PG CH S1-03 (DSC)

TWO YEAR MASTER'S DEGREE COURSE

(CBCS in Accordance with NEP 2020)

SEMESTER - I

PHYSICAL CHEMISTRY-I

CHEMISTRY

Hiranya Chandra Bhuyan School of Science and Technology

KRISHNA KANTA HANDIQUI STATE OPEN UNIVERSITY

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August 2026

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ISBN: 978-93-7839-009-8

Printed and published by the Registrar on behalf of Krishna Kanta Handiqui State Open University

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COURSE INTRODUCTION

This course has been designed for postgraduate learners enrolled in the M.Sc. Chemistry programme. It aims to provide a comprehensive understanding of the fundamental principles and applications of physical chemistry, with special emphasis on thermodynamics, non-equilibrium processes, polymer chemistry, and surface phenomena.

The course introduces the concepts of thermodynamic functions, spontaneity, and equilibrium, enabling students to understand the criteria for chemical stability and the role of free energy in determining reaction feasibility. Advanced topics such as Maxwell relations, equations of state, and real gas behaviour help bridge the gap between idealized models and real-world systems.

A significant portion of the course focuses on non-ideal systems, including solutions and electrolytes, where concepts like activity, fugacity, and partial molar properties are explored in detail. The study of phase equilibria and multicomponent systems equips students with the ability to interpret phase diagrams and understand complex equilibria relevant to industrial and research applications.

The course also introduces non-equilibrium thermodynamics, emphasizing irreversible processes, entropy production, and coupled phenomena such as thermoelectric effects, along with important principles like Onsager’s reciprocal relations and Prigogine’s minimum entropy production.

In addition, the course provides a thorough introduction to polymer chemistry, covering classification, synthesis, molecular weight determination, and structural properties of polymers in solution. Students will gain insight into polymerization mechanisms and kinetics, which are essential for modern materials science and industrial chemistry.

Additionally, the course explores surface chemistry and catalysis, including adsorption phenomena, surfactants, micelle formation, colloidal stability, and mechanisms of heterogeneous catalysis. These topics are crucial for understanding processes in areas such as environmental chemistry, nanotechnology, and chemical engineering.

Overall, this course aims to develop analytical thinking, problem-solving skills, and a deeper conceptual understanding of physical chemistry principles, while also highlighting their applications in research, industry, and emerging scientific fields.

UNIT-WISE DESCRIPTION

Unit 1: Basic Concepts of Thermodynamics

This unit introduces the fundamental principles of thermodynamics, including system and surroundings, thermodynamic states, and equilibrium. It covers state and path functions, internal energy, enthalpy, heat, and work along with the mathematical formulation of the first law. Concepts of thermochemistry, Hess's law, and the second law of thermodynamics are discussed, along with entropy and Clausius inequality.

Unit 2: Thermodynamic Functions, Spontaneity, Equilibrium and Maxwell Relations

Unit 2 focuses on thermodynamic potentials such as Helmholtz and Gibbs free energy and their role in determining spontaneity and equilibrium. It includes the Gibbs–Helmholtz equation, Le Chatelier's principle, and Maxwell's relations with applications. Thermodynamic equations of state are also introduced.

Unit 3: Thermodynamics of Real Gases and Gas Mixtures

This unit deals with deviations from ideal gas behavior and introduces the thermodynamics of real gases and mixtures. Concepts such as partial molar properties, fugacity, and fugacity coefficients are explained along with their determination and applications in real systems.

Unit 4: Thermodynamics of Non-Ideal Solutions and Electrolytes

This unit explains the behavior of ideal and non-ideal solutions with emphasis on activity and activity coefficients. Different scales of activity, ionic activity coefficients, and their applications to chemical equilibria in electrolyte systems are discussed.

Unit 5: Phase Equilibrium Concept and Three-Component Systems

This unit covers thermodynamic criteria for phase equilibrium and the Gibbs phase rule. It introduces reduced phase rule and triangular phase diagrams for ternary systems such as water-acetic acid-chloroform. Applications of three-component systems are also discussed.

Unit 6: Basic Concepts of Non-Equilibrium Thermodynamics

This unit introduces irreversible processes and entropy production. It explains generalized forces and flows, linear laws of non-equilibrium thermodynamics, phenomenological equations, and Onsager's reciprocal relations.

Unit 7: Coupled Flows, Stationary States and Local Sustenance of Order

Unit 7 discusses coupled transport processes and thermoelectric effects such as Seebeck, Peltier, and Thomson effects. It also explains non-equilibrium stationary states, Prigogine's principle of minimum entropy production, and the thermodynamic basis of order in living systems.

Unit 8: Introduction to Polymer Chemistry

This unit introduces polymers, monomers, and repeat units along with classification based on structure and properties. Concepts of degree of polymerization, natural and synthetic polymers, thermoplastics, thermosetting polymers, fibres, elastomers, and plastics are covered.

Unit 9: Average Molecular Weights of Polymers and their Determination

This unit explains polydispersity and different average molecular weights (number, weight, viscosity average). Methods for molecular weight determination such as viscosity, osmotic pressure, light scattering, and size exclusion chromatography are discussed.

Unit 10: Dimensions of Polymer Chains in Solution

Unit 10 focuses on the configuration and dimensions of polymer chains in solution. Concepts such as root mean square end-to-end distance, radius of gyration, random flight model, chain stiffness, and theta solvent are explained.

Unit 11: Polymerisation Reactions

This unit deals with mechanisms of polymer formation including chain and step polymerization. It introduces cationic, anionic, coordination polymerization, and ring-scission processes. Kinetics of free radical polymerization, step polymerization, and copolymerization are also discussed.

Unit 12: Surface Chemistry and Surfactants

This unit covers the nature of surfaces and adsorption processes. It includes physical and chemical adsorption, adsorption isotherms (Langmuir and BET), and surface area determination. Surfactants, micelle formation, CMC, reverse micelles, and microemulsions are also discussed.

Unit 13: Chemisorption

This unit explains chemisorption on different types of surfaces and electrical aspects of surface chemistry. Concepts such as electrical double layer, zeta potential, its measurement, and its role in colloidal stability are included.

Unit 14: Mechanism of Heterogeneous Catalysis

This unit focuses on the kinetics and mechanisms of heterogeneous catalysis. It explains models such as Langmuir-Hinshelwood and Eley-Rideal, along with unimolecular and bimolecular surface reactions.

UNIT 1: BASIC CONCEPTS OF THERMODYNAMICS

UNIT STRUCTURE

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1.4 Thermodynamic State and Thermodynamic Equilibrium
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1.6 Intensive and Extensive Variables
1.7 Internal Energy
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1.10 Second Law of Thermodynamics
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1.13 Let Us Sum Up
1.14 Answers to Check Your Progress
1.15 Further Reading
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1.1 LEARNING OBJECTIVES

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

- learn the basics of thermodynamic systems
- learn about the zeroth and the first law of thermodynamics
- describe thermochemical principles for calculating different properties
- explain the second law of thermodynamics.

1.2 INTRODUCTION

Thermodynamics, which is derived from the Greek words therme, meaning heat, and dynamis, meaning power or force, is the branch of science that deals with the phenomenological study of the relationships between heat, work, and various forms of energy. In the study of thermodynamics, it is first essential to learn the fundamental concepts such as the thermodynamic system and its surroundings, which refer to the part of the universe being studied and the part that is not being studied, respectively. The behaviour of thermodynamic systems is governed by the fundamental laws, starting with the Zeroth Law of Thermodynamics, which deals with the concept of temperature. The First Law of Thermodynamics is based on the law of conservation of energy and relates to the concepts of heat, work and internal energy. The Second Law of Thermodynamics is based on the law of conservation of energy and introduces the concept of entropy.

1.3 THERMODYNAMIC SYTEMS AND SURROUNDINGS

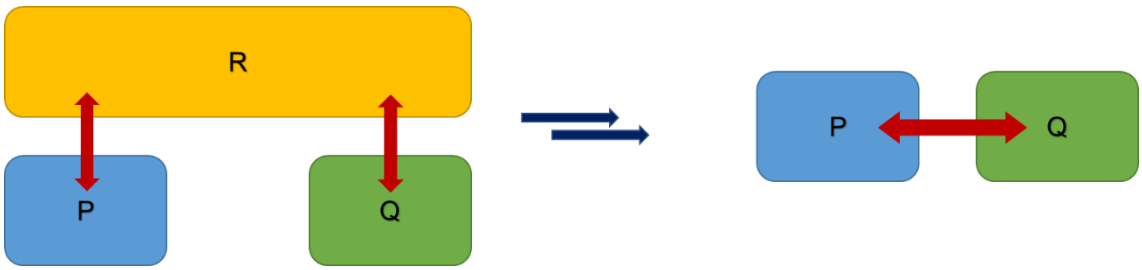
In order to carry out investigations based on thermodynamic principles, one needs to distinguish between system and surroundings. A thermodynamic system is a well-defined portion of matter under investigation separated from the rest of the universe by some boundary. The rest of the universe (barring the system) is called as surroundings. For example, if the temperature of a glass of water is measured, then the glass of water is the system and rest is surroundings.

Thermodynamics systems are separated from surroundings by walls or boundaries (may be real or imaginary) which are categorised based on whether the wall or boundary allows transfer of heat (energy) or not. A diathermal (also called *diabatic*) wall or boundary allows the transfer of heat between the system and the surroundings while an adiabatic wall restricts the same.

Thermodynamic systems are divided into further categories depending upon whether energy and matter can be exchanged with the surroundings or not:
Isolated system: Such a system does not exchange energy or matter the with surroundings.
Closed system: In a closed system, energy is allowed to be transferred to or from the surroundings, but matter cannot be exchanged.
Open system: Exchange of both energy and matter are allowed.

1.4 THERMODYNAMIC STATE AND THERMODYNAMIC EQUILIBRIUM

An unusually given name, the “zeroth” law in thermodynamics, was formulated after the other three laws, namely the “first”, “second” and “third” laws were formulated. However, the realizations of the “zeroth” law was so fundamental and profound that it has to be placed before all other existing fundamental laws of thermodynamics and hence the name was given as “zeroth law”. The statement of the zeroth law is “if two bodies P and Q are separately in thermal equilibrium with a third body R, then P and Q are also in thermal equilibrium”.
A schematic representation of the statement of the zeroth law is shown below, where the double-headed arrow represents thermal equilibrium between the two bodies.



The statement of the zeroth law is deceptively simple. But, at the time of its formulation, the concept of thermal equilibrium itself was empirical, because temperature was measured in some empirical way. People built different types of thermometers e.g., mercury thermometer, air thermometer, etc., and temperature was measured in a

relative sense. For example, the temperature at which ice melts was "hypothesized" to be 0 °C (T_0) and the boiling water temperature was "hypothesized" to be 100 °C (T_{100}). At 0 °C, the height of the material (say mercury) in the thermometer is h_0, and correspondingly h_{100} for temperature of 100 °C. These two heights are related by coefficient of thermal expansion (β) of the material and the temperature difference (ΔT) by $h_{100} = h_0(1 + \beta\Delta T)$ which rearranges to $h_{100} - h_0 = 100\beta h_0$. For any arbitrary temperature T and corresponding height h_T, the same approach gives $h_T - h_0 = T\beta h_0$. Hence, the arbitrary temperature T can be calculated as, $T = 100\,(h_T - h_0)/(h_{100} - h_0)\,°C$. Even though a practical means of measuring temperature was measured, it was still an empirical realisation based on a lot of hypotheses. The zeroth law established that if the temperatures of systems "P" and "Q" are same with system "R" when measured separately, then the temperatures of systems "P" and "Q" are bound to be same. That is temperature is not just an empirical concept, but an inherent property of the system that characterises "thermal equilibrium". Thus, the zeroth law put a profound meaning to the concept of temperature. The essence of the zeroth law of temperature is nicely summarised as *"the Zeroth Law provides the logical foundation for defining temperature consistently;* ***without it, temperature could not be treated as a scientifically measurable property rather than a subjective sensation****." (H. B. Callen, Thermodynamics and an Introduction to Thermostatistics, 2nd ed., Wiley, 1985, p. 26.)*.

1.5 STATE FUNCTION AND PATH FUNCTION

In thermodynamics, the properties of a system are divided into state functions and path functions. Properties which depend only on the state of the system, but not on how that state is reached (i.e., the path to reach the state) are called state functions. On the other hand, properties which depend not only on the state of the system, but also on the path to reach a particular thermodynamics state of the system are called path functions. Mathematically, state and path functions can be defined in terms of Euler's relation criterion by identifying whether a thermodynamic function is an exact or inexact differential. Suppose, a thermodynamic property z is a function of two variables x and y. Then, from basic calculus,

$$dz = \left(\frac{\partial z}{\partial x}\right) dx + \left(\frac{\partial z}{\partial y}\right) dy$$

Now, if

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

Then dz is an exact differential and is a state function. However, if

$$\frac{\partial^2 z}{\partial x \partial y} \neq \frac{\partial^2 z}{\partial y \partial x}$$

then, z is an inexact differential and it is a path function.

For example, consider the volume (V) of a system of one mole of an ideal gas which is a function of temperature (T) and pressure (P), with V = RT/P.

$$dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial P}\right) dP$$

Since, $V = \frac{RT}{P}$

$$\left(\frac{\partial V}{\partial T}\right) = \frac{R}{P} \Rightarrow \left(\frac{\partial^2 V}{\partial P \partial T}\right) = -\frac{R}{P^2}$$

$$\left(\frac{\partial V}{\partial P}\right) = -\frac{RT}{P^2} \Rightarrow \left(\frac{\partial^2 V}{\partial T \partial P}\right) = -\frac{R}{P^2}$$

Thus, here $\left(\frac{\partial^2 V}{\partial P \partial T}\right) = \left(\frac{\partial^2 V}{\partial T \partial P}\right)$, and so dV is an exact differential, or V is a state function.

1.6 INTENSIVE AND EXTENSIVE VARIABLES

Certain thermodynamic properties depend on the size of the system or the amount of matter present there, while others don't. Those which do not depend on the size of the system are called as intensive properties or variables. On the other hand, extensive properties are the ones that depend on the size of system. For example, temperature of water in a one litre and a two litre bottles are same. Thus, temperature is an intensive property. One the other hand energy, volume, etc. of these two bottles will be obviously different, so these properties are extensive properties. Note that in thermodynamics, often many properties are expressed in the units of per mole which are referred as molar quantities. All molar quantities are intensive properties, because even though a property can be extensive, recasting it to per mole basis gives a new property that remains same, irrespective of the amount of matter there.

