of this interval is a result of a delay in sodium and calcium channel inactivation; without proper channel inactivation, the threshold potential is reached prematurely and thus arrhythmia tends to result. These drugs, known as pro-arrhythmic agents, include antimicrobials, antipsychotics, methadone, and, ironically, antiarrhythmic agents. The use of such agents is particularly frequent in intensive care units, and special care must be exercised when QT intervals are prolonged in such patients: arrhythmias as a result of prolonged QT intervals include the potentially fatal torsades de pointes, or TdP.

Role of diet

Diet may be a variable in the risk of arrhythmia. Polyunsaturated fatty acids, found in fish oils and several plant oils, serve a role in the prevention of arrhythmias. By inhibiting the voltage-dependent sodium current, these oils shift the threshold potential to a more positive value; therefore, an action potential requires increased depolarization. Clinically therapeutic use of these extracts remains a subject of research, but a strong correlation is established between regular consumption of fish oil and lower frequency of hospitalization for atrial fibrillation, a severe and increasingly common arrythmia.

5.8.2 Nernst–Planck Equation

The time dependent form of the Nernst–Planck equation is a conservation of mass equation used to describe the motion of a charged chemical species in a fluid medium. It extends Fick’s law of diffusion for the case where the diffusing particles are also moved with respect to the fluid by electrostatic forces: It is named after Walther Nernst and Max Planck.

Equation of Nernst–Planck equation

$E = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}$. It describes the flux of ions under the influence of both an ionic concentration gradient “c and an electric field

$$\frac{\partial c}{\partial t} = -\nabla \cdot J \quad | \quad J = -\left[D\nabla c - uc + \frac{Dze}{k_{\mathrm{B}}T}c\left(\nabla\phi + \frac{\partial \mathbf{A}}{\partial t}\right)\right]$$

$$\Longleftrightarrow \quad \frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c - uc + \frac{Dze}{k_{\mathrm{B}}T}c\left(\nabla\phi + \frac{\partial \mathbf{A}}{\partial t}\right)\right]$$

Where J is the diffusion flux density, t is time, D is the diffusivity of the chemical species, c is the concentration of the species, z is the valence of ionic species, e is the elementary charge, k_B is the Boltzmann constant, T is the temperature, u is velocity of fluid, ϕ is the electric potential, $\mathbf{A}$ is the magnetic vector potential.

If the diffusing particles are themselves charged they are influenced by the electric field. hence the nernst–planck equation is applied in describing the ion-exchange kinetics in soils.

Setting time derivatives to zero, and the fluid velocity to zero (only the ion species moves),

$$J = -\left[D\nabla c + \frac{Dze}{k_{\mathrm{B}}T}c\left(\nabla\phi + \frac{\partial \mathbf{A}}{\partial t}\right)\right]$$

In the static electromagnetic conditions, one obtains the steady state Nernst–Planck equation

$$J = -\left[D\nabla c + \frac{Dze}{k_{\mathrm{B}}T}c(\nabla\phi)\right]$$

Finally, in units of mol/($m^2 \cdot s$) and the gas constant R, one obtains the more familiar form:

$$J = -D\left[\nabla c + \frac{zF}{RT}c(\nabla\phi)\right]$$

where F is the Faraday constant equal to $N_A e$.

5.8.3 Hodges - Huxley Equations

The Hodgkin–Huxley model, or conductance-based model, is a mathematical model that describes how action potentials in neurons are initiated and propagated. It is a set of nonlinear differential equations that approximates the electrical characteristics of excitable cells such as neurons and cardiac myocytes. It is a continuous-time dynamical system.

Alan Hodgkin and Andrew Huxley described the model in 1952 to explain the ionic mechanisms underlying the initiation and propagation of action potentials in the squid giant axon. They received the 1963 Nobel Prize in Physiology or Medicine for this work.

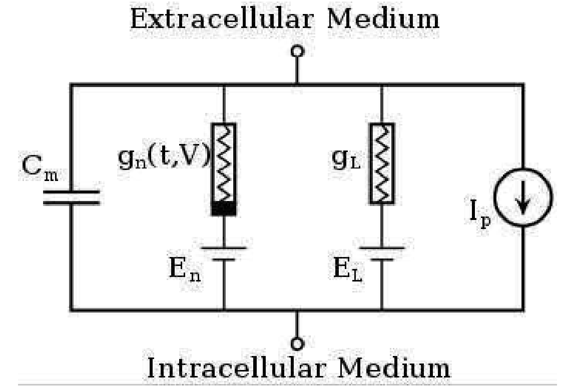


Fig. 5.18 *Basic components of Hodgkin–Huxley-type models*

Basic components of Hodgkin–Huxley model

The typical Hodgkin–Huxley model treats each component of an excitable cell as an electrical element (as shown in the figure). The lipid bilayer is represented as a capacitance (C_m). Voltage-gated ion channels are represented by electrical conductances (g_n, where n is the specific ion channel) that depend on both voltage and time. Leak channels are represented by linear conductances (g_L). The electrochemical gradients driving the flow of ions are represented by voltage sources (E_n) whose voltages are determined by the ratio of the intra- and extracellular concentrations of the ionic species of interest. Finally, ion pumps are represented by current sources (I_p).[clarification needed] The membrane potential is denoted by V_m.

Mathematically, the current flowing through the lipid bilayer is written as

$$I_c = C_m \frac{\mathrm{d}V_m}{\mathrm{d}t}$$

and the current through a given ion channel is the product

$$I_i = g_i(V_m - V_i)$$

where V_i is the reversal potential of the *i*-th ion channel. Thus, for a cell with sodium and potassium channels, the total current through the membrane is given by:

$$I = C_m \frac{\mathrm{d}V_m}{\mathrm{d}t} + g_K(V_m - V_K) + g_{Na}(V_m - V_{Na}) + g_l(V_m - V_l)$$

where I is the total membrane current per unit area, C_m is the membrane capacitance per unit area, g_K and g_{Na} are the potassium and sodium conductances per unit area, respectively, V_K and V_{Na} are the potassium and sodium reversal potentials, respectively, and g_l and V_l are the leak conductance per unit area and leak reversal potential, respectively. The time dependent elements of this equation are V_m, g_{Na}, and g_K, where the last two conductances depend explicitly on voltage as well.