1.7 INTERNAL ENERGY

Before going to the statement of the internal energy and the first law of thermodynamics, it is important to dig out some history from the time when heat was not understood. In the late 18th century, it was thought when something hot is touched, a "hot liquid" called the "caloric fluid" flows into the hand. Because it was thought to be some physical liquid, it was also assumed that this caloric fluid could not be created and can only be moved around. However, this view was challenged in 1798 by Count Rumford, who noticed something unusual while making brass cannons. He observed that a huge metal drill spinning inside a brass cannon made the metal got so hot that water placed on it started to boil. If heat was a liquid, it should have been consumed eventually. But as long as the drill kept running, the heat was continuously produced. This proved heat wasn't a liquid; rather a form of energy from motion. Later, James Joule wanted to develop a more precise understanding of heat. He built a simple machine: a falling weight tied to a string that spun a paddle in a bucket of water. The mechanical work of the falling weight spun the paddle, which stirred the water and the water got warmer. Since mechanical work (the falling weight) was heating the water, the revolutionary equivalence of heat and work was established by Joule's experiment. Note that Joule not only established the equivalence qualitatively, but did so quantitatively. He measured the rise in temperature of given mass of water when a specific amount of mechanical work was done. A specific weight falling through a distance always increased the temperature of a given amount of water by a constant amount.

The missing piece: Many experiments were performed by scientists to understand heat and work in detail. One of such experiments was the "Ice Calorimeter" experiment

of Lavoisier and Laplace. They tried to measure how much energy was inherently present inside a substance. They put a hot object inside a chamber surrounded by ice and measured exactly how many ounces of ice melted into water. Since the ice stayed at a constant temperature while it melted, they realized the energy from the hot object was being transferred into some "internal state" of the ice to turn it into water, without raising the temperature of the ice itself. This was a clue about something “internal” about heat transfer.

Furthermore, Joule repeated his paddle-wheel experiment with mercury and found that a given amount of mechanical work raised the temperature of mercury much higher compared to that of water, i.e., for same input, there was different output.
All these experiments suggested that there was a missing piece in the equivalence of heat and work. Rudolf Clausius and Lord Kelvin found this missing piece and called it as the “internal energy” of a system. Presently, internal energy U is defined as the total kinetic and potential energy of the molecular constituents (i.e., of molecules, ions, etc.) present in the system. We may note that just like the volume, U is also a state function.

1.8 FIRST LAW OF THERMODYNAMICS

The mathematical form of the first law of thermodynamics:

Collecting all the historical findings above, the mathematical form of the first law is given as

$$dQ = dU - dW \qquad (1.1)$$

Which means if a system is heated by an amount dQ, a part of it increases the internal energy of the system by an amount dU and the rest of the heat is used to do $(-dW)$ amount of work by the system (we may note that in chemistry, the work done *on* the system *by* the surroundings is defined as $+dW$). Note that the heat energy absorbed is converted into internal energy and work done. So, the first law aligns with the principle of conservation of energy.

Elaborating the work done: An interesting way to elaborate thermodynamic work done is in terms of contraction (or expansion) of a gas confined in a cylinder which has a moveable piston on one side. If the gas is cooled, the pressure inside will decrease, and the piston will be pushed by the external pressure P_{ext}, contracting the system. Suppose, the piston is moved (in the inward direction) by an extent dL with force *F*. Then the work done by the surroundings (on the system) is given by:

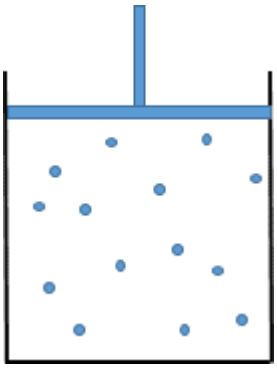
$$dW = FdL$$

$$\Rightarrow dW = \frac{F}{A} A\, dL$$

Where, A is the surface area of the piston. Since work is done by the external pressure on the piston, $F/A = P_{ext}$ is the external pressure and $dV = -A\, dL$ is the change (here, a decrease) in volume when the piston is moved, work done becomes:

$$dW = -P_{ext}\, dV \qquad (1.2)$$

This is an important result involving pressure and volume as the central quantities.



If the contraction is done reversibly, then in every step, the external pressure and the internal pressure P_{int} (it is denoted as just the pressure P) are approximately equal i.e., $P_{ext} \approx P_{int}$. Thus, the reversible work done is

$$dW_{rev} = -P_{int}\, dV$$

Thus, for a series of reversible expansion from volume V_1 to V_2 in increments of dV, the total reversible work done is

$$W_{rev} = -\int_{V_1}^{V_2} P_{int}\, dV \qquad (1.3)$$

If we enforce a cyclic process, say a reversible expansion from volume V_1 to V_2 and then a compression from volume V_2 to V_1 , all done, then from the first law of thermodynamics, the following cyclic integrals are interrelated as:

$$\oint dQ = \oint dU - \oint dW$$

Since, the initial and final states are same, the internal energy change during the whole process, $\Delta U = \oint dU = 0$ (as the internal energy U is a state function). Thus,

$$\oint dQ = -\oint dW \qquad (1.4)$$

Thus, all the heat supplied would be fully converted to work in a cyclic process. Note that this is true even for an irreversible cyclic process also. This is because, internal energy is a state function and it does not depend on whether the change is carried out reversibly or irreversibly. Since, the initial and final states are same, $\oint dU = 0$ even for an irreversible process. The fact that all the heat can be converted into work during a cyclic process hints at efficiency, which will be needed for Carnot's engine while we discuss the second law of thermodynamics.

Coming back to the reversible and work done, if a cyclic process of expansion and the compression back to the initial state is performed following exactly the same path, then

$$W_{rev}^{cyclic} = W_{rev}^{expansion} + W_{rev}^{compression}$$

$$W_{rev}^{cyclic} = -\int_{V_1}^{V_2} P_{int}\, dV - \int_{V_2}^{V_1} P_{int}\, dV = 0$$

We can represent it in general as

$$\oint dW_{rev} = 0 \qquad (1.5)$$

Thus, the work done in a reversible cyclic process is 0.

If the cyclic process is performed irreversibly, then $P_{ext} \approx P_{int}$. So the irreversible expansion work against a constant external pressure P_{ext} is

$$W_{irr}^{expansion} = -P_{ext}(V_2 - V_1)$$

After the expansion, the internal pressure is different and hence we need to apply a different (constant) external pressure ($P_{ext}^{'}$) to compress. Thus,

$$W_{irr}^{compression} = -P'_{ext}(V_1 - V_2)$$

$$W_{irr}^{cyclic} = -P_{ext}(V_2 - V_1) + \{-P'_{ext}(V_1 - V_2)\} \neq 0$$

We can represent it in general as

$$\oint dW_{irr} \neq 0 \qquad (1.6)$$

The work done in an irreversible cyclic process is non-zero.

Reversible work done *by the system* is greater than the irreversible work done:

Let us assume that expansion of a gas done reversibly and irreversibly. In the irreversible expansion, $P_{ext} < P_{int}$ and in the reversible expansion, $P_{ext} \approx P_{int}$. So, in both the cases, the work done by the system, –*W* will be:

$-W_{irr}^{expansion} = \int_{V_1}^{V_2} P_{ext}\, dV$, and $-W_{rev}^{expansion} = \int_{V_1}^{V_2} P_{int}\, dV$, so:

$$-W_{rev}^{expansion} > -W_{irr}^{expansion} \qquad (1.7)$$

This conclusion will again be important during the discussion of the Carnot engine.

The P-V curve:

The variation of pressure with respect to volume or vice versa is very important, as this has to do with expansion and compression of gases which is at the heart of thermodynamics. The general shape of the P-V graph is shown in **Figure 1.1**.

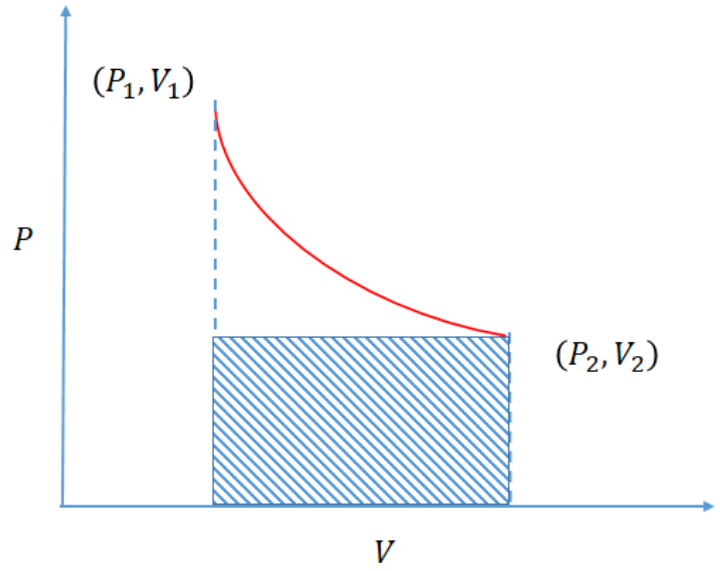


Figure 1.1: Variation of pressure with respect to volume. The shaded region is the associated irreversible P-V work done ($-W_{irr}$) by the system against constant pressure.

The curve ( ) is the general shape of the P-V plot and integration over the whole plot gives the area under the curve as shown by the shaded plus unshaded region and represents the associated reversible P-V work done ($-W_{rev}$) by the system.

The enthalpy function:

A state function, the enthalpy H, was defined as sum of the internal energy U and the product PV (of the two functions P and V) so that for experiments in laboratory which are usually performed in a constant pressure condition, the heat supplied dQ equals the change dH in this state function H. This can be shown as follows.

From first law, we knew $dQ = dU - dW$. As $dW = -P_{ext}\, dV$, and as for processes at constant pressure, $P_{ext} = P_{int}$ (i.e., P), so there $dQ = dU + PdV$

On the other hand, $dH = d(U + PV) = dU + PdV + VdP$. As at constant pressure *P*, *dP = 0*, this gives that for processes at constant pressure, $dH = dU + PdV$, and so:

$$dQ = dH = dU + PdV \qquad (1.8)$$

Where $$H = U + PV \qquad (1.9)$$

Note that as for the common constant-pressure condition, change of enthalpy equals the heat supplied, so enthalpy is sometimes called the heat content of the system.

Thermodynamic changes in isothermal process for an ideal gas system:

Temperature (T) remains constant during an isothermal process. Under such condition, the thermodynamic quantities of an ideal gas take special forms as discussed below.

a) Internal energy: Since there is no potential energy of interaction among the ideal gas molecules, the internal energy of an ideal gas is solely thermal energy i.e., the energy

possessed due to non-zero temperature. Thus, if T is constant, $dT = 0$ which means $dU = 0$ for an ideal gas at isothermal condition.

b) Heat: Since $dU = 0$, from the first law, $dQ = -dW$. Hence, all the energy supplied as or withdrawn from a system containing ideal gas will totally be converted into work under isothermal conditions.

c) Enthalpy: The change in enthalpy associated with any process carried under isothermal condition for a system of ideal gas is equal to zero as shown below.

$$dH = d(U + PV) = d(U + nRT) = dU + nRdT = 0$$

d) Reversible work done in an expansion: If an ideal gas undergoes expansion from volume V_1 to V_2, the work done is given by

$$W = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT\ ln\left(\frac{V_2}{V_1}\right) \qquad (1.10)$$

Heat Capacity of gases:

Heat capacity of a substance is the amount of heat required to raise its temperature by unit amount. Thus, if dQ amount of heat raises the temperature of a substance by dT, then heat capacity

$$C = \frac{dQ}{dT}$$

In case of solids or liquids, the volume of the substance remains practically constant while raising the temperature. However, in case of gases the volume changes if the temperature is not raised under constant volume condition. Hence, two types of heat capacities are defined in case of gases: heat capacity at constant pressure (C_P) and heat capacity at constant volume (C_V).

Expression for C_P:

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \qquad (1.11)$$

Since at constant pressure, $\partial Q = \partial H$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad (1.12)$$

Expression for C_V:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \qquad (1.13)$$

At constant volume condition, $\partial Q = \partial U$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (1.14)$$

C_P is always greater than C_V :

When a gas is heated at constant volume, no work is done and the heat is used to increase its internal energy. At constant pressure, the gas will expand and do some work. So, a part of the supplied heat is used to do the work and a part is used to raise

the temperature. Hence at constant pressure, more heat is required to raise the temperature of the gas by unit amount. Hence, $\boldsymbol{C_P > C_V}$.

Relation between $\boldsymbol{C_P}$ and $\boldsymbol{C_V}$ for an ideal gas:

$$dU = C_V dT$$
$$dH = C_P dT$$
$$\Rightarrow dU + PdV = C_P dT$$
$$\Rightarrow C_V dT + PdV = C_P dT$$
$$\Rightarrow (C_P - C_V)dT = PdV$$
$$\Rightarrow (C_P - C_V) = P\frac{dV}{dT}$$

Differentiating the ideal gas equation *PV = nRT* with respect to T at constant P,

$$P\frac{dV}{dT} = nR$$

Hence,

$$C_P - C_V = nR \qquad (1.15)$$

For 1 mole of ideal gas,

$$C_P - C_V = R$$

Thermodynamic changes in adiabatic process of an ideal gas:

In an adiabatic process, the heat content of a system remains constant, i.e.,

$$dQ = 0$$

So according to the first law of thermodynamics,

$$dU = dW$$

Change in internal energy:

From equation (1.14)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$
$$\Rightarrow dU = C_V dT$$

Integrating, from temperature T_1 to T_2 and corresponding internal energy U_1 to U_2

$$\Delta U = U_2 - U_1 = C_V(T_2 - T_1) \qquad (1.16)$$

Change in enthalpy:

From equation (1.9)

$$H = U + PV$$
$$\Rightarrow H = U + nRT$$
$$\Rightarrow dH = dU + nRdT$$

Integrating from temperature T_1 to T_2 and corresponding enthalpy H_1 to H_2 and using equation (1.16)

$$\Delta H = H_2 - H_1 = C_V(T_2 - T_1) + nR(T_2 - T_1)$$
$$\Delta H = H_2 - H_1 = (C_V + nR)(T_2 - T_1)$$

Since $C_P - C_V = nR$

$$\Delta H = H_2 - H_1 = C_P(T_2 - T_1) \qquad (1.17)$$

Relationship between T and V in an adiabatic process for an ideal gas:
In an adiabatic process,

$$dU = dW$$
$$\Rightarrow C_V dT = P_{ext}\, dV$$

For a reversible process, $P_{ext} \approx P_{int}$

$$C_V dT = P_{int}\, dV$$
$$C_V dT = \frac{nRT}{V} dV$$

Integrating from temperature T_1 to T_2 and corresponding volume V_1 to V_2

$$\int_{T_1}^{T_2} C_V \frac{dT}{T} = \int_{V_1}^{V_2} \frac{nR}{V} dV$$
$$\Rightarrow C_V\, ln\left(\frac{T_2}{T_1}\right) = nR\, ln\left(\frac{V_2}{V_1}\right)$$
$$\Rightarrow\ ln\left(\frac{T_2}{T_1}\right)^{C_V} = ln\left(\frac{V_2}{V_1}\right)^{nR}$$
$$\Rightarrow \left(\frac{T_2}{T_1}\right)^{1} = \left(\frac{V_2}{V_1}\right)^{nR/C_V}$$
$$\Rightarrow\ T\, V^{nR/C_V} = constant$$
$$\Rightarrow\ T\, V^{(C_P - C_V)/C_V} = constant$$
$$\Rightarrow\ TV^{\frac{C_P}{C_V}-1} = constant$$
$$\Rightarrow\ TV^{\gamma-1} = constant \qquad (1.18)$$

Equation (1.18) is the relation between T and V in an adiabatic change for an ideal gas where $\gamma = \frac{C_P}{C_V}$ is a constant for a given gas (e.g., 5/3 for the monatomic gases).