Ionic current characterization

In voltage-gated ion channels, the channel conductance g_l is a function of both time and voltage ($g_n(t, v)$ in the above figure , while in leak channels g_l is a constant (g_l in the figure). The current generated by ion pumps is dependent on the ionic species specific to that pump. The following sections will describe these formulations in more detail.

Voltage-gated ion channels

Using a series of voltage clamp experiments and by varying extracellular sodium and potassium concentrations, Hodgkin and Huxley developed a model in which the properties of an excitable cell are described by a set of four ordinary differential equations. Together with the equation for the total current mentioned above, these are:

$$I = C_m \frac{\mathrm{d}V_m}{\mathrm{d}t} + \bar{g}_{\mathrm{K}} n^4 (V_m - V_K) + \bar{g}_{\mathrm{Na}} m^3 h (V_m - V_{Na}) + \bar{g}_l (V_m - V_l),$$

$$\frac{dn}{dt} = \alpha_n(V_m)(1-n) - \beta_n(V_m)n$$

$$\frac{dm}{dt} = \alpha_m(V_m)(1-m) - \beta_m(V_m)m$$

$$\frac{dh}{dt} = \alpha_h(V_m)(1-h) - \beta_h(V_m)h$$

$p = (n, m, h)$, α_p and β_p $\bar{g}_n$ where I is the current per unit area, and α_i and β_i are rate constants for the i-th ion channel, which depend on voltage but not time. is the maximal value of the conductance. n, m, and h are dimensionless quantities between 0 and 1 that are associated with potassium channel activation, sodium channel activation, and sodium channel inactivation, respectively. For

taken the form

$$\alpha_p(V_m) = p_\infty(V_m)/\tau_p$$

$$\beta_p(V_m) = (1 - p_\infty(V_m))/\tau_p.$$

p_∞ and $(1 - p_\infty)$ are the steady state values for activation and inactivation, respectively, and are usually represented by Boltzmann equations as functions of V_m.

In the original paper by Hodgkin and Huxley, the functions α and β are given by

$$\alpha_n(V_m) = \frac{0.01(10+V)}{\exp\left(\frac{10+V}{10}\right)-1} \qquad \alpha_m(V_m) = \frac{0.1(25+V)}{\exp\left(\frac{25+V}{10}\right)-1} \qquad \alpha_h(V_m) = 0.07\exp\left(\frac{V}{20}\right)$$

$$\beta_n(V_m) = 0.125\exp\left(\frac{V}{80}\right) \qquad \beta_m(V_m) = 4\exp\left(\frac{V}{18}\right) \qquad \beta_h(V_m) = \frac{1}{\exp\left(\frac{30+V}{10}\right)+1}$$

Where, $V = V_{rest} = Vm$ denotes the negative depolarization in mV.

While in many current software programs, Hodgkin–Huxley type models generalize α and β to

$$\frac{A_p(V_m - B_p)}{\exp\left(\frac{V_m - B_p}{C_p}\right) - D_p}$$

In order to characterize voltage-gated channels, the equations are fit to voltage clamp data. For a derivation of the Hodgkin–Huxley equations under voltage-clamp. Briefly, when the membrane potential is held at a constant value (i.e., voltage-clamp), for each value of the membrane potential the nonlinear gating equations reduce to equations of the form: ‘

$$m(t) = m_0 - [(m_0 - m_\infty)(1 - e^{-t/\tau_m})]$$
$$h(t) = h_0 - [(h_0 - h_\infty)(1 - e^{-t/\tau_h})]$$
$$n(t) = n_0 - [(n_0 - n_\infty)(1 - e^{-t/\tau_n})]$$

Thus, for every value of membrane potential V_m the sodium and potassium currents can be described by

$$I_{\mathrm{Na}}(t) = \bar{g}_{\mathrm{Na}} m(V_m)^3 h(V_m)(V_m - E_{\mathrm{Na}}),$$
$$I_{\mathrm{K}}(t) = \bar{g}_{\mathrm{K}} n(V_m)^4 (V_m - E_{\mathrm{K}}).$$

In order to arrive at the complete solution for a propagated action potential, one must write the current term I on the left-hand side of the first differential equation in terms of *V*, so that the equation becomes an equation for voltage alone. The relation between *I* and *V* can be derived from cable theory and is given by

$$I = \frac{a}{2R}\frac{\partial^2 V}{\partial x^2},$$

where *a* is the radius of the axon, *R* is the specific resistance of the axoplasm, and x is the position along the nerve fiber. Substitution of this expression for I transforms the original set of equations into a set of partial differential equations, because the voltage becomes a function of both x and t. The Levenberg–Marquardt algorithm is often used to fit these equations to voltage-clamp data. While the original experiments treated only sodium and potassium channels, the Hodgkin–Huxley model can also be extended to account for other species of ion channels.

Leak channels

Leak channels account for the natural permeability of the membrane to ions and take the form of the equation for voltage-gated channels, where the conductance g_{leak} is a constant. Thus, the leak current due to passive leak ion channels in the Hodgkin-Huxley formalism is $I_l = g_{leak}(V - V_{leak})$.

Pumps and exchangers

The membrane potential depends upon the maintenance of ionic concentration gradients across it. The maintenance of these concentration gradients requires active transport of ionic species. The sodium-potassium and sodium-calcium exchangers are the best known of these. Some of the basic properties of the Na/Ca exchanger have already been well-established: the stoichiometry of exchange is 3 Na^+: 1 Ca^{2+} and the exchanger is electrogenic and voltage-sensitive. The Na/K exchanger has also been described in detail, with a 3 Na^+: 2 K^+ stoichiometry.