Relationship between T and P in an adiabatic process for an ideal gas:
Using ideal gas equation in (1.18)

$$T\left(\frac{RT}{P}\right)^{\gamma-1} = constant$$

$$T^{\gamma}\left(\frac{R}{P}\right)^{\gamma-1} = constant$$

$$\Rightarrow T^{\gamma} P^{(1-\gamma)} = constant \qquad (1.19)$$

Equation (1.19) is the relation between T and P in an adiabatic change from an ideal gas.

Relationship between P and V in an adiabatic process for an ideal gas:
Using ideal gas equation in (1.18)

$$\left(\frac{PV}{R}\right) V^{\gamma-1} = constant$$
$$\Rightarrow PV^{\gamma} = constant \qquad (1.20)$$

Equation (1.20) is the relation between P and V in an adiabatic change from an ideal gas.

1.9 CONCEPT OF THERMOCHEMISTRY AND HESS'S LAW

In the context of thermodynamic experiments, energy in the form of heat is, either absorbed or released due to chemical change. This is mainly due to some changes occurring during chemical reactions. The study of thermal changes accompanying chemical transformations constitute the soul of thermochemistry. We can identify two types of thermal changes associated with chemical transformations: 1. Exothermic processes where the surroundings gain heat from the system, i.e., the system gives out heat, 2. Endothermic processes where the surroundings lose heat to the system or in other words, the system absorbs heat. Before thoroughly diving deep into thermochemistry, a few thermodynamic quantities need to be introduced.

Standard Heat/Enthalpy of Reaction ($\Delta \boldsymbol{H^0_{rxn}}$):

Heat/Enthalpy of Reaction for a chemical reaction is the difference between the heat contents of the products and the reactants when stoichiometric gram molecular weights of the reactants in the chemical equation have reacted completely under standard conditions forming the products.

For example, the standard enthalpy of reaction for the formation of ammonia

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g) \qquad \Delta H^0_{rxn} = -46.0\ kJ\ mol^{-1}$$

Similarly, the standard enthalpy of reaction of formation of magnesium oxide

$$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(g) \qquad \Delta H^0_{rxn} = -601.7\ kJ\ mol^{-1}$$

$$\Delta H^0 = Heat\ content\ of\ product - Heat\ content\ of\ reactants$$

For example, consider a schematic reaction

$$A + B \rightarrow C + D$$

$$\Delta H^0 = \left(H^0_C + H^0_D\right) - \left(H^0_A + H^0_B\right)$$

$$\Delta H^0 = \left(\Delta H^0_{f_C} + \Delta H^0_{f_D}\right) - \left(\Delta H^0_{f_A} + \Delta H^0_{f_B}\right)$$

Where, $\Delta H^0_{f_i}$: standard heat/enthalpy of formation of the ith species.

Generalizing,

$$\Delta H^0 = \sum \Delta H^0_{f_{products}} - \sum \Delta H^0_{f_{reactants}}$$

Standard Enthalpy of Formation ($\Delta \boldsymbol{H^0_f}$)

The standard enthalpy of formation is the enthalpy change when one mole of a compound is formed from its constituent elements in their most stable forms under standard conditions (1 bar pressure and usually 298 K). The enthalpy of formation of elements in their standard states is 0.

Standard Enthalpy of Combustion ($\Delta \boldsymbol{H^0_C}$)

The standard enthalpy of combustion is the enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions. Combustion reactions are highly exothermic. The end product of complete combustion are usually CO_2 and H_2O for organic compounds.
For example, the standard enthalpy of combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^0 = -890.3\ kJ\ mol^{-1}$$

Standard Enthalpy of Neutralization (ΔH_{neut}^0)
The standard enthalpy of neutralization is the enthalpy change when one mole of water is formed from the reaction of an acid and a base in dilute solution under standard conditions. For example,

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + 2H_2O(l) \qquad \Delta H_c^0 = -57.3\ kJ\ mol^{-1}$$
$$NaOH(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) \qquad \Delta H_c^0 = -57.4\ kJ\ mol^{-1}$$

Since the main reaction in neutralization of strong acid by strong base is

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The enthalpies of neutralization strong acid-base pairs are very close.

Standard Enthalpy of Atomization (ΔH_{atom}^0):
Definition:
The standard enthalpy of atomization is the enthalpy change required to form one mole of gaseous atoms from a substance (element or compound) in its standard state. For example,

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \qquad \Delta H_{atom}^0 = 121.0\ kJ.mol^{-1}$$
$$Na(s) \rightarrow Na(g) \qquad \Delta H_{atom}^0 = 107.0\ kJ.mol^{-1}$$

Example of some calculations of different enthalpies:
1. The enthalpy of combustion of glucose is -2816 kJ.mol^{-1} at room temperature. Calculate the enthalpy of formation of glucose. Given that the enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ are –393.5 and –285.9 kJ.mol^{-1}

Solution: The reaction involved in combustion of glucose is

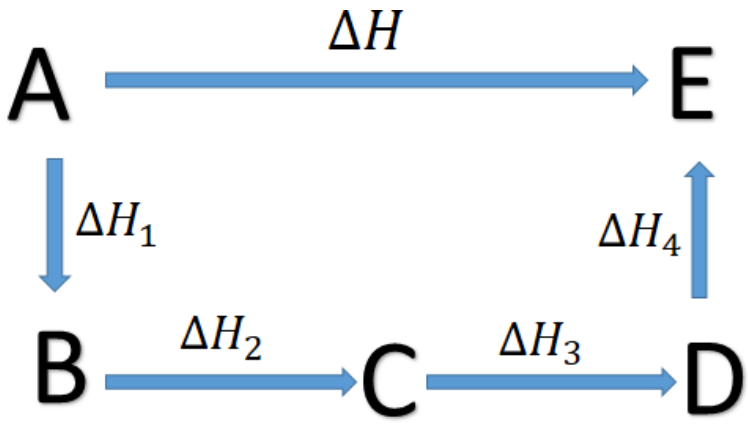
$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l), \quad \Delta H_C^0 = -2816\ \text{kJ}.mol^{-1}$$

$$\Delta H_C^0 = \sum \Delta H_f^0\ (products) - \sum \Delta H_f^0\ (reactantts)$$
$$\Delta H_C^0 = 6 \times \Delta H_f^0(CO_2) + 6 \times \Delta H_f^0(H_2O) - \Delta H_f^0(C_6H_{12}O_6) - \Delta H_f^0(O_2)$$

The standard enthalpy of formation of O_2 is 0. Hence,

$$-2816.0\ \text{kJ}.mol^{-1} = 6 \times (-393.5\text{kJ}.mol^{-1}) + 6 \times (-285.9\ \text{kJ}.mol^{-1}) - \Delta H_f^0(C_6H_{12}O_6)$$
$$\Delta H_f^0(C_6H_{12}O_6) = -1260.4\ \text{kJ}.mol^{-1}$$

Hess's Law of constant heat summation:
Hess's Law of Constant Heat Summation states that the total enthalpy change of a chemical reaction is the same, regardless of whether the reaction occurs in a single step or a series of multiple steps. This is shown pictorially below



According to the Hess law, for the reaction cycle shown in the figure

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

Hess's law is a direct consequence of the fact that enthalpy is a state function.

1.10 SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics, another profound generalisation about thermodynamic behaviour of real life systems, is expressible in several equivalent forms as given below. It seems strange that the following apparently diverse statements reflect the same underlying rule of nature and so are inherently equivalent!

Kelvin-Planck statement:
It is impossible to construct a device, operating in a cycle, the sole effect of which is the absorption of heat from a single heat reservoir and the complete conversion of that heat into work. The truth of this statement can be realised by considering the heat engines which turn heat into work, but in that process must transfer some part of the heat absorbed from the source to a reservoir at a lower temperature (e.g., the outside).

Clausius statement:
It is impossible to construct a device whose sole effect is the transfer of heat from a cool reservoir to a hot reservoir, essentially implying that heat cannot spontaneously flow from a colder body to a hotter body, as we know from our everyday experiences.

Statement in terms of entropy:
During a spontaneous thermodynamic process, the entropy function of the universe (i.e., of the system and its surroundings) must increase, while for a reversible process, value of that function for the universe remains constant. We'll define and learn more about that enigmatic thermodynamic function 'entropy' later.

The Carnot Cycle:
Sadi Carnot while trying to understand about the efficiency of steam engine stumbled upon the question – can a theoretical heat engine is possible with 100% efficiency? To answer this question, he imagined a theoretical heat engine that involves four reversible operations involving some ideal gas, as schematically shown below:

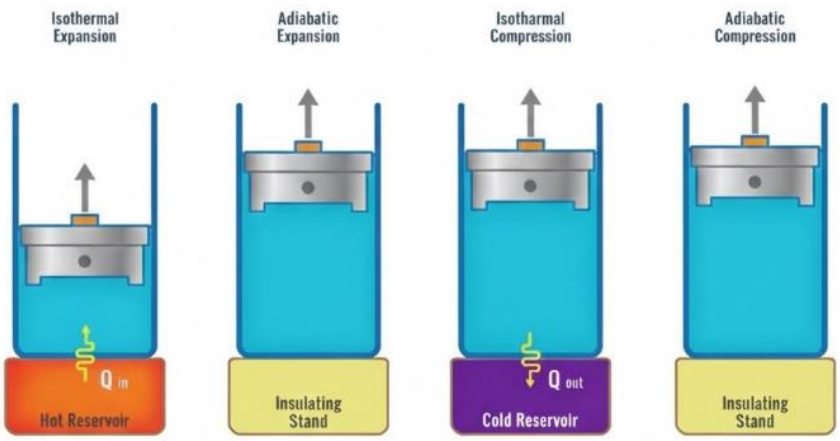


Figure 1.2: Schematic representation of the processes in Carnot cycle

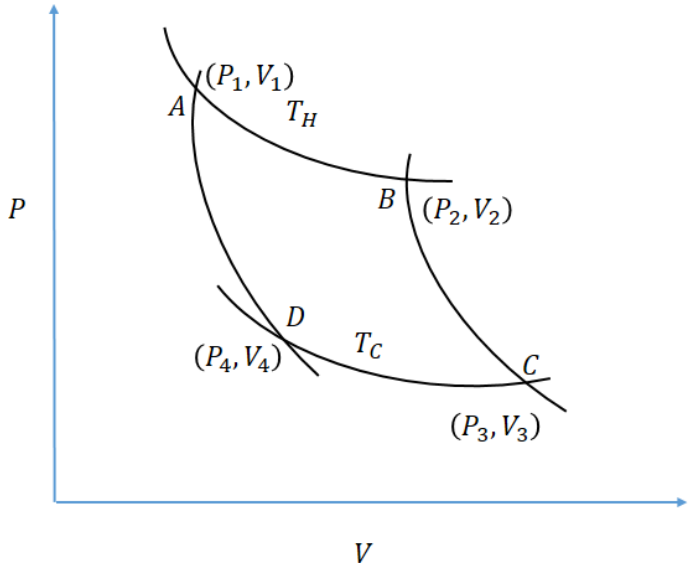


Figure 1.3: The P-V curves in the reversible cyclic processes of the Carnot engine

1. Isothermal reversible expansion: An amount of heat is supplied to the system from a hot heat reservoir at temperature T_H. The vessel containing the gas is such that heat cannot pass in or out of the system from the side walls or the piston, but possible only through the bottom. Since, the temperature is constant, all the supplied heat is converted into work. Let Q_H amount of heat is absorbed in this process and W_1 amount of work is done and the gas expands while the pressure decreases. Suppose, the system was initially at pressure P_1 and volume V_1 and after the expansion, they become P_2 and V_2, respectively.

$$Q_H = -W_1 = RT_H \, ln\left(\frac{V_2}{V_1}\right) \qquad (1.21)$$

2. Adiabatic reversible expansion: The container is now placed at an insulating stand so that heat cannot flow out of the container, but no heating is done at this stage either. The gas still expands till it stops. So, some work (W_2) is done under adiabatic expansion from pressure and volume of P_2 and V_2 to P_3 and V_3, respectively. At this

stage, the temperature of the gas decrease (T_C) as the expansion takes place at the expense of internal energy in absence of external heating. Hence,

$$\Delta U = W_2$$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$
$$\Delta U = C_V \Delta T = C_V(T_H - T_C) = W_2 \qquad (1.22)$$

3. Isothermal reversible compression: Now the container is shifted to a cold reservoir such that heat ($-Q_C$) will flow out of the container and compression of volume takes place from pressure and volume of P_3 and V_3 to P_4 and V_4. Since all the heat taken out is converted into work of compressing the volume, the temperature (T_C) of the system remain constant.

$$-Q_C = W_3 = RT_C \, ln\left(\frac{V_4}{V_3}\right) \qquad (1.23)$$

4. Adiabatic reversible compression: Again, the container is placed at an insulating stand so that heat cannot flow out of the container, but no outflow of heat occurs at this stage either. The gas still contracts and some work (W_4) is done under adiabatic compression from pressure and volume of P_4 and V_4 to P_1 and V_1, respectively completing the total cycle. At this stage, the temperature of the gas increases as the compression takes place at the expense of internal energy in absence of external heating. The final temperature as it reaches to the initial state becomes T_H. Hence,

$$\Delta U = W_4$$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$
$$\Delta U = C_V \Delta T = C_V(T_H - T_C) = W_4 \qquad (1.24)$$

Note that in step 1, Q_H amount of heat goes into the system and in step 3, $-Q_C$ amount of heat comes out of the system giving the total amount of heat involved in the process as ($Q_H + Q_C$). Since the system comes back to its original state, the change in internal energy, $\Delta U = 0$. Hence the total work done $-W_{tot}$ is equal to $Q_H + Q_C$. The efficiency of the Carnot engine is defined as

$$\eta = \frac{Total\ work\ done}{Total\ supplied\ heat} = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H}$$

From equations (1.21) and (1.23),

$$\frac{Q_C}{Q_H} = \frac{-RT_C ln\left(\frac{V_4}{V_3}\right)}{RT_H ln\left(\frac{V_2}{V_1}\right)}$$

From steps 2 and 4,

$$C_V ln\left(\frac{T_2}{T_1}\right) = R ln\left(\frac{V_3}{V_2}\right)$$
$$C_V ln\left(\frac{T_2}{T_1}\right) = R ln\left(\frac{V_4}{V_1}\right)$$

From these two equations,

$$\frac{V_4}{V_3} = \frac{V_2}{V_1}$$

Combining these,

$$\eta = 1 - \frac{T_C}{T_H} \qquad (1.25)$$

Thus in order to achieve efficiency of 1, we must have either $T_C = 0\ K$ or $T_H = \infty$. Both of these are not physically viable and hence efficiency cannot be 100%.