Mathematical properties of Hodgkin–Huxley model

$V_m(t), n(t), m(t)$, and $h(t)$. The Hodgkin–Huxley model can be thought of as a differential equation system with four state variables, that change with respect to time *t*. The system is difficult to study because it is a nonlinear system and cannot be solved analytically. However, there are many numerical methods available to analyze the system. Certain properties and general behaviors, such as limit cycles, can be proven to exist.

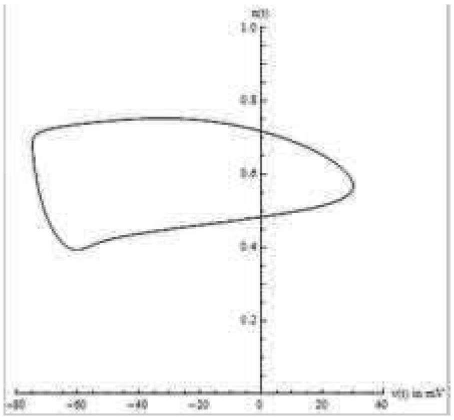


Fig. 5.19 *Simulation of the Hodgkin–Huxley model in Phase Space*

Center manifold

Because there are four state variables, visualizing the path in phase space can be difficult. Usually two variables are chosen, voltage *n*(*t*), allowing one to visualize the limit cycle. However, one must be careful because this is an ad-hoc method of visualizing the 4-dimensional system. This does not prove the existence of the limit cycle.

A better projection can be constructed from a careful analysis of the Jacobian of the system, evaluated at the equilibrium point. Specifically, the eigenvalues of the Jacobian are indicative of the center manifold's existence. Likewise, the eigenvectors of the Jacobian reveal the center manifold's orientation. The Hodgkin–Huxley model has two negative eigenvalues and two complex eigenvalues with slightly positive real parts. The eigenvectors associated with the two negative eigenvalues will reduce to zero as time t increases. The remaining two complex eigenvectors define the center manifold. In other words, the 4-dimensional system collapses onto a 2-dimensional plane. Any solution starting off the center manifold will decay towards the center manifold. Furthermore, the limit cycle is contained on the center manifold.

Bifurcations

If the injected current *I* were used as a bifurcation parameter, then the Hodgkin–Huxley model undergoes a Hopf bifurcation. As with most neuronal models, increasing the injected current will increase the firing rate of the neuron. One consequence of the Hopf bifurcation is that there is a minimum firing rate. This means that either the neuron is not firing at all (corresponding to zero frequency), or firing at the minimum firing rate. Because of the all-or-none principle, there is no smooth increase in action potential amplitude, but rather there is a sudden 'Jump' in amplitude. The resulting transition is known as a canard.

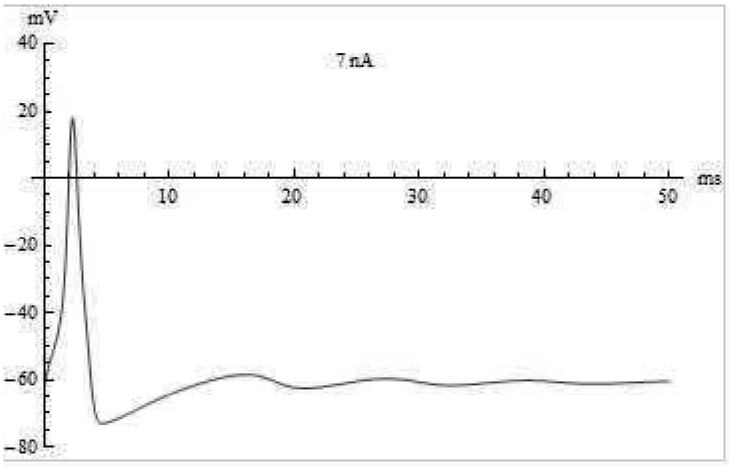


Fig. 5.20 *The voltage in i(t) of the Hodgkin–Huxley model*

Improvements and alternative models

The Hodgkin–Huxley model is regarded as one of the great achievements of 20th-century biophysics. Nevertheless, modern Hodgkin–Huxley-type models have been extended in several important ways:

- Additional ion channel populations have been incorporated based on experimental data.
- The Hodgkin–Huxley model has been modified to incorporate transition state theory and produce thermodynamic Hodgkin–Huxley models.
- Models often incorporate highly complex geometries of dendrites and axons, often based on microscopy data.
- Stochastic models of ion-channel behavior, leading to stochastic hybrid systems.
- The Poisson–Nernst–Planck (PNP) model is based on a mean-field approximation of ion interactions and continuum descriptions of concentration and electrostatic potential.

Several simplified neuronal models have also been developed (such as, the FitzHugh–Nagumo model), facilitating efficient large-scale simulation of groups of neurons, as well as mathematical insight into dynamics of action potential generation.

5.8.4 Core Conductor Models

A simple core conductor is a long thin membrane tube filled with an electrically conducting medium (e.g., axoplasm) on the inside and bathed on the outside by another electrically conducting liquid (e.g., extracellular fluid). This membrane tube is usually a cylinder with a diameter that is substantially larger than its length. For short length (i.e., small, compared to the length constant l) increments along the cylinder, the resistance to electric current flow over the membrane is substantially greater than the core resistance. Because of these relative resistances, electric current inside the core conductor tends to travel parallel to the cylinder axis for a long distance before leaking out a significant fraction across the membrane. This simple physical notion serves as the foundation for a cable theory approach of steady-state current and potential distributions in neural core conductors; the membrane capacitance must also be taken into account for transient cable features.