1.11 CONCEPT AND PHYSICAL SIGNIFICANCE OF ENTROPY

It follows form the efficiency of Carnot cycle that

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

In fact, for an infinite number of Carnot cycles, we can write that

$$\sum \frac{Q_i}{T_i} = 0$$

In the limit of infinitesimally small Carnot cycles, we can replace Q_i by dQ and since Carnot cycle is cyclic and reversible,

$$\oint \frac{dQ(rev)}{T} = 0$$

$$\oint dS = 0$$

Where

$$dS = \frac{dQ(rev)}{T}$$

Is defined as the infinitesimal change in a state function called entropy of the system. The justification of this lies in the fact that the cyclic integral of the differential of only a state function is always zero – as was also the case with the internal energy U, where we found that $\oint(dQ + dW) = 0$, leading to the idea that $(dQ + dW)$ must equal the differential of some state function, that state function being identified and denoted as U. Here, similarly, as $\oint dQ(rev)/T$ is found to be zero, so $dQ(rev)/T$ must equal differential of some state function, here which is the entropy S.

Physical significance of entropy:

Entropy is understood as the measure of disorderliness of a system. This means that more is the entropy of a system, more would be the disorderliness of that system. However, there is a microscopic, statistical connection to entropy as well. As the number of microscopic states available to a system increases, the system can arrange itself among those states according to the physical properties of the system. For example, consider a hypothetical system of 4 particles with three available microscopic energy states with energy 1, 2 and 3 units. The physical property under observation is total energy of 6 units. Then, either two particles can occupy the 2-unit energy state and the remaining two occupy the 1-unit energy state, or one particle can occupy the 3-unit energy state and remaining three occupy the 1-unit energy state – in both these cases the total energy comes out to be 6 units. This sort of various microscopic arrangements leads to disorderliness, and this gets expressed as entropy.

1.12 CLAUSIUS INEQUALITY

The Clausius inequality is a mathematical expression of the Second Law of Thermodynamics formulated by Rudolf Clausius. It provides a quantitative way to distinguish between reversible and irreversible processes and leads directly to the concept of entropy.

$$\oint \frac{dQ}{T} \leq 0$$

For a reversible process,

$$\oint \frac{dQ_{rev}}{T} = 0$$

And for an irreversible process,

$$\oint \frac{dQ_{irr}}{T} < 0$$

The physical meaning of this inequality is that in real processes some energy becomes unavailable for useful work. This happens because irreversibility generates entropy. Thus the Clausius inequality quantifies the direction of natural processes.

Traditionally, however, Clausius inequality is expressed more in the more popular form ***dQ / T ≤ dS***. This popular form is found from the idea that *S* being a state function, the cyclic integral of *dS* is zero. Thus, the cyclic integral of *dQ/T* is smaller of equal to that of *dS*, thus implying *dQ/T ≤ dS*, which is the aforesaid form.

We are now in a position to appreciate and properly learn the statement of the second law of thermodynamics in terms of entropy, to which statement the Clausius inequality is directly intertwined. This statement states that $dS_{univ} \geq 0$, where S_{univ} is the entropy of the universe, and the greater than sign stands for spontaneous processes while the equal to sign stands for reversible processes. Now, as entropy is an additive property, $dS_{univ} = dS + dS_{surr}$ where *dS* and dS_{surr} , understandably, stands for entropy change of the system and of the surroundings. However, it can be shown that dS_{surr} always equals – *dQ/T*, so that $dS_{univ} = dS - dQ/T$. Thus, the statement expression $dS_{univ} \geq 0$ implies $dS - dQ/T \geq 0$, or that $dS \geq dQ/T$, or, $dQ/T \leq dS$.

W CHECK YOUR PROGRESS

Q1. A glass of water is an example of a) open system, b) closed system

Q2. Which of the following quantities are state functions or path functions: internal energy, internal energy per mole of an ideal gas, work done? Explain your answer.

Q3. Explain why C_P is always greater than C_V for a gas.

Q4. Calculate the enthalpy change for the transition graphite ⇌ diamond from the standard enthalpy of combustion ($\Delta H^0_{combustion}$) values of $-393.5\ kJ.mol^{-1}$ and $-393.4\ kJ\ mol^{-1}$ for graphite and diamond, respectively.

2 1.13 LET US SUM UP

Thermodynamics systems are divided into isolated, closed and open systems depending upon whether mass and energy are transferable from or to the systems. The zeroth law laid the foundation of thermal equilibrium and establishes that temperature remains constant in a system at thermal equilibrium. The first law of thermodynamics is the conservation of energy and states that if heat is supplied to a system, then a part it gets converted to internal energy and the rest is used to do work. The second law establishes the concept of entropy and proves that no machine can have 100% efficiency.

K 1.14 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: a) open system

Answer to Q2: Internal energy: extensive property, internal energy per mole of an ideal gas: intensive property. Because the second property is per mole, so it is independent of the amount of the substance.

Answer to Q3: Because, at constant pressure a part of the supplied heat is used to do the work and only a part is used to raise the temperature at constant temperature, while at constant volume condition, the total heat supplied is used to raise the temperature. So at constant pressure, more heat is required to raise the temperature by unity.

Answer to Q4:

$C(s, graphite) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^0_{combustion} = -393.5\ kJ.mol^{-1}$

$C(s, diamond) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^0_{combustion} = -393.4\ kJ.mol^{-1}$

Subtracting the second reaction from the first

$C(s, graphite) \rightarrow C(s, diamond) \quad \Delta H^0_{combustion} = 1.9\ kJ.mol^{-1}$

O 1.15 FURTHER READING

- P.W. Atkins. *Physical Chemistry*. Oxford University Press.
- B.R. Puri, L.R. Sharma, Madan S. Pathania. *Principles of Physical Chemistry*
- I.N. Levine. *Physical Chemistry.* Mc Graw Hill (India)
- K.L. Kapoor. *A Textbook of Physical Chemistry, Vol. II.* Mc Graw Hill (India)

M 1.16 MODEL QUESTIONS

Q1. Give one example of each of open system, closed systems and isolated systems.

Q2. Calculate efficiency of a Carnot cycle for which temperatures during the isothermal expansions and compressions are 373 K and 273 K, respectively.

Q3. State the physical significance of entropy.

Q4. Calculate the work reversible work done during an isothermal expansion of an ideal gas from volume $10\ dm^3$ to $50\ dm^3$ at 300 K.

UNIT 2: THERMODYNAMIC FUNCTIONS, SPONTANEITY, EQUILIBRIUM AND MAXWELL RELATIONS

UNIT STRUCTURE

2.1 Learning Objectives
2.2 Introduction
2.3 Helmholtz and Gibbs Free Energy
2.4 Criteria of Spontaneity and Equilibrium
2.5 Gibbs-Helmholtz Equation
2.6 Le Chatelier's Principle and Its Applications
2.7 Maxwell's Relations and Their Applications
2.8 Thermodynamic Equations of State
2.9 Let Us Sum Up
2.10 Answers to Check Your Progress
2.11 Further Reading
2.12 Model Questions

2.1 LEARNING OBJECTIVES

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

- learn about the Helmholtz and Gibbs free energies
- explain the different criteria for spontaneity and equilibrium
- explain Le Chatelier's principle
- apply Maxwell's relations
- describe thermodynamic equation of state

2.2 INTRODUCTION

In **Unit 1**, we were introduced to the fundamental laws of thermodynamics that govern energy and heat transfer. In this unit, we shall be discussing the various thermodynamic functions that will aid us in determining whether or not a process or a reaction will spontaneously take place and under what circumstances it will be at equilibrium. The laws dealing with Gibbs Free Energy and Helmholtz Free Energy shall be developed to aid us in determining spontaneity. The temperature dependence of free energy shall also be examined in this chapter by discussing the Gibbs-Helmholtz Equation. Le Chatelier's Principle shall be introduced in this chapter to discuss how systems in equilibrium respond to changes in their environment. Various mathematical equations, such as Maxwell Relations and Thermodynamic Equations of State, shall be introduced which will aid us in interrelating different properties of thermodynamics.

2.3 HELMOHLTZ AND GIBBS FREE ENERGY

For discussing spontaneity of processes under certain conditions, two additional state functions are defined, based on the concepts of the internal energy *U*, the enthalpy *H* and the entropy *S* that we have already discussed. The Helmholtz free energy *A* is defined as $A = U - TS$, while the Gibbs free energy *G* is defined as $G = H - TS$. The universally valid criterion of spontaneity based on entropy (i.e., $dS_{univ} > 0$, implying $dS + dS_{surr} > 0$) evidently involves the consideration of entropy changes for both the system and the surroundings. But the criteria in terms of these two functions, of course valid only under certain common conditions, involve the changes in these state functions only for the system, which is an obvious advantage, though there lies the disadvantage of satisfying the said definite conditions.

The Helmholtz free energy *A* is also called the work function, because under the condition of constant temperature, the decrease in *A* gives the maximum possible work that can be done *by the system*. This is because: As $A = U - TS$, so $(dA)_T = dU - TdS = dU - dQ_{rev}$ (as $dS = dQ_{rev} / T$), and so $-(dA)_T = dQ_{rev} - dU = -dW_{rev}$ (from the 1st law). We earlier discussed that $-dW_{rev}$ is the maximum possible work done by the system. [You probably remember that a similar case was found about the enthalpy function, for which the isobaric decrease in the enthalpy *H* equals the heat released $-dQ$, and so enthalpy is also called as the heat content.] On the other hand, the Gibbs free energy *G* is also called the *net work function*, because under the condition of constant temperature and pressure, the decrease in *G* gives the maximum possible non-mechanical work (termed net work) that can be done *by the system*. This is shown as: $G = H - TS = U + PV - TS$, so $(dG)_{T,P} = dU + PdV - TdS = dU + PdV - dQ_{rev}$, and so, $-(dG)_{T,P} = dQ_{rev} - dU - PdV = -dW_{rev} - PdV$. As PdV is the mechanical work done by the system, so $-dW_{rev} - PdV$ is the maximum possible net work done by the system.

2.4 CRITERIA OF SPONTANEITY AND EQUILIBRIUM

Thermodynamics studies the relationships between heat, work, and energy in physical and chemical processes. Two central concepts in thermodynamics are spontaneity and equilibrium. Spontaneity determines whether a process (i.e., a change) can occur naturally under the given conditions, while equilibrium represents the state where no further net change occurs in the system.

Spontaneous Process: A spontaneous process is a process that occurs naturally without continuous external intervention. Spontaneity does not necessarily imply that the process is fast; it only indicates the direction in which a process tends to occur. Some examples of spontaneous process are heat flowing from a hot body to a cold body expansion of a gas into a vacuum, dissolution of salt in water etc. Spontaneity depends on thermodynamic conditions such as temperature, pressure, and the nature of the system.

Non-Spontaneous Processes: A non-spontaneous process does not occur on its own and requires external work input. For example, heat flowing from a cold body to a hot body requires electrical work (as in present-day refrigerators), compression of a gas requires external work etc.

Thermodynamic equilibrium: It is the state in which a system experiences no net macroscopic change with time. At equilibrium, all driving forces for change vanish.

Criteria of Spontaneity Based on Entropy: According to the second law of thermodynamics, the total entropy of the universe increases for a spontaneous process. For any process

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

For a spontaneous process: $\Delta S_{univ} > 0$

At equilibrium: $\Delta S_{univ} = 0$

Gibbs Free Energy Criterion:

For processes ***occurring at constant temperature and pressure***, in a system *where only P-V work is allowed*, spontaneity is determined by considering the change of Gibbs free energy of the system.

Spontaneous processes: $\Delta G < 0$

At equilibrium: $\Delta G = 0$

This criterion is widely used in chemistry and chemical thermodynamics.

Helmholtz Free Energy Criterion:

For processes ***occurring at constant temperature and volume***, in a system *where only P-V work is allowed,* the change of Helmholtz free energy of the system is considered to judge spontaneity.

Spontaneous processes: $\Delta A < 0$

At equilibrium: $\Delta A = 0$.

As was stated above, the last two criteria involve change of a function (G or A) only of the system, not requiring the same for the surroundings, unlike for the case of the criterion based on entropy. These two criteria can be easily derived from the entropy-based criterion, as detailed below.

As $dS_{univ} \geq 0$ and as $dS_{surr} = -dQ/T$, so $dS - dQ/T \geq 0$ or $dS \geq dQ/T$ (we came across it as one form of the Clausius inequality), implying $dQ - TdS \leq 0$. Next, to derive $\Delta A \leq 0$ for processes at constant T and V, we note that for a system where only P-V work is allowed, work done $dW = -P_{ext}\, dV$ and so at constant volume, $dW = 0$ giving $dQ = dU - dW = dU$. So we get $dU - TdS \leq 0$. Next, as $A = U - TS$, we get $dA = dU - TdS - SdT$, and so at constant T & V, $dA = dU - TdS$, implying $dA \leq 0$. Integrating, we get $\Delta A \leq 0$.

Similarly, to derive $\Delta G \leq 0$ for processes at constant T and P, we note that here also $dW = -P_{ext}\, dV$ and so at constant pressure P, where external pressure P_{ext} need equal the system pressure P, $dW = -P\, dV$. This gives $dQ = dU - dW = dU + PdV$. So, the above relation $dQ - TdS \leq 0$ here implies $dU + P\, dV - T\, dS \leq 0$. Next, as $G = H - TS = U + PV - TS$, we get $dG = dU + PdV + VdP - TdS - SdT$, and so at constant T and P, $dG = dU + P\, dV - T\, dS$, implying $dG \leq 0$. Integrating, we get $\Delta G \leq 0$.

2.5 GIBBS–HELMHOLTZ EQUATION

From $G = H - TS = U + PV - TS$, we get $dG = dU + PdV + VdP - TdS - SdT$. Now, for a simple, inert closed system allowing only *P-V* work and containing an unreactive substance (e.g., some nitrogen gas), the reversible work done dW_{rev} equals $-P\,dV$ (as $dW = -P_{ext}\,dV$ while for reversible process $P_{ext} = P$) and so, $TdS = dQ_{rev} = dU - dW_{rev} = dU - (-PdV) = dU + PdV$. This relation, $TdS = dU + PdV$, for a system containing such an inert substance, is known in thermodynamics as a *fundamental equation*. Substituting this equation in the above expression for dG, we get another *fundamental equation*: $dG = VdP - SdT$.