5.8.5 Electrocardiography

Electrocardiography is the process of producing an Electrocardiogram (ECG or EKG[a]). It is an electrogram of the heart which is a graph of voltage versus time of the electrical activity of the heart using electrodes placed on the skin. These electrodes detect the small electrical changes that are a consequence of cardiac muscle depolarization followed by repolarization during each cardiac cycle (heartbeat). Changes in the normal ECG pattern occur in numerous cardiac abnormalities, including cardiac rhythm disturbances (such as atrial fibrillation and ventricular tachycardia), inadequate coronary artery blood flow (such as myocardial ischemia and myocardial infarction), and electrolyte disturbances (such as hypokalemia and hyperkalemia). Traditionally, 'ECG' usually means a 12-lead ECG taken while laying down as discussed below. However, other devices can record the electrical activity of the heart such as a Holter monitor but also some models of smartwatch are capable of recording an ECG (starting with the Apple Watch in 2018). ECG signals can be recorded in other contexts with other devices.

In a conventional 12-lead ECG, ten electrodes are placed on the patient's limbs and on the surface of the chest. The overall magnitude of the heart's electrical potential is then measured from twelve different angles ('Leads') and is recorded over a period of time (usually ten seconds). In this way, the overall magnitude and direction of the heart's electrical depolarization is captured at each moment throughout the cardiac cycle. There are three main components to an ECG: the P wave, which represents the depolarization of the atria; the QRS complex, which represents the depolarization of the ventricles; and the T wave, which represents the repolarization of the ventricles. During each heartbeat, a healthy heart has an orderly progression of depolarization that starts with pacemaker cells in the sinoatrial node, spreads throughout the atrium, and passes through the atrioventricular node down into the bundle of His and into the Purkinje fibers, spreading down and to the left throughout the ventricles. This orderly pattern of depolarization gives rise to the characteristic ECG tracing. To the trained clinician, an ECG conveys a large amount of information about the structure of the heart and the function of its electrical conduction system. Among other things, an ECG can be used to measure the rate and rhythm of heartbeats, the size and position of the heart chambers, the presence of any damage to the heart's muscle cells or conduction system, the effects of heart drugs, and the function of implanted pacemakers.

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5.9 PALAROGRAPHY THEORY

In an electrolysis-cell, having one polarizable electrode and other non-polarizable electrode, there occurs a phenomenon, which can be studied by means of current voltage curves. With the help of the current voltage-curve, the solution can be analysed. This method is known as *voltametry*. The technique in which the polarizable electrode consists of dropping-mercury is known as *polarography.*

The dropping mercury electrode (DME). As the name suggests, the electrode is mercury in the form of a succession of droplets coming out from a glass capillary (internal diameter 0.03 to 0.05 mm). This has two advantages, first it provides the high hydrogen overvoltage and secondly, the electrode surface is continually renewed, and hence, cannot become fouled. The diagrammatic representation of the apparatus is shown in Fig. 5.21.

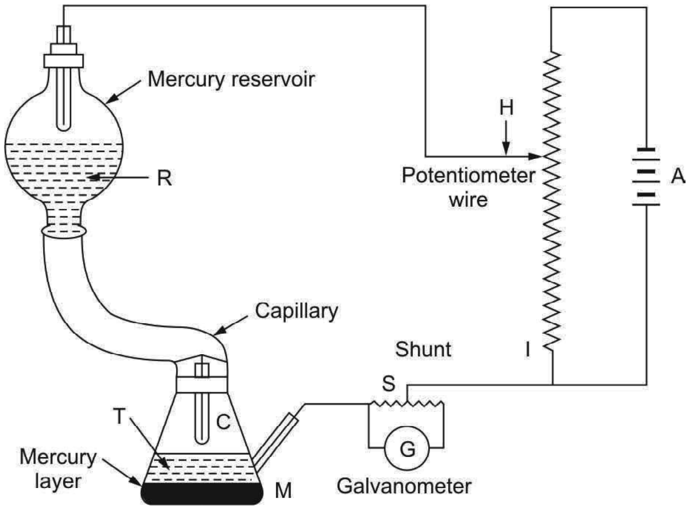

Fig. 5.22 *Essential features of a polarograph*

The flask contains the experimental solution, which is saturated with an inert gas (nitrogen or hydrogen) by passing the gas through the tube *T.C* is a capillary from which the mercury falls at the rate of 20 to 30 drops per minute. The mercury level *M* serves as anode. The applied voltage is varied by means of a sliding contact along a potentiometer wire *I*. The galvanometer *G* is provided with a shunt *S* to measure the current strength. The current voltage curve is thus obtained. The curve is obtained by automatic registering apparatus, known as *polarograph* and the curve so obtained is known as *polarogram*. The polarographic analysis of a solution of 0.1 M $CaCl_2$ containing Cu^{+2}, Pb^{+2}, Cd^{2+}, Mn^{2+}, etc., as impurities is shown in Fig. 5.23. The different species occupy their characteristic positions with respect to voltage in the polarogram, as shown below:

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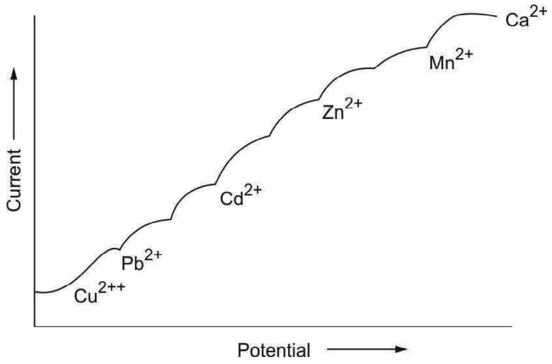

Fig. 5.23 *Polarogram of* $CaCl_2$ *(0.1 M) containing* Cu^{++}, Pb^{++}, Zn^{++}, Cd^{++}, Mn^{++}, *etc., as impurities*

Theory of current voltage curves: Using the cell shown in Fig. 5.22, we can obtain the polarogram of 0.001M $CdCl_2$ in 0.01 MKCl. This is shown in Fig. 5.23.

The curve in Fig 5.23 can be divided into three regions, i.e., *L*, *M* and *N*. At low potential (region) *L*, the current is very small due to the reduction of traces of impurities; this is known as *residual current*. On increasing the negative potential, the reduction of Cd^{++} ion starts, resulting in a sharp increase of current. When Cd^{++} ion is reduced completely, the current becomes almost constant (region *N*). This saturation is due to the local depletion of Cd^{++} ions in the vicinity of the DME. At this stage, the value of limiting current, i.e., *PO*, is known as the diffusion-current and depends upon the concentration of the reducible species.

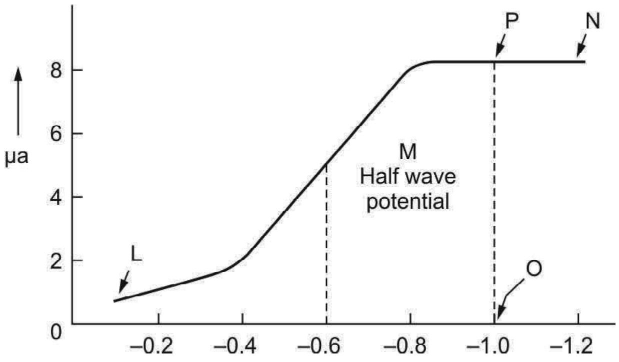

Fig. 5.24 *Polarogram of* $CdCl_2$ *(0.001 M) in KCl*

If *n* be the number of electrons involved in the cathodic reduction process; *C* the concentration of reducible substance in millimoles per litre, *D* the coefficient of diffusion of the reducible substance in cm^2/sec, *m* is the mass of mercury flowing through the capillary in mg/sec and t be the time between successive drops in seconds, the diffusion current i_d can be expressed using the relation.

$$i_d = 607nCD^{\frac{1}{2}}\ m^{\frac{2}{3}}\ t^{\frac{1}{6}}$$

This is known as *Ilkovic equation* and can be used to estimate *n* or *D* under the conditions of the experiment. In practical polarography, stationary micro-electrodes are seldom used as it decreases the diffusion current and these have been replaced by rotating platinum electrode.

There are numerous uses to which polarography can be put to both in qualitative and quantitative analysis. Substances can be identified by knowing their characteristic half wave potentials ($E_{1/2}$), i.e., the potential at the point on the polarogram where the current is half the diffusion current. Polarographic analysis is very useful in determining the structures of the organic compounds.

5.9.1 Llkovic Equation

Ilkovic equation: In polarography, the Ilkovic equation is a relationship between the diffusion current (id) and the concentration of the non-polarisable electrode, i.e. the material reduced or oxidised at the falling mercury electrode (polarisable electrode).

Qualitative information can also be determined from the half-wave potential of the polarogram (the current vs. Potential plot in a polarographic experiment). The value of the half-wave potential is related to the standard potential for the redox reaction being studied. This technique and especially the differential pulse anodic stripping voltammetry (dpasv) method can be used for environmental analysis, and especially for marine study for characterisation of organic matter and metals interactions.

The ilkovic equation is a relation used in polarography relating the diffusion current (id) and the concentration of the depolarizer (c), which is the substance reduced or oxidized at the dropping mercury electrode. The ilkovic equation has the form

$$I_\mathrm{d} = knD^{1/3} m_r^{2/3} t^{1/6} c$$

Where:

- *k* is a constant which includes π and the density of mercury, and with the faraday constant f has been evaluated at 708 for maximal current and 607 for average current
- *d* is the diffusion coefficient of the depolarizer in the medium (cm^2/s)
- *n* is the number of electrons exchanged in the electrode reaction, m is the mass flow rate of hg through the capillary (mg/s)
- *t* is the drop lifetime in seconds,
- *c* is depolarizer concentration in mol/cm^3.

The equation is named after the scientist who derived it, the slovak chemist dionýz ilkovič (1907–1980).

5.9.2 Half Wave Potential and its Signification

A half-wave potential (AA) is one in which the polarographic wave current equals half of the diffusion current (BB). Each element and its various valence states and chemical forms have their own half-wave potential in a specific supporting electrolyte. The chemical species producing the current is thus identified by seeing a current peak at a given half-wave potential.

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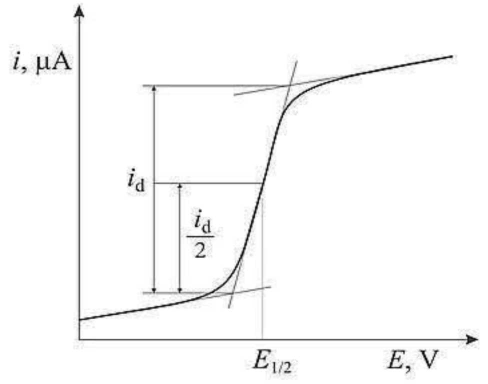

Fig. 5.25 *Half Wave Potential*

Signification of Half Wave Potential: Each element and its various valence states and chemical forms have their own half-wave potential in a specific supporting electrolyte. The chemical species producing the current is thus identified by seeing a current peak at a given half-wave potential.

5.10 INTRODUCTION TO CORROSION

Corrosion is a general term used to describe various interactions between a material and its environment leading to a degradation in the material properties. Corrosion is a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide, carbonate or sulfide. It is the gradual destruction of materials (usually a metal) by chemical and/or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulfates. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal and results in a distinctive orange colouration.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

The chemistry of corrosion is complex; it can be considered an electrochemical phenomenon. During corrosion at a particular spot on the surface of an object made of iron, oxidation takes place and that spot behaves as an anode. The electrons released at this anodic spot move through the metal and go to another spot on the metal and reduce oxygen at that spot in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water in moist air condition of atmosphere. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as a cathode.