Gibbs-Helmholtz equation means a set of equations (all obtainable from the above fundamental equation) that discusses how the Gibbs free energy *G* of a substance, or its change *ΔG* during a chemical or physical transformation, changes with the change in temperature. Generally, Gibbs-Helmholtz equation means either of the two relations:

$$\text{(i) } (\partial(G/T)/\partial T)_P = -H/T^2 \quad \text{and} \quad \text{(ii) } (\partial(\Delta G/T)/\partial T)_P = -\Delta H/T^2 \qquad (2.1)$$

However, some Indian authors have also named two other related equations

$G = H + T(\partial G/\partial T)_P$ and $\Delta G = \Delta H + T(\partial \Delta G/\partial T)_P$ as Gibbs-Helmholtz equations!

To derive all these relations, we note that the above fundamental equation implies $(\partial G/\partial T)_P = -S$, so that $G = H - TS = H + T(\partial G/\partial T)_P$ (this is the third equation). Next, considering *G/T* as a product of two functions *G* and *1/T*, we get that $(\partial(G/T)/\partial T)_P$ equals $(1/T).(\partial G/\partial T)_P + G.(\partial(1/T)/\partial T)_P = (1/T).(-S) + G.(-1/T^2) = -S/T - G/T^2 = -(TS+G)/T^2 = -H/T^2$, giving (i). Next, applying relation (i) for the initial state i and the final state f of the system corresponding to a transformation, we get $(\partial(G_i/T)/\partial T)_P = -H_i/T^2$ and $(\partial(G_f/T)/\partial T)_P = -H_f/T^2$. Subtracting, we would get:

$(\partial(G_f/T)/\partial T)_P - (\partial(G_i/T)/\partial T)_P = -H_f/T^2 + H_i/T^2 = -(H_f - H_i)/T^2$, giving equation (ii).

The Gibbs-Helmholtz equation (ii) is particularly useful in discussing temperature dependence of transformations, such as of chemical reactions and of physical state transitions. Considering the well-known relation $\Delta_r G° = -RT \ln K$, where $\Delta_r G°$ is the standard Gibbs free energy change for a reaction and *K* is the equilibrium constant, we get $\Delta_r G°/T = -R \ln K$, implying:

$$(\partial \ln K/\partial T)_P = \Delta_r H°/(RT^2) \qquad (2.2)$$

This well-known relation, useful in treatments on chemical equilibrium, is called the van't Hoff equation. Thus we see that for an endothermic reaction, $\Delta_r H°$ is positive and so $(\partial(\ln K)/\partial T)_P$ is positive, implying that the equilibrium constant increases with an increase in temperature, thus shifting the equilibrium to the right, tending to negate the rise in temperature. Similarly, for an exothermic reaction, $\Delta_r H°$ is negative, so the equilibrium constant would decrease with a rise in temperature. This is exactly what is known from the Le Chatelier's principle also!

2.6 LE CHATELIER'S PRINCIPLE AND ITS APPLICATION

Le Chatelier's Principle states that if a system at equilibrium is subjected to some change, the equilibrium shifts in the direction that tends to undo the effect of the change.

There are three primary factors that can alter the state of a chemical equilibrium: concentration, temperature and pressure. Note that addition of a catalyst has no effect on the position of equilibrium. It merely increases the speed at which equilibrium is reached by accelerating both the forward and backward reactions equally. Below, we discuss how the Le Chatelier's principle comes into play in response to changes in various factors.

Effect of Change of Concentration:

When the concentration of a substance in an equilibrium system is changed, the system shifts to consume the added substance or replace the removed substance. Consider the following reaction

$$\underset{Pale\ yellow}{Fe^{3+}(aq)} \quad + \quad \underset{Colourless}{SCN^{-}(aq)} \quad \leftrightharpoons \quad \underset{Dark\ brown}{FeSCN^{2+}(aq)}$$

Adding reactant component e.g. ferric chloride ($FeCl_3$) or potassium thiocyanate ($KSCN$) is added, the concentration of Fe^{3+} or SCN^{-} ions increases. According to Le Chatelier's Principle, the equilibrium shifts to the right, increasing the concentration of the dark brown colour of the product complex. On the other hand, if the complex $FeSCN^{2+}$ is added, the equilibrium shifts to the left.

In general, increasing the concentration of the reactant(s) shifts the equilibrium towards the right (product) and increasing the concentration of the product(s) shifts the equilibrium towards the left (reactant).

Effect of Change of Temperature

As a chemical equilibrium involves two opposing reactions, clearly, one would be exothermic (evolves heat) and the other one endothermic (absorbs heat). For example, consider this equilibrium:

$$N_2O_4(g) \rightleftarrows 2NO_2(g), \qquad \Delta H = 59.0\ kJ$$

Since the forward reaction is endothermic, the backward reaction is exothermic. Therefore, increasing the temperature favours the endothermic reaction and hence the forward reaction will be favoured to maintain the equilibrium. On the other hand, decreasing the temperature favours the exothermic reaction and hence the backward reaction will be favoured. In last unit, this generalisation was mathematically verified.

Effect of Change of Pressure

Pressure comes into play when the reactants or products involve gaseous species. For example, consider this equilibrium

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

Since here 4 moles of the gaseous reactants can react to produce 2 moles of the gaseous product, upon formation of the product the pressure tends to decrease. If the pressure is increased, then according to Le Chatelier's principle, the system will try to decrease is pressure and hence also the total number of moles of gaseous species.

Hence, the reaction will go in forward direction with increasing pressure. Decreasing the pressure will drive the reaction in the backward direction.

2.7 MAXWELL'S RELATIONS AND THEIR APPLICATIONS

So far, four energy related thermodynamic functions have been discussed in previous sections which are internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G). For an inert closed system discussed in Section 2.5, these energy-based thermodynamics functions are mathematically related, via the following set of four mutually equivalent fundamental equations, to the other thermodynamic variables pressure, temperature, volume and entropy, as:

$$dU = TdS - PdV \qquad (2.3)$$

$$dH = TdS + VdP \qquad (2.4)$$

$$dA = -SdT - PdV \qquad (2.5)$$

$$dG = -SdT + VdP \qquad (2.6)$$

Derivations of the other three relations from equation (2.3), the one already derived in Section 2.5, are rather obvious. Recalling the defining expressions for these functions, namely *H = U + PV, A = U – TS, G = H – TS = U + PV – TS*, we get *dH = dU + P dV + V dP, dA = dU – T dS – S dT* and *dG = dU + P dV + V dP – T dS – S dT*. You can now easily verify that substitution of *dU = T dS – P dV* in the above expressions of *dH, dA* and *dG* results in equations (2.4), (2.5) and (2.6)

For such an inert simple system, let us now consider U as a function of S and V, H as a function of S and P, A as a function of T and V, and G as a function of T and P, i.e.:

$$U = U(S, V)$$

$$H = H(S, P)$$

$$A = A(T, V)$$

$$G = G(T, P)$$

So, their differential forms are given as:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad (2.7)$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \qquad (2.8)$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \qquad (2.9)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad (2.10)$$

Comparing (2.3) and (2.7)

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S \qquad (2.11)$$

Comparing (2.4) and (2.8)

$$T = \left(\frac{\partial H}{\partial S}\right)_P \qquad V = \left(\frac{\partial H}{\partial P}\right)_S \qquad (2.12)$$

Comparing (2.5) and (2.9)

$$S = -\left(\frac{\partial A}{\partial T}\right)_V \qquad P = -\left(\frac{\partial A}{\partial V}\right)_T \qquad (2.13)$$

Comparing (2.6) and (2.10)

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T \qquad (2.14)$$

Equation 2.11 can be further differentiated as:

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial V \partial S} \qquad \left(\frac{\partial P}{\partial S}\right)_V = -\frac{\partial^2 U}{\partial S \partial V}$$

Since, energy *U* is a state function, Euler's reciprocity equality holds and one can write

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (2.15)$$

Similarly, equation 2.12 can be further differentiated as

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial^2 H}{\partial P \partial S} \qquad \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P}$$

Again enthalpy being a state function, Euler's reciprocity equality holds and one can write

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad (2.16)$$

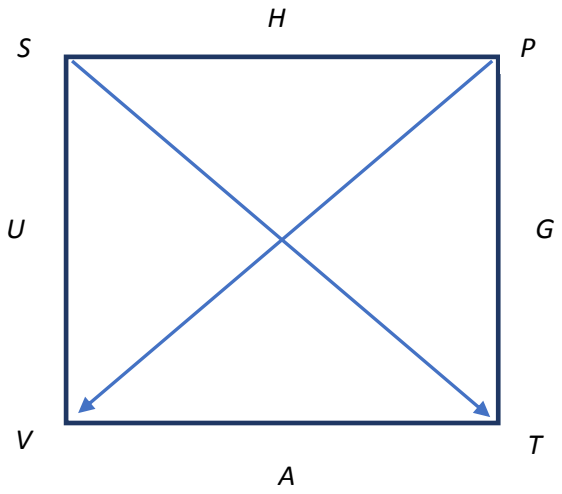
Following the same procedure with equations 2.13 and 2.14 (do that yourself), we get:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (2.17)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (2.18)$$

Collectively, the four equations (2.15) to (2.18) are called as **Maxwell's relations**, valid for the aforesaid type of inert closed systems. The Maxwell's relations are important because they give how entropy changes (difficult to measure experimentally) with respect to other thermodynamic variables in terms of derivatives of experimentally measureable quantities.

Maxwell's relations can be mentally recalled by using a mnemonic device called as the thermodynamic square.



In this square, the thermodynamic functions *H*, *G*, *A* and *U* appear at the sides of the square and the variables on which these functions depend on appear at the corners of the square. The variables at the corners appear in the derivatives while the corresponding constant variables (which appear as subscripts) are indicated by the arrow. For example, considering the opposite sides U and G, one obtains

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{and} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

2.8 THERMODYNAMIC EQUATIONS OF STATE

Thermodynamic equation of state relates different fundamental thermodynamic quantities of a given thermodynamic system (which is a closed, inert one, just as the one we came across very recently). This can be understood in the same spirit of the ideal gas equation or the equation of state for ideal gases ($PV = nRT$) that relates the fundamental variables P, V and T. However, a thermodynamic equation of state is a general one, which is applicable for any substance and in any physical state (i.e., gas, liquid or solid), unlike the ideal gas equation which is applicable only for an ideal gas. Below, we would derive two thermodynamic equations of state, involving different thermodynamic functions.

Let us start with the first fundamental equation, Equation (2.3), $dU = T\,dS - P\,dV$. Dividing this with dV and imposing the condition of constant temperature, we get:

$$(\partial U/\partial V)_T = T\,(\partial S/\partial V)_T - P$$

Now substituting the third Maxwell relation, Equation (2.17), therein, we get:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (2.19)$$

Equation (2.19) is the **thermodynamic equation** of state relating internal energy with pressure, temperature and volume.

To derive the other thermodynamic equation of state that relates enthalpy with other variables, we instead start with the second fundamental equation, namely Equation (2.4), *dH = T dS + V dP*, and divide that with dP while imposing the condition of constant temperature, leading to:

$(\partial H/\partial P)_T = T\,(\partial S/\partial P)_T + V.$

Now substituting the fourth Maxwell relation, Equation (2.18), therein, we get:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (2.20)$$

Equation (2.20) is the thermodynamics equation of state involving enthalpy, and it gives the variation of enthalpy against pressure at constant temperature in terms of an easily measureable quantity $\left(\frac{\partial V}{\partial T}\right)_P$.

It is interesting to verify whether these generalised thermodynamic equation of states remain valid for known specific cases, such as that of an ideal gas. As an ideal gas obeys the ideal gas equation *PV = nRT*, so for it *P = nRT/ V*. Considering the equation of state (2.19), we find that its RHS will become, $T\,(\partial P/\partial T)_V - P = T\,(nR/V) - P = P - P = 0$. This would imply $(\partial U/\partial V)_T = 0$, which is indeed a true and well-known relation for ideal gases. From the other thermodynamic equation of state (2.20), we may similarly find that $(\partial H/\partial P)_T = 0$ for ideal gases.

W CHECK YOUR PROGRESS

Q1. Which of the following is a right choice for describing spontaneity of the process

$$A \rightarrow B\,, \qquad \Delta\chi = m$$

Where

a) χ is entropy and m is positive at constant temperature and internal energy
b) χ is Helmholtz energy and m is positive at constant temperature and internal energy
c) χ is Gibbs energy and m is positive at constant temperature and internal energy

Q2. Predict whether the reaction will move in forward or backward direction when the temperature is a) increased, b) decreased

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) \qquad \Delta H = -92.38\ kJ$$

Give justification of your prediction

Q3. Obtain the Maxwell's relation based on the opposite sides H and A of the thermodynamic square

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

2 2.9 LET US SUM UP

The criteria for equilibrium under different thermodynamic conditions are
At constant U and $V \rightarrow$ Entropy is maximum.

At constant T and $V \rightarrow$ Helmholtz free energy is minimum.

At constant T and $P \rightarrow$ Gibbs free energy is minimum.

The criteria for spontaneity under different thermodynamic conditions are

At constant U and $V \rightarrow$ Entropy change is positive.

At constant T and $V \rightarrow$ Helmholtz free energy change is negative.

At constant T and $P \rightarrow$ Gibbs free energy change is negative.

Le Chatelier's principle states that a system in thermodynamic equilibrium tries to nullify the any effect e.g. change in concentration, pressure, temperature etc that can disturb the equilibrium. The Maxwell's relations are very important in thermodynamics, which connects experimentally less measurable quantities to the ones which can be measured easily.

K 2.10 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: (a) χ is entropy and m is positive at constant temperature and internal energy

Answer to Q2: If temperature is increased, then the backward reaction is favoured, because the backward reaction is exothermic. If temperature is decreased, the forward reaction is favoured, because the forward reaction is endothermic

Answer to Q3: Follow the last part of **section 2.7** to derive these Maxwell's relations.

O 2.11 FURTHER READING

- P.W. Atkins. *Physical Chemistry*. Oxford University Press.
- B.R. Puri, L.R. Sharma, Madan S. Pathania. *Principles of Physical Chemistry*
- I.N. Levine *Physical Chemistry.* Mc Graw Hill (India)
- K.L. Kapoor *A Textbook of Physical Chemistry, Vol. II.* Mc Graw Hill (India)

M 2.12 MODEL QUESTIONS

Q1. Which of the following is a right choice for describing spontaneity of the process

$$A \rightarrow B\,, \qquad \Delta\chi = m$$

Where

a) χ is entropy and m is negative at constant temperature and pressure

b) χ is Helmholtz and m is negative at constant temperature and pressure

b) χ is Gibbs and m is negative at constant temperature and pressure

Q2. Which of the following is a right choice for describing spontaneity of the process

$$A \rightarrow B\,, \qquad \Delta\chi = m$$

Where

a) χ is entropy and m is negative at constant temperature and volume

b) χ is Helmholtz and m is negative at constant temperature and volume
b) χ is Gibbs and m is negative at constant temperature and volume.