Forms of Corrosion

1. **General corrosion:** General corrosion is characterized by an overall attack on the surface. The corrosion takes place without distinguished anodic and cathodic areas.
2. **Galvanic corrosion**: When two different metals are electrically connected and in contact with an electrolyte (=liquid), they will form a galvanic cell where the more noble material is cathodic and the less noble anodic. The anodic material will corrode. The electropotentials of metals can be measured in different water solutions and listed in galvanic series, as for seawater in the diagram. The corrosion rate depends on:
    - The surface area ratio between cathode and anode (a bigger anode area compared to the cathode area reduces the galvanic effects, e.g. stainless steel fasteners on a cast iron pump).
    - The magnitude of potential difference (compare aluminium bronze in contact with stainless steel and cast iron in contact with stainless steel).
    - The conductivity of the electrolyte (liquid).
3. **Pitting corrosion:** Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which compete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause corrosion pits of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an autocatalytic process.
4. **Crevice corrosion:** Crevice corrosion refers to corrosion occurring in confined spaces to which the access of the working fluid from the environment is limited. These spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles**.** When dust, sand and other corrosive substances are deposited on surfaces, they create an environment where water will accumulate and corrode the part.
5. **Intergranular corrosion:** InterGranular Corrosion (IGC), also known as intergranular attack (IGA), is a form of corrosion where the boundaries of crystallites of the material are more susceptible to corrosion than their insides**.**

    6. Stress corrosion: Stress corrosion is another form of corrosion that is important to many fields including civil structures. Stress-corrosion occurs **when a material exists in a relatively inert environment but corrodes due to an applied stress**. The stress may be externally applied or residual.

7. **Erosion corrosion**: Erosion corrosion is a combination of electrochemical corrosion (i.e. general corrosion) and the action of a high speed fluid, eroding the corrosion product. The pits formed by erosion corrosion usually have bright surfaces free from corroded material. The attacks are generally localized to areas with turbulent flow and are promoted by gas bubbles and solid particles.
8. **Cavitation corrosion:** Cavitation corrosion appears in areas where vapour bubbles are formed due to low pressure. When the bubbles implode on a surface the protective oxide is destroyed and eroded away and after that built up again. The process is repeated and characteristic deep holes of cavitation corrosion are formed on the surface. It can usually be seen on the trailing edge of impellers and propellers.
9. **Selective corrosion:** Selective corrosion occurs in metals in which the alloying elements are not uniformly distributed. Typical examples of this type of corrosion are:
    - Dezincification of brass, where by zinc is dissolved and leave behind a porous copper material.
    - Graphitization of cast iron, whereby the iron is dissolved and leave behind a network of graphite of low mechanical strength.

Homogeneous Theory

Specifically, corrosion can be used to describe any process that involves the degradation or deterioration of metal elements. The best-known case is rust formation involving steel. The process is typically electrochemical, having the characteristics of a battery. When atoms of metals are exposed to an environment containing water, the metal can produce electrons. This action can be confined locally to create a crack or pit. This could extend further to the surrounding area, leading to general wastage. Confined corrosion that results in pitting is capable of producing fatigue, and corrosive agents such as seawater could result in immense growth of the crack. Corrosion also arises in a higher rate in areas involving microstructural changes, mainly due to welding.

Corrosion theory involves four essential components:

1. Cathode
2. Anode
3. Electrical connection that exists between the cathode and anode for the electron current flow
4. Electrolyte or a conducting environment to facilitate ionic movement

Corrosion theory entails that the process involves an anodic reaction. This type of reaction is produced through dissolving metal, which generates electrons. This is further consumed by another process called cathodic reaction. These two processes balance the charges produced. The sites generating these processes may be found close or far apart, depending on the situation.

The electrons generated by the process need to be consumed through cathodic reaction. This should be close to the process of corrosion itself. Hydrogen ions and electrons react to build atomic hydrogen, and later, hydrogen gas. When hydrogen forms, further corrosion can be prevented through a thin gas film at the metal surface. This film serves as a polarizer, which is functional in decreasing metal-to-water contact, reducing corrosion. Thus, anything that breaks the barrier film tends to hasten the speed of corrosion.

Corrosion Monitoring

Corrosion monitoring is the use of a Corrator (corrosion meter) or set of methods and equipment to provide offline or online information about corrosion rate expressed in mpy (mill per year). For better care and to take or improve preventive measures to combat and protect against corrosion.

Corrosion Monitoring is a process that evaluates and monitors equipment components, structures, process units, and facilities for signs of corrosion. Monitoring programs aim to identify certain conditions in order to extend the life and serviceability of assets while increasing safety and reducing replacement costs. Corrosion monitoring covers all types of corrosion and materials.

The key advantage to implementing corrosion monitoring is to detect early warning signs of corrosion and to determine trends and processing parameters that may induce a corrosive environment. Processing parameters that may need to be altered include temperature, pressure, pH, etc. Additionally, corrosion monitoring serves to measure the effectiveness of corrosion prevention methods in order to determine if different inspection and/or monitoring techniques should be utilized.

A wide variety of corrosion measurement techniques are used for corrosion monitoring some of them are:

- Weight loss coupons
- Electrical resistance
- Linear polarization
- Hydrogen penetration
- Galvanic current

Protection from Corrosion

Various treatments are used to slow corrosion damage to metallic objects which are exposed to the weather, salt water, acids, or other hostile environments. Some unprotected metallic alloys are extremely vulnerable to corrosion, such as those used in neodymium magnets, which can spall or crumble into powder even in dry, temperature-stable indoor environments unless properly treated to discourage corrosion.

- **Surface treatments**: When surface treatments are used to deter corrosion, great care must be taken to ensure complete coverage, without gaps, cracks, or pinhole defects. Small defects can act as an “Achilles’ heel”, allowing corrosion to penetrate the interior and causing extensive damage even while the outer protective layer remains apparently intact for a period of time.
- **Applied coatings**: Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier

of corrosion-resistant material between the damaging environment and the structural material. Aside from cosmetic and manufacturing issues, there may be tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, but if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with active metal such as zinc or cadmium.

- **Reactive coatings**: If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These chemicals form an electrically insulating or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are famous for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).
- **Anodization:** Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores, several nanometers wide, appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area.
- **Controlled permeability formwork**: Controlled Permeability Formwork (CPF) is a method of preventing the corrosion of reinforcement by naturally enhancing the durability of the cover during concrete placement. CPF has been used in environments to combat the effects of carbonation, chlorides, frost and abrasion.
- **Cathodic protection**: Cathodic Protection (CP) is a technique to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.
- **Anodic protection:** Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g. stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, such as solutions of sulfuric acid. Anodic protection is an electrochemical method of corrosion protection by keeping metal in passive state.

Check Your Progress

16. Define the SHE.
17. What is an electrocardiography?
18. Define the polarography.
19. What do you understand by the Ilkovic equation?
20. How will you define the half wave potential?
21. What is intergranular corrosion?
22. Give an example of selective corrosion.
23. What are the four essential components of Corrosion theory?

5.11 ANSWERS TO 'CHECK YOUR PROGRESS'

1. In chemistry, the transport number is also termed as 'Ion transport number' or the 'Transference number'. It is the fraction of the total electrical current carried in an electrolyte by a given ionic species '***i***' and is denoted by,

$$t_i = \frac{I_i}{I_{tot}}$$

2. A quantitative measure of an ion's ability to move under the influence of a potential difference in solution: It is the speed of movement under the influence. of unit potential difference.
3. According the Kohlrausch law, the current carried by an ion is proportional to its ionic conductance. The speed of an ion in a solution at any concentration is proportional to the conductance of the ion at that concentration. Thus, we have

Current carried by the cation $\mu \ \lambda_0^+$

Current carried by the anion $\mu \ \lambda_0^-$

Total current $\propto \left(\lambda_0^+ + \lambda_0^-\right)$

$\therefore$ Transport number of cation, $t_+ = \dfrac{\lambda_0^+}{\lambda_0^+ + \lambda_0^-}$ and

Transport number of an anion, $t_- = \dfrac{\lambda_0^-}{\lambda_0^+ + \lambda_0^-}$

4. Equivalent Conductivity (L): The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity. It is denoted by L.
5. Electrochemistry deals with the processes at the interface between an electron conductor and an ion conductor. By application of a potential, electronic

surface charges aggregate at this interface inducing possibly electrochemical reactions, for example at a metal-water interface.

6. Electrocapillarity or electrocapillary phenomena are the phenomena related to changes in the surface energy (or interfacial tension) of the Dropping Mercury Electrode (DME), or in principle, any electrode, as the electrode potential changes or the electrolytic solution composition and concentration change.
7. Gouy-Chapman theory is an electrostatic model of the spatial distribution of ions adsorbed, but not immobilized, by a charged particle surface reacting with an aqueous electrolyte solution. These ions are relatively free to move about while reacting with surface charge either by accumulation (positive adsorption) or depletion (negative adsorption) in the interfacial region.
8. It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode.
9. Electrode reactions are characterized by charge transfer across the interface. The charge can be carried by electrons or by ions. It is shown here that when both mass and charge cross the interface, the charge must be carried by the ionic species, not by the electrons, as a result of the very large difference in the time scale for electron and ion transfer.
10. Most widely used semiconductors are Silicon (Si), Germanium (Ge), Selenium (Se) etc., that exists as simple semiconductors and compound semiconductors such as Gallium Arsenide (GaAs), Indium Phosphate (InP), Gallium Nitride (GaN) etc.
11. Tunneling is a quantum mechanical phenomenon when a particle is able to penetrate through a potential energy barrier that is higher in energy than the particle's kinetic energy.
12. An electrocatalyst is a catalyst that participates in electrochemical reactions. Electrocatalysts are a specific form of catalysts that function at electrode surfaces or, most commonly, may be the electrode surface itself.
13. Electrocatalysis can be defined as the heterogeneous catalysis of electrochemical reactions, which occur at the electrode-electrolyte interface and where the electrode plays both the role of electron donor/acceptor and of catalyst.
14. Hydrogen gas is released in the process of electrolysis of water.
15. The process of electrolysis of water is also called water spilting.
16. The Standard Hydrogen Electrode (abbreviated as SHE), also called Normal Hydrogen Electrode (NHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials.
17. Electrocardiography is the process of producing an Electrocardiogram (ECG or EKG[a]). It is an electrogram of the heart which is a graph of voltage versus time of the electrical activity of the heart using electrodes placed on the skin. These electrodes detect the small electrical changes that are a consequence of cardiac muscle depolarization followed by repolarization during each cardiac cycle (heartbeat).