Q3. Predict whether the reaction will move in forward or backward direction when the pressure is a) increased, b) decreased

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

Give justification of your prediction.

Q4. List the differences between Gibbs and Helmholtz free energy.

Q5. Derive the thermodynamic equation of states involving enthalpy.

UNIT 3: THERMODYNAMICS OF REAL GASES AND GAS MIXTURES

UNIT STRUCTURE

3.1 Learning Objectives
3.2 Introduction
3.3 Deviations from Ideal Gas Behaviour
3.4 Partial Molar Properties
3.5 Thermodynamics of Gases and Gas Mixtures
3.6 Fugacity and Fugacity Coefficient
3.7 Determination of Fugacity
3.8 Let Us Sum Up
3.9 Answers to Check Your Progress
3.10 Further Reading
3.11 Model Questions

3.1 LEARNING OBJECTIVES

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

- understand real gas and its deviation from ideality
- evaluate partial molar properties
- describe the concept of fugacity and fugacity coefficient
- understand and determine fugacity

3.2 INTRODUCTION

In the previous discussions, the behaviour of gases was considered as ideal for the sake of simplicity. However, real gases do not always obey the assumptions of the Ideal Gas Law, especially at high pressures and low temperatures. In this unit, the properties of real gases will be discussed and the reasons for the deviation from the behaviour of an ideal gas will be explained. The concept of Partial Molar Properties will then be discussed in order to understand the behaviour of the thermodynamic properties when the components are added to the mixture. Lastly, the concept of Fugacity and the Fugacity Coefficient will be discussed in order to understand the behaviour of real gases more accurately.

3.3 DEVIATIONS FROM IDEAL GAS BEHAVIOUR

The deviation from ideal behaviour is captured in terms of a quantity named compressibility factor (Z) which is defined as

$$Z = \frac{(PV)_{real}}{(PV)_{ideal}} = \frac{(PV)_{real}}{nRT}$$

In general, the subscript “real” is dropped and it the expression appear as

$$Z = \frac{PV}{nRT}$$

For an ideal gas, $Z = 1$. For a real gas the value of Z deviates from 1 and is a measure of how much is the deviation from ideality. Experimentally, the variation of compressibility factor vs. pressure was obtained for various gases; for the particular temperature of 0 °C these are as shown in the **Figure 3.1** below. Clearly, all the gases deviate more or less from the ideal behaviour. Further, it should be noted that the actual shape of such a plot for a given gas (say, N_2) depends on the temperature also: as the temperature is lowered, the gases tend to develop a dip as seen here for methane and carbon dioxide at 0 °C. Thus, for every gas there is a temperature, termed the *Boyle's temperature*, at which the given real gas behaves like an ideal gas, with its *Z* value practically equalling 1 over an appreciable range of pressure (starting from zero). For example, for N_2 the Boyle's temperature is around 153 °C.

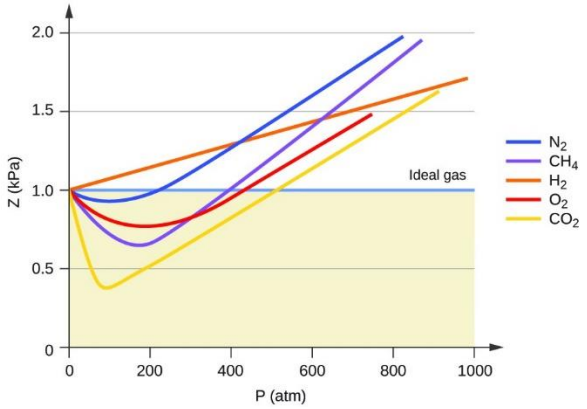


Figure 3.1: Deviation of real gases from ideal behaviour.

The deviations from ideal behaviour are attributed to limitations of two assumptions of kinetic theory of gases.

1. The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas. This assumption is valid only at low pressures and high temperature. When the pressure is high, total volume occupied by the gas molecules small. However, the individual molecules being “incompressible” maintains the same molecular volume even at high pressure. Hence, under high pressure conditions, the molecular volume is not negligible compared to the total volume occupied by the gas. On the other hand, volume is proportional to temperature. Hence at low temperature the total volume of the gas decreases and again the individual molecular volume becomes non-negligible (with respect to the total volume).

2. The forces of attraction between gas molecules are negligible. Again at conditions of high pressure or low temperature, the total volume of the gas is small. Hence, the intermolecular spaces decrease leading to appreciable forces of attraction and repulsion. The attractive forces between gas molecules cause the gas molecules to be attracted to each other reducing the pressure of the gas. Conversely, the repulsive forces between gas molecules cause the gas molecules to repel each other causing

them to hit the walls of the container with greater force, which increases the pressure of the gas.

In case of ideal gas, the equation of states or the ideal gas equation sets the starting point of further studies. Thus, it is imperative to have some equations of state for the real gases. The very first equation of state was given by Johannes Diderick van der Walls in 1873. His approach was to retain the form of the ideal gas equation, but correcting the pressure and volume terms with respect to real gases. Through detailed reasoning (clearly beyond the scope of this course on thermodynamics) that tried to correct the two aforementioned limitations in the assumptions of kinetic theory, van der Waals arrived at the following equation of state for the real gas, known as the van der Waals equation. [However, it should be kept in mind that there are several other equations of state for real gases, put forward by different scientists, though these are not as popular as the above one.]

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Where 'a' and 'b' are constants, these constants having different values for different gases. Here the constant 'a' signifies how much the actual pressure deviates from the ideal-gas pressure, arising because of the gas molecules about to collide with the container walls getting partially pulled back due to the attraction from the other nearby molecules. The constant 'b' signifies the deviation of the observed volume from the ideal-gas volume, arising because of the moving gas molecules not being able to move freely around the whole container volume due to presence of the other molecules having some small volume.

3.4 PARTIAL MOLAR PROPERTIES

An inherent assumption in the thermodynamics discussed so far is that the system is a closed system where matter cannot be exchanged with the surroundings. But, in an open system, matter can be exchanged. Furthermore, the system can be multicomponent, such as a mixture, say a solution. Then the thermodynamic functions not only depend on the macroscopic properties like temperature, pressure and volume, but also on the amounts of each substance present. For example, Gibbs free energy which is expressed as a function of T and P for closed systems, will become

$$G \rightarrow G(T, P, n_1, n_2, \cdots\cdots, n_k) \qquad (3.1)$$

Where n_i is the amount (number of moles) of the ith component in the system having k different components. The differential of G then becomes

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\cdots,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\cdots,n_k} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\cdots,n_k} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\cdots,n_k} dn_2 + \cdots\cdots + \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_1,n_2\cdots,n_{k-1}} dn_k$$

We can generalize this to any arbitrary extensive thermodynamic function *X* as:

$$X = X(T, P, n_1, n_2, \cdots\cdots, n_k)$$

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P,n_1,n_2,\cdots,n_k} dT + \left(\frac{\partial X}{\partial P}\right)_{T,n_1,n_2,\cdots,n_k} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T,P,n_2,\cdots,n_k} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T,P,n_1,\cdots,n_k} dn_2 + \cdots\cdots + \left(\frac{\partial X}{\partial n_k}\right)_{T,P,n_1,n_2\cdots,n_{k-1}} dn_k$$

Here $\left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$ is the partial molar property/quantity of *X* for the ith component which is usually represented by $\bar{X}_i$.

Some examples are,

Partial molar volume of the ith component, $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$

Partial molar internal energy of the ith component, $\bar{U}_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$

Partial molar entropy of the ith component, $\bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$

Partial molar enthalpy of the ith component, $\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$

Hence, partial molar quantity of the ith component with respect to any thermodynamic function (X) is defined as the change in X, per mole increase of the component i, when an infinitesimal amount (dn_i) of that component is added to the system, without changing pressure, temperature and the amounts of any other substances. Another equivalent definition also exists of partial molar quantity which states it as the change in X when 1 mole of the component i is added to a system (without changing anything else), which is so large that the addition of this component has practically no impact on the composition of the system.

The partial molar volume of the ith species in an ideal solution is equal to its molar volume in pure state. However, in all situations, the 'total volume' (actually speaking, just the volume V) of a solution is expressible as the sum of the products of the number of mole and the partial molar volume of each component, as: $V = \sum_i n_i \bar{V}_i$

Actually, such a relation is true for any kind of partial molar quantity $\bar{X}_i$, so that

$$X = \sum_i n_i \bar{X}_i$$

Chemical potential: The most important partial molar quantity is the chemical potential (μ_i) which is defined as the partial molar Gibbs free energy.

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k} \qquad (3.2)$$

Hence, chemical potential is the change in Gibbs free energy per mole of a multicomponent system when an infinitesimal amount (dn_i) of the *i*-th component is added at constant temperature, pressure and constant amounts of other components. As we have seen the differential form of Gibbs free energy

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\cdots,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\cdots,n_k} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\cdots,n_k} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\cdots,n_k} dn_2 + \cdots\cdots + \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_1,n_2\cdots,n_{k-1}} dn_k$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\cdots,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\cdots,n_k} dP + \mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots + \mu_k dn_k$$

At constant temperature and pressure, this means,

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots + \mu_k dn_k = \sum_i \mu_i dn_i \qquad (3.3)$$

Just what we wrote for the arbitrary extensive function X is true for G also, so:

$$G = \sum_i n_i \mu_i$$

For n moles of a pure substance, obviously, $G = n\mu$.

Gibbs-Duhem Equation:

Since

$$G = \sum_i \mu_i n_i$$

The total differential of G at constant temperature and pressure is

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots + \mu_k dn_k + n_1 d\mu_1 + n_2 d\mu_2 + \cdots\cdots + n_k d\mu_k$$

Applying equation (3.3), we find that at constant temperature and pressure

$$(dG)_{T,P} = (dG)_{T,P} + n_1 d\mu_1 + n_2 d\mu_2 + \cdots\cdots + n_k d\mu_k$$

$$\Rightarrow n_1 d\mu_1 + n_2 d\mu_2 + \cdots\cdots + n_k d\mu_k = 0$$

$$\Rightarrow \sum n_i d\mu_i = 0 \qquad (3.4)$$

This is the *Gibbs-Duhem equation*, the significance of this being that the variation of chemical potential of species in a thermodynamic system is not independent of each other. To elaborate it more, consider a binary solution having two components A and B.

Applying Gibbs-Duhem equation,

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\Rightarrow n_A d\mu_A = -n_B d\mu_B$$

Since n_A and n_B are non-negative, this equation means that if the chemical potential of component A increases, that of the component B would decrease.

Variation of chemical potential with temperature and pressure:

From equation (3.3)

$$(dG)_{n_1,n_2,\cdots,n_k} = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\cdots,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\cdots,n_k} dP$$

We will replace the set $(n_1, n_2, \cdots, n_k)$ in the subscript by the symbol n_j , getting

$$(dG)_{nj} = \left(\frac{\partial G}{\partial T}\right)_{P,nj} dT + \left(\frac{\partial G}{\partial P}\right)_{T,nj} dP$$

From equation (2.6), for a closed system where the numbers of moles are constant,

$$dG = VdP - SdT$$

Comparing the two equations

$$\left(\frac{\partial G}{\partial T}\right)_{P,nj} = -S \qquad (3.5)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,nj} = V \qquad (3.6)$$

We can now differentiate equation (3.5) with respect to n_i as

$$\frac{\partial^2 G}{\partial n_i \partial T} = -\left(\frac{\partial S}{\partial n_i}\right)_{P,N} \qquad (3.7)$$

Similarly, differentiating equation (3.6) we get

$$\frac{\partial^2 G}{\partial n_i \partial P} = -\left(\frac{\partial V}{\partial n_i}\right)_{T,N} \qquad (3.8)$$

According to the mathematical expression for the chemical potential,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$$

Differentiating with respect to T, we get

$$\frac{\partial^2 G}{\partial T \partial n_i} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} \qquad (3.9)$$

Differentiating chemical potential with respect to P, we get

$$\frac{\partial^2 G}{\partial P \partial n_i} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} \qquad (3.10)$$

Comparing equations (3.7) and (3.9) and imposing the requirement that G is an exact differential (i.e., that Euler's reciprocity relation is obeyed), we get

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial n_i}\right)_{P,N} = -\bar{S}_i \qquad (3.11)$$

Where, $\bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{P,N}$ is the partial molar entropy by definition.

Similarly, comparing equation (3.8) and (3.10) and imposing the requirement that G is an exact differential,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial n_i}\right)_{T,N} = \bar{V}_i \qquad (3.12)$$

Where, $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,N}$ is the partial molar volume by definition.

Hence, the variations of chemical potential with respect to temperature and pressure are the negative of partial molar entropy and partial molar volume itself, respectively.

Entropy of a substance is always positive, hence, chemical potential decrease with the increase in temperature as per equation (3.11). Since, entropy in the gaseous state is more than the liquid state followed by solid state, the trend in the decrease in chemical potential when temperature increases follows the trend accordingly as shown below in **Figure 3.2**. Note that the slope of the curve for the gaseous phase is steepest, indicating fastest decreasing in chemical potential as temperature increases as the gaseous phase has maximum molar entropy. Following this logic, the slopes for the liquid and solid states follows. Furthermore, at the melting point (T_m), solid and liquid phases are in equilibrium and hence same chemical potential. Similarly at the boiling point (T_b), the chemical potentials for the liquid and gaseous phases are equal.