18. In an electrolysis-cell, having one polarizable electrode and other non-polarizable electrode, there occurs a phenomenon, which can be studied by means of current voltage curves. With the help of the current voltage-curve, the solution can be analysed. This method is known as *voltametry*. The technique in which the polarizable electrode consists of dropping-mercury is known as *polarography.*
19. - In polarography, the Ilkovic equation is a relationship between the diffusion current (id) and the concentration of the non-polarisable electrode, i.e. the material reduced or oxidised at the falling mercury electrode (polarisable electrode).
20. A half-wave potential (AA) is one in which the polarographic wave current equals half of the diffusion current (BB). Each element and its various valence states and chemical forms have their own half-wave potential in a specific supporting electrolyte. The chemical species producing the current is thus identified by seeing a current peak at a given half-wave potential.
21. InterGranular Corrosion (IGC), also known as intergranular attack (IGA), is a form of corrosion where the boundaries of crystallites of the material are more susceptible to corrosion than their insides.
22. Dezincification of brass, where by zinc is dissolved and leave behind a porous copper material is an example of selective corrosion.
23. The four essential components of Corrosion theory are:
    - Cathode
    - Anode
    - Electrical connection that exists between the cathode and anode for the electron current flow
    - Electrolyte or a conducting environment to facilitate ionic movement

5.12 SUMMARY

- The concept and measurement of transport number were introduced by Johann Wilhelm Hittorf in the year 1853. When the ions in a solution have different ion transport numbers then this gives liquid junction potential.
- The fraction of the current carried by a given ionic species in the solution is called the transport number of Hittorf's number or transference number of the ion and designated by the symbols t_+ and t_-.
- The equivalent conductance of an electrolyte may be defined as the conductance of a volume of solution containing one gram equivalent of dissolved substance, the solution being placed between two parallel electrodes, 1 cm apart, and large enough to contain between them all of the solution.
- The Debye-Hückel theory was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes. It was further modified by Lars Onsager in 1927 with the following postulates.

NOTES

- Electrolytes are chemicals that break into ions in water. Aqueous solutions containing electrolytes conduct electricity. Strong electrolytes include the strong acids, strong bases, and salts. These chemicals completely dissociate into ions in aqueous solution.
- The verification of the Debye-Hückel-Onsager equation is more difficult for electrolytes of unsymmetrical valence types (different Z^+ and Z^- values) since determination of the value of w can be done only on knowing the mobility's of the individual ions at infinite dilution and also the transference numbers of the ions.
- The validity for Onsager theory is also provided by conductance measurements of a number of electrolytes made at 0^0C and 100^0C. At both temperatures, the observed slope of the plot of agrees with the calculated result within the limits of experimental error.
- The activity coefficients of different electrolytes can be determined based on measurements of vapor pressure, freezing point, solubility or electromotive force. The results obtained by the various methods are in good agreement with each other and hence they may be regarded as reliable.
- The 'Debye-Hückel Limiting Law' is applicable only at very low concentrations of solute. This law enables calculation of the mean activity coefficient from basic properties of the solution. The name 'Limiting Law' is applied because in the limit of arbitrarily low molalities, i.e., as the concentration of the solute gets closer and closer to zero, all solutions are expected to behave in a manner consistent with the expression.
- The Butler–Volmer equation is named after John Alfred Valentine Butler and Max Volmer. Also sometimes known as **Erdey-Grúz–Volmer** equation, it is one of the most fundamental relationships in electrochemical kinetics.
- The Butler–Volmer equation has been widely used to analyze the electron transfer for electrochemical simulation. Though it has been approximately used for numerous applications, but the Butler–Volmer equation is specifically approximated for finding the activation over-potential or over-voltage.
- For approximation of Butler–Volmer equation, there are some approximation equations, such as Tafel, linear low polarization, and hyperbolic sine approximation.
- Semiconductors that exists in pure form without any impurities added are called as intrinsic semiconductors. Consider the semiconductor Silicon, Si with atomic number 14.

5.13 KEY TERMS

- **Transport number:** Ion transport number, also called the transference number, is the fraction of the total electrical current carried in an electrolyte by a given ionic species, Differences in transport number arise from differences in electrical mobility.

- **Electrolytic conductivity:** Conductivity (electrolytic) Conductivity (or specific conductance) of an electrolyte solution is a measure of its ability to conduct electricity. The SI unit of conductivity is siemens per meter (S/m).
- **Debye- Hückel theory:** It was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes.
- **Molecular conductance:** Molecular conductance is defined as the conductance of a volume of solution containing one mole of solute, the solution being placed between the two electrodes of 1cm apart and large enough to contain in between them all the solutions.

5.14 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define Ionic Mobilities.
2. What is molecular conductance?
3. Equivalent conductivity decreases in the various concentration of electrolytic solution.
4. What is the value of K (Boltzmann constant) in Debye-Hückel-Onsagar equation?
5. Differentiate between strong and weak electrolyte.
6. State the Debye-Hückel limiting law.
7. What do you understand by activity coefficient of different electrolytes?
8. Drive the thermodynamics of electrified interface equation.
9. Define the electrocapillary.
10. What do you understand by thermodynamic electrified interfaces?
11. What is Butter Volmer equation?
12. Define the intrinsic semiconductor.
13. What do you understand by quantization of charge transfer?
14. Differentiate between the intrinsic and extrinsic semiconductor.
15. What is electrocatalysis?
16. Define the anode and cathode.
17. What do you understand by bioelectrochemistry?
18. State Nernst-Plank equation.
19. What is palarograpgy?
20. What is controlled permeability formwork?

Long-Answer Questions

1. Explain in detail about the electrochemistry of solution giving examples.
2. Describe Debye-Hückel-Onsagar equation with the help of examples.

3. Drive the Debye-Hückel-Onsagar equation for symmetrical and unsymmetrical electrolyte.
4. Elaborate on the thermodynamics of electrified interface equation.
5. Explain in detail about the Derivation of Electrocapillary and Lippmann equation (surface excess)
6. Describe the Butler-Volmer equation and approximation of the equation.
7. Analyse the quantum aspects of charge transfer at electrode solution interface.
8. Elaborate on the semiconductor and their types.
9. Interpret the electrocatalysis with the help of examples.
10. Illustrate the hydrogen electrode.
11. Elaborate on the electrochemistry and threshold membrane phenomena
12. Derive the Nernst-Plank and Hodge-Huxley equation.
13. Comprehend the electrocardiography with examples.
14. Elaborate on the polarography with appropriate examples.
15. Explain in detail about the corrosion with their types.

5.15 FURTHER READING

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