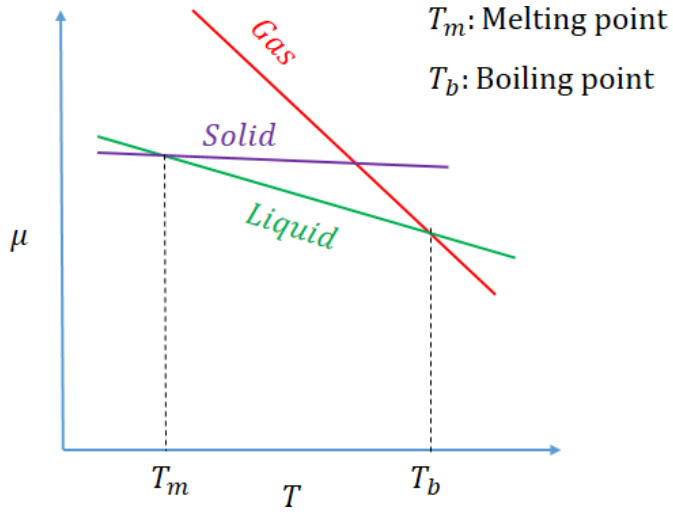


Figure 3.2: Variation of the chemical potential with temperature for solid, liquid and the gas phase

3.5 THERMODYNAMICS OF GASES AND GAS MIXTURES

Chemical Potentials for a mixture of an ideal gas:

Consider a system containing k different ideal gases having n_j $(i = 1,2,\cdots,k)$ mole of the jth type of gas. The ideal has equation then becomes

$$PV = (n_1 + n_2 + \cdots + n_k)RT$$

$$V = (n_1 + n_2 + \cdots + n_k)\frac{RT}{P}$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} = \frac{RT}{P}$$

Using equation (3.13),

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{RT}{P}$$

$$\Rightarrow d\mu_i = RT\frac{dP}{P} \qquad (3.13)$$

If we consider only the *i*-th type of ideal gas with its partial pressure p_i, then we get

$$p_i = \frac{n_i RT}{V} \qquad (3.14)$$

Putting

$$V = (n_1 + n_2 + \cdots + n_k)\frac{RT}{P} = n_{tot}\frac{RT}{P}$$

$$p_i = \frac{n_i RT}{n_{tot}\frac{RT}{P}} = \left(\frac{n_i}{n_{tot}}\right)P = x_i P$$

Where x_i is the mole fraction of the *i*-th component gas. Rewriting equation (3.14) as

$$d\mu_i = RT\frac{d(x_i P)}{x_i P} = RT\frac{dp_i}{p_i}$$

Integrating, for the system considered to be in a given (i.e., constant) temperature

$$\mu_i = \mu_i^0 + RT\ ln\ p_i \qquad (3.15)$$

This equation (3.15) is the relation relating chemical potential of a component in an ideal gas mixture, at a given temperature. Here μ_i^0 is the constant of integration the physical significance of which will be seen later. Thus, the chemical potential μ_i of a particular species in a mixture of ideal gases depends on its partial pressure p_i, and clearly, it increases with its partial pressure p_i. If the partial pressure of the *i*-th species is unity then, clearly, $\mu_i = \mu_i^0$.

Clearly, for a pure ideal gas instead of an ideal gas mixture, $\mu_i = \mu$ and p_i = P, yielding

$$\mu = \mu^\circ + RT\ ln\ P \qquad (3.16)$$

Also, from equation (3.14)

$$p_i = \left(\frac{n_i}{V}\right)RT = c_i RT$$

Here the number of moles of the *i*-th species (n_i) per unit volume, i.e., (n_i/V) is the molar concentration (c_i) of that species.

We can rewrite equation (3.16) as $\mu_i = \mu_i^0 + RT\ ln(\ c_i RT)$, so

$$\mu_i = \mu_i^0 + RT\ ln(RT) + RT\ln c_i$$

Since $RT\ ln(RT)$ is a constant at a given temperature, we can define a new constant as $\mu_{i,c}^0 = \mu_i^0 + RT\ ln(RT)$, which yields:

$$\mu_i = \mu_{i,c}^0 + RT \ln c_i \qquad (3.17)$$

The ideal gas obeys the characteristic thermodynamic behaviour of its internal energy and enthalpy being independent of volume and pressure, both functions being dependent only on the temperature. In Section 2.8 within the last Unit, we found that for an ideal gas, both $(\partial U/\partial V)_T$ and $(\partial H/\partial P)_T$ equal zero. This will remain true even in an ideal gas mixture. An important consequence of this result, along with the above expressions about chemical potential of an ideal gas and of the components within an ideal gas mixture, is the fact that change of internal energy or enthalpy during isothermal-isobaric mixing of some ideal gases is always zero, while the change of Gibbs free energy is always negative. Here isothermal-isobaric mixing means mixing of several gases, all at a given temperature and a given pressure.

Let us consider several ideal gases (denoted as *1, 2, ….., k*) with respective amounts ($n_1, n_2, ,,,,,, n_k$) existing separated (by compartment walls within a large container) before mixing, all at a given temperature T and a given pressure P. Initially before mixing, the internal energy U_{ini} and the enthalpy H_{ini} of the combined (un-mixed) gas system are respectively $U_{ini} = \sum_i n_i \bar{U}_i$ and $H_{ini} = \sum_i n_i \bar{H}_i$. Finally after mixing, the internal energy U_{fin} and the enthalpy H_{fin} of the mixed gas system are respectively $U_{fin} = \sum_i n_i \bar{U}_i$ and $H_{fin} = \sum_i n_i \bar{H}_i$. As for any component gas in an ideal gas mixture, the temperature before and after mixing are the same given temperature, so the partial molar internal energy or enthalpy values of each component gas will remain same before and after mixing. So, during mixing of the gases, the change in internal energy $\Delta_{mix}U$ (also called the internal energy of mixing) or in enthalpy $\Delta_{mix}H$ (the enthalpy of mixing) will be, respectively,

$$\Delta_{mix}U = U_{fin} - U_{ini} = \sum_i n_i \bar{U}_i - \sum_i n_i \bar{U}_i = 0 \qquad (3.18)$$

$$\Delta_{mix}H = H_{fin} - H_{ini} = \sum_i n_i \bar{H}_i - \sum_i n_i \bar{H}_i = 0 \qquad (3.19)$$

However, for the Gibbs free energy of mixing, $\Delta_{mix}G$, the case would be quite different. As the partial molar Gibbs free energy $\bar{G}_i$, i.e., the chemical potential μ_i, depends on the partial pressure p_i in addition to the temperature T as per relation (3.15) for ideal gases, and as the partial pressure p_i before mixing will be the given pressure P while after mixing it will become $p_i = x_i P$, so

$$\begin{aligned}\Delta_{mix}G = G_{fin} - G_{ini} &= \sum_i n_i \left(\mu_i^0 + RT\ ln\ (x_i\ P)\right) - \sum_i n_i \left(\mu_i^0 + RT\ ln\ P\right) \\ &= \sum_i n_i \left(\mu_i^0\right) - \sum_i n_i \left(\mu_i^0\right) + \sum_i n_i \left(RT\ ln\ (x_i\ P)\right) - \sum_i n_i \left(RT\ ln\ P\right) \\ &= RT \sum_i n_i \ln x_i\end{aligned}$$

As above we got $n_i = x_i\ n_{tot}$, so here $\Delta_{mix}G = n_{tot}\ RT \sum_i x_i \ln x_i$

Now, as all mole fractions $x_i < 1$, so any $\ln x_i < 0$, implying that the sum $\sum_i x_i \ln x_i$ is always negative. This means that for isothermal-isobaric mixing of several ideal gases, $\Delta_{mix}G$, the Gibbs free energy change for mixing, is always negative. As per the well-known criterion of spontaneity for isothermal-isobaric processes, we so find that such

mixing of ideal gases is always a spontaneous process, as is experimentally obvious for our familiar nearly-ideal gases. Thus, for such mixing of ideal gases we write

$$\Delta mixG = n_{tot}\, RT \sum_i x_i \ln x_i < 0 \qquad (3.20)$$

For the said isothermal-isobaric mixing of gases, occurring at constant temperature and pressure, the entropy of mixing $\Delta_{mix}S$ will obviously be related to above quantities $\Delta_{mix}H$ and $\Delta_{mix}G$ as: $\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$. Substituting equations (3.19) and (3.20), this clearly yields the following relation, with $\Delta_{mix}S$ being always positive:

$$\Delta_{mix}S = -n_{tot}\, R \sum_i x_i \ln x_i > 0 \qquad (3.21)$$

However, for non-ideal real gases and their gas mixtures, none of the above relations (3.13) to (3.21) are exactly true, though in general these remain approximately valid. For the real gases, to do exact mathematical treatments, we need to define the *fugacity* function and to base our calculations on that function, as detailed in the next section.

3.6 FUGACITY AND FUGACITY COEFFICIENT

As mentioned above, for real gases and their mixtures, equations (3.15) and (3.16), relating the chemical potential with the partial pressure, are not exactly valid. Hence, a new function called the fugacity function (f) was introduced (rather, invented) for real gases which replaces the partial pressures or the pressure in equations (3.15) and (3.16), as shown below. Thus, fugacity f (for a pure gas) or f_i (for a component i in a gas mixture) is a sort of *effective pressure* of a real gas, and it somewhat differs from the actual observed pressure or partial pressure, due to the intermolecular interactions among the gas molecules in a real gas system.

$$\mu_i = \mu_i^0 + RT\ ln\ f_i \qquad (3.22)$$

$$\mu = \mu^\circ + RT\ ln\ f \qquad (3.23)$$

Thus, the difference in the chemical potential for a pure gas or a component at two pressure or partial pressure values is expressible in terms of the ratio of their fugacity values, such as for a pure gas:

$$\Delta\mu = \mu_2 - \mu_1 = RT\ ln\frac{f_2}{f_1} \qquad (3.24)$$

The ratio $\phi = \frac{f}{P}$ is called as fugacity coefficient. The fugacity coefficient (ϕ) is a dimensionless correction factor that measures how much a real gas deviates from the ideal gas behaviour. We may note that $\phi = 1$ means the gas is behaving ideally, $\phi < 1$ means attractive force between molecules are predominating and $\phi > 1$ means repulsive force between molecules are predominating. At moderate pressures and ordinary temperatures, the fugacity coefficient generally remains smaller than 1.

An invented function such as fugacity or fugacity coefficient would not have much use if it can't be determined by relating it to some measurable properties. In the next section, we discuss how to determine the fugacity and hence also the fugacity coefficient.

3.7 DETERMINATION OF FUGACITY

Integrating equation (3.23) for a pure gas with respect to pressure P keeping the temperature as constant gives

$$\left(\frac{\partial \mu}{\partial P}\right)_T = RT\left(\frac{\partial \ln f}{\partial P}\right)_T$$

Since the molar volume $\bar{V}_m = \left(\frac{\partial \mu}{\partial P}\right)_T$

$$\frac{\bar{V}_m}{RT} = \left(\frac{\partial \ln f}{\partial P}\right)_T$$

$$\Rightarrow RT(d \ln f) = \bar{V}_m dP$$

The deviation in volume of real gas from an ideal gas can be expressed as

$$\alpha = \frac{RT}{P} - \bar{V}_m$$

$$\Rightarrow \alpha\, dP = RT\, \frac{dP}{P} - \bar{V}_m\, dP$$

$$\Rightarrow \bar{V}_m\, dP = RT \frac{dP}{P} - \alpha\, dP$$

$$\Rightarrow RT(d \ln f) = RT(d \ln P) - \alpha\, dP$$

Integrating over pressure range 0 to P gives,

$$ln\left(\frac{f}{P}\right) = -\frac{1}{RT}\int_0^P \alpha\, dP$$

Experimentally, the values of the deviation in volume α is measured at different pressures over the range 0 to P. The area under the curve obtained in this way is equal to $(-RT\ ln(f/P))$ from which $ln(f/P)$ and finally the fugacity *f* can be determined.

W CHECK YOUR PROGRESS

Q1. State the significances of the van der Waals constants a and b.
Q2. Explain the significance of the Gibbs-Duhem equation.
Q3. How is a partial molar quantity of an extensive thermodynamic function defined? State a very popular example of a partial molar quantity.

2 3.8 LET US SUM UP

Real gases deviate from ideal behaviour, hence, correction to ideal gas pressure and volumes are done by introducing constants a and b. The van der Waals equation is a popular equation of state for the real gases. For multicomponent systems, partial molar quantities are the thermodynamic variables. Chemical potential is one of the most important partial molar quantities which is the change in free energy when 1 mole of a component is added to a multicomponent system so large that its composition does not practically change. For real gases, pressure is replaced by fugacity which is obtained by considering finite volumes of real molecules and attraction among them.

K 3.9 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: The van der Waals constant '*a*' signifies how much the pressure deviates from the ideal pressure. The constant '*b*' signifies the deviation from ideal volume.

Answer to Q2: Gibbs-Duhem equation signifies that for a multi-component system, the change in chemical potential of one component is dependent on that of other components.

Answer to Q3: The partial molar quantity $\bar{X}_i$ for the *i*-th component of an extensive thermodynamic function *X* is defined as the change in the function *X*, per mole increase of the component i, when an infinitesimal amount (dn_i) of that component is added to the system, without changing pressure, temperature and the amounts of any other substances. Thus,

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_1,n_2,\cdots,n_{i-1},\cdots,n_{i+1,\ldots}n_k}$$

The chemical potential μ_i is a very popular example of a partial molar quantity. It is the partial molar Gibbs free energy, i.e., $\mu_i = \bar{G}_i$.

O 3.10 FURTHER READING

- P.W. Atkins. *Physical Chemistry*. Oxford University Press.
- B.R. Puri, L.R. Sharma, M.S. Pathania. *Principles of Physical Chemistry*
- I.N. Levine. *Physical Chemistry.* Mc Graw Hill (India)
- K.L. Kapoor. *A Textbook of Physical Chemistry, Vol. I & II.* Mc Graw Hill (India)
- G.W. Castellan. *Physical Chemistry*. Addison-Wesley
- A.S. Negi, S.C. Anand. *A Textbook of Physical Chemistry,* New Age International

M 3.11 MODEL QUESTIONS

Q1. What is meant by the Boyle's temperature?
Q2. Explain why both the change of internal energy and the change of enthalpy, during isothermal-isobaric mixing of some ideal gases, must be zero.
Q3. Show that mixing of some ideal gases initially kept at the same temperature and pressure would always be spontaneous.
Q4. What is meant by fugacity of a gas? How can it be experimentally determined?

UNIT 4: THERMODYNAMICS OF NON-IDEAL SOLUTIONS AND ELECTROLYTES

UNIT STRUCTURE

4.1 Learning Objectives
4.2 Introduction
4.3 Ideal and Non-Ideal Solutions
4.4 Activity and Activity Coefficient
4.5 Different Scales of Activity and Activity Coefficient
4.6 Ionic Activity Coefficients
4.7 Applications to Chemical Equilibria
4.8 Let Us Sum Up
4.9 Answers to Check Your Progress
4.10 Further Reading
4.11 Model Questions

4.1 LEARNING OBJECTIVES

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

- know the basics of ideal and non-ideal solutions.
- explain the concept of activity and activity coefficients for non-ionic and ionic solution
- describe applications of thermodynamics to chemical equilibrium

4.2 INTRODUCTION

In many chemical processes, reactions occur in mixtures rather than in pure substances, making it important to understand the thermodynamics of solutions. This unit begins with the basic ideas of ideal and non-ideal solutions, where the behaviour of mixtures is compared with the predictions of Raoult's Law that governs ideal solution behaviour, and the deviations from it as observed in real solutions. To describe these deviations more accurately, the concepts of Activity and Activity Coefficient are introduced for both non-ionic and ionic solutions. These quantities allow real solutions to be treated within a thermodynamic framework similar to ideal systems. Finally, the unit applies these thermodynamic ideas to the study of Chemical Equilibrium, showing how equilibrium conditions and equilibrium constants can be understood in terms of activities rather than simple concentrations. Together, these concepts provide the foundation for analysing real chemical reactions in solution.

4.3 IDEAL AND NON-IDEAL SOLUTIONS

An ideal solution is a mixture where the interactions between different molecules are identical to the interactions between similar molecules. For example, a binary solution with components of liquid A and B, three types of interactions are possible, between

$A-A$, $B-B$ and $A-B$. When the solution is ideal, all the interactions are identical. In reality, many solutions act very close to ideal e.g., in a binary solution of benzene and toluene, the benzene-benzene, toluene-toluene and benzene-toluene interactions are nearly identical as benzene and toluene are structurally quite similar. Another example of a nearly ideal solution is a binary mixture of H_2O and D_2O. On the other hand, a binary solution of water and ethanol is non-ideal as the ethanol-ethanol, ethanol-water and water-water interactions differ.

Raoult's law: It is a law that is obeyed by ideal liquid solutions, and for non-ideal solutions there are deviations from this law. This law states that partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution.

In case of a binary solution with components of liquid A and B having n_A and n_B moles, respectively, the corresponding mole fractions are

$$x_A = \frac{n_A}{n_A + n_B} \qquad (4.1)$$

$$x_B = \frac{B}{n_A + n_B} \qquad (4.2)$$

Note that $x_A + x_B = 1$. If p_A^0 and p_B^0 are the vapour pressures of pure A and pure B liquids, then the corresponding partial pressures of the vapour of the solution are

$$p_A^{partial} = x_A p_A^0 \qquad (4.3)$$

$$p_B^{partial} = x_B p_B^0 \qquad (4.4)$$

If the vapour behaves like an ideal gas, then following the Dalton's law, total vapour pressure (P) is given by

$$P = p_A^{partial} + p_B^{partial} = x_A p_A^0 + x_B p_B^0 \qquad (4.5)$$

A solution with more than one liquid components is ideal if it follows Raoult's law at all concentrations and temperatures.

Vapour pressure of ideal solutions:

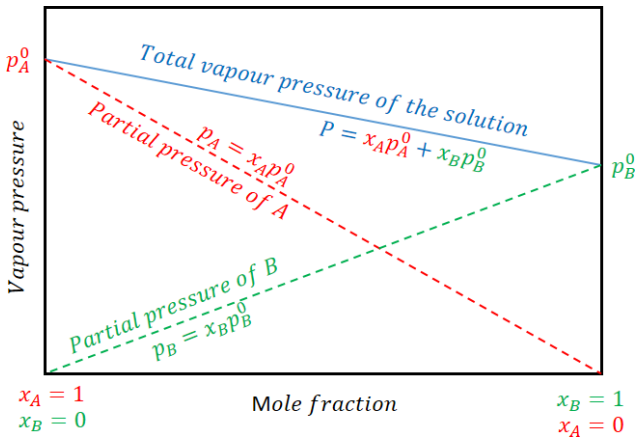


Figure 4.1: Vapour pressure of ideal solution vs. mole fraction of the constituents

The above figure shows how the total vapour pressure (P) of a binary ideal solution varies with the mole fractions and hence the partial pressures of the vapours of the constituents vary. For the left-most point, when $x_A = 1$ and $x_B = 0$ meaning that the liquid (a binary solution of A and B, but with the number of moles of B being zero) is pure A. Hence the total vapour pressure is the pressure of the vapour from pure A i.e., $P = p_A^0$. This can be seen in the left vertical axis of the figure. On the other extreme, when $x_A = 0$ and $x_B = 1$ meaning that the liquid (a binary solution, but with the number of moles of A being zero) is pure B. Hence the total vapour pressure is the pressure of the vapour from pure B i.e. $P = p_B^0$. This can be seen in the right vertical axis of the figure. When both the mole fractions are nonzero, the total pressure is the summation of the vapour pressure of the constituents weighted by the respective mole fractions. This is found to be a straight line joining the two above-mentioned points.

Chemical Potentials of Ideal Solutions:

The vapour of a binary solution behave ideally is actually a mixture of two ideal gases. So we can use equation (**3.16**). Furthermore, there is a liquid vapour equilibrium established in the binary solution. So chemical potential of the liquid phase is equal to that of the vapour phase. Thus, we can write for the component A of the binary mixture

$$\mu_A(l) = \mu_A(g) = \mu_A^0(g) + RT\ ln\ p_A^{partial} \qquad (4.6)$$

For the pure liquid A,

$$\mu_A^0(l) = \mu_A^0(g) + RT\ ln\ \ p_A^0 \qquad (4.7)$$

Rewriting equation (4.6)

$$\mu_A(l) = \mu_A^0(g) + RTln\ p_A^0 + RT\ln p_A^{partial} - RTln\ p_A^0$$

$$\Rightarrow\ \mu_A(l) = \left(\mu_A^0(g) + RTln\ p_A^0\right) + RT\ ln\left(p_A^{partial} \Big/ P_A^0\right)$$

$$\Rightarrow\ \mu_A(l) = \mu_A^0(l) + RT\ ln\left(p_A^{partial} \Big/ P_A^0\right) \qquad (4.8)$$

Since, $p_A^{partial}/p_A^0 = x_A$ according to equation (4.3)

$$\mu_A(l) = \mu_A^0(l) + RT \ln x_A \qquad (4.9)$$

Similarly for the component B

$$\mu_B(l) = \mu_B^0(l) + RT \ln x_B \qquad (4.10)$$

4.4 ACTIVITY AND ACTIVITY COEFFICIENT

For component A of an ideal binary solution as discussed above,

$$x_A = \frac{p_A}{p_A^0}$$

In case of a non-ideal solution, the mole fraction is replaced by activity and pressure is replaced by fugacity. Thus we define activity (a_A) as

$$a_A = \frac{f_A}{f_A^0}$$

Where, f_A is the fugacity of component A in solution and f_A^0 is the fugacity of pure A.

In case of an ideal solution, activity of each component is equal to the respective mole fraction in the binary solution. The relationship between activity and mole fraction for an ideal solution is shown graphically below in **Figure 4.2**.

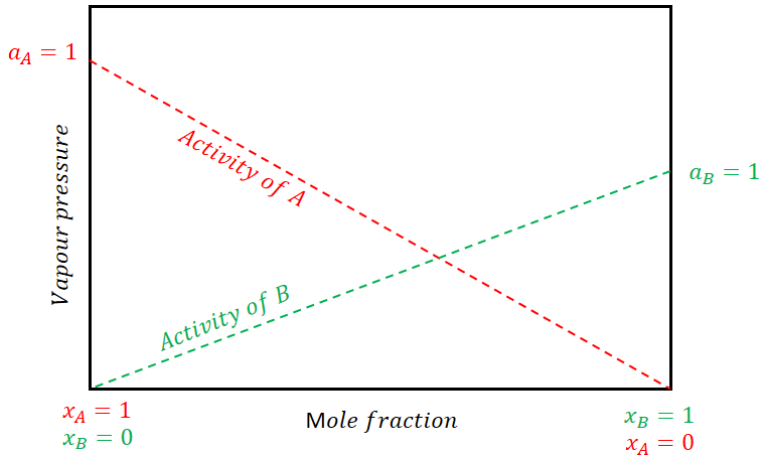


Figure 4.2: Relation between activity and mole fraction in a binary ideal solution

For a non-ideal solution $a_A = \gamma_A x_A$, where γ_A is the activity coefficient of the component A. Similar would be the case for the component B.

4.5 DIFFERENT SCALES OF ACTIVITY AND ACTIVITY COEFFICIENT

Different scales are:

a) Mole Fraction Scale (Raoult's Law Standard State):

$$a_A = \gamma_A \, x_A$$

This scale is used for the solvent in liquid solutions, and for both the solvent and the solute for liquid-liquid solutions.

b) Partial Pressure Scale (for gases):

The partial pressure scale is used for gases and fugacity is the central quantity.

$$a_A = \frac{f_A}{f_A^0}$$

c) Molality Scale:

$$a_B = \gamma_B \, m_B$$

Where, m_B is the molality (in mol kg^{-1} unit) of a solute component B in the solution. This scale is popularly used for solution of a solid solute in a liquid solvent, including those involving an ionic solid solute.

4.6 IONIC ACTIVITY COEFFICIENTS

So far, we have discussed solution of non-electrolytes which means that the components in the solution do not dissociate into ions. But, when an ionic solute compound dissolves in a strongly polar solvent such as water, the molecules of ionic solute dissociates into ions. In real solutions, these ions interact with one another due to electrostatic forces. Due to these interactions, electrolyte solutions deviate from ideal behaviour. To account for this non-ideal behaviour, the concepts of ionic activity and ionic activity coefficient are used. For electrolyte solutions, we cannot measure the activity of individual ions separately. Therefore, the concept of mean ionic activity coefficient ($\gamma_\pm$) is introduced. Before going further, it is important to understand another concept called as ionic strength.

Ionic strength $I = \frac{1}{2}\sum m_i Z_i^2$ where, Z_i is the charge on ith ionic species, and m_i is the molality of that species.

For example, ionic activity of a 0.20 molal solution of $CaCl_2$ in water (at 25°C) can be calculated by considering the dissociation of the salt in solution

$$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$$

Hence effective concentration of Ca^{2+} in solution is 0.20 m (molal) and that of Cl^- is $2 \times 0.20\ \mathrm{m} = 0.40\ \mathrm{m}$. Moreover, the charge on calcium ion is +2 and that on chloride ion is –1. Hence, ionic strength for this solution is

$$I = \frac{1}{2}(0.20 \times (2)^2 + 0.40 \times (-1)^2) = 0.60\ \mathrm{m}$$

The mean ionic activity coefficient of an extremely dilute electrolyte solution is given by the Debye-Huckel theory. The mathematical expression is

$$log\ \gamma_\pm = -A\ |Z^+ Z^-|\ \sqrt{I}$$

Where A is a constant called Debye-Huckel constant which depends on temperature, nature and density of the solvent, its value for water at 25 °C being 0.509 mol$^{-1/2}$ kg$^{1/2}$.

Z^+, Z^- are the charges on the positive and the negative ions, respectively. The expression $|Z^+ Z^-|$ means this quantity is always positive and we will ignore any sign on the negatively charged ion. We need further note that $\gamma_\pm$ is dimensionless.
The mean ionic activity of the aforementioned $CaCl_2$ solution can be calculated 25 ℃ as:

$$log\ \gamma_\pm = -0.509 \times 2 \times 1 \times \sqrt{0.60} = -0.789$$

$$\gamma_\pm = antilog\ (-0.789) \approx 0.16$$

4.7 APPLICATIONS TO CHEMICAL EQUILIBRIA

Let us consider a reversible reaction in some generalized form which can be written as

$$a\ A + b\ B \rightleftharpoons y\ Y + z\ Z$$

That is a moles of A reacts with b moles of B to give y moles of Y and z moles of Z.
The equilibrium constant for this reaction is

$$K_{eq} = \frac{[Y]^y[Z]^z}{[A]^a[B]^b} \qquad (4.11)$$

If we assume the reactants and products to be ideal gases, then we can write the Gibbs free energy of the reactant ($G^{reactant}$) and product ($G^{product}$) sides in terms of chemical potential (μ) as μ is the free energy per mole. Hence,

$$G^{recatnt} = \mu_A a + \mu_B b \qquad (4.12)$$

$$G^{product} = \mu_Y y + \mu_Z z \qquad (4.13)$$

$$\Delta G = G^{product} - G^{recatnt}$$

$$\Delta G = (\mu_Y y + \mu_Z z) - (\mu_A a + \mu_B b)$$

Since at equilibrium $\Delta G = 0$

$$(\mu_Y y + \mu_Z z) - (\mu_A a + \mu_B b) = 0$$

Using equation (3.16)

$$\left((\mu_Y^0 + RT \ln p_Y)y + (\mu_Z^0 + RT \ln p_Z)z\right) - \left((\mu_A^0 + RT \ln p_A)a + (\mu_B^0 + RT \ln p_B)b\right) = 0$$

Where, p_i is the partial pressure of species i and μ_i^0 is the standard chemical potential of the that species.

$$\left[(y\mu_Y^0 + z\mu_Z^0) - \left(a\mu_A^0 + b\mu_B^0\right)\right] + RT[(y \ln p_Y + z \ln p_Z) - (a \ln p_A + b \ln p_B)] = 0$$

$$\Rightarrow RT \ln\left(\frac{p_Y^y p_Z^z}{p_A^a p_B^b}\right) = -\left[(y\mu_Y^0 + z\mu_Z^0) - \left(a\mu_A^0 + b\mu_B^0\right)\right]$$

$$\Rightarrow RT \ln\left(\frac{p_Y^y p_Z^z}{p_A^a p_B^b}\right) = -\Delta G^0$$

Where, ΔG^0 is the free energy of the reaction under standard condition (25 ℃, $1\ atm\ pressure$). Thus,

$$\frac{p_Y^y p_Z^z}{p_A^a p_B^b} = e^{-\frac{\Delta G^0}{RT}} \qquad (4.14)$$

At constant temperature, the right hand side of the equation (4.14) is a constant (K_P)

$$\frac{p_Y^y p_Z^z}{p_A^a p_B^b} = K_P \qquad (4.15)$$

K_P is the equilibrium constant of the gaseous reaction in terms of partial pressures of the reactants and products.

The equilibrium constant can be represented in terms of concentrations and mole fractions of the reactants and products also using equations (3.17) and (4.9), respectively.

$$\frac{c_Y^y c_Z^z}{c_A^a c_B^b} = K_c \qquad (4.16)$$

$$\frac{x_Y^y x_Z^z}{x_A^a x_B^b} = K_x \qquad (4.17)$$

Where K_c and K_x are the equilibrium constants in terms of concentrations and mole fractions respectively.

Combining equations (4.14) and (4.15), we can write

$$K_P = e^{-\frac{\Delta G^0}{RT}} \qquad (4.18)$$

$$\Rightarrow \Delta G^0 = -RT \ln K_P \qquad (4.19)$$

Relation between K_P and K_c:

For a mixture of ideal gases, we can write,

$$p_i V = n_i RT$$
$$\Rightarrow p_i = \frac{n_i}{V} RT$$
$$\Rightarrow p_i = c_i RT$$

Where, $i = A, B, Y, Z$, the reactants and products, p_i and c_i are the partial pressure and concentration of the ith species.

From equation (4.5.5)

$$K_P = \frac{p_Y^y p_Z^z}{p_A^a p_B^b}$$
$$K_P = \frac{c_Y^y c_Z^z}{c_A^a c_B^b} (RT)^{((y+z)-(a+b))}$$
$$K_P = K_C (RT)^{\Delta n} \qquad (4.20)$$

Relation between K_P and K_x:

For a mixture of ideal gases, we can write using Dalton's law,

$$p_i = x_i P$$

Where, $i = A, B, Y, Z$, the reactants and products, x_i is the mole fraction of the ith species and P is the total pressure.

From equation (4.15)

$$K_P = \frac{p_Y^y p_Z^z}{p_A^a p_B^b}$$

$$K_P = \frac{x_Y^y x_Z^z}{x_A^a x_B^b}(RT)^{((y+z)-(a+b))}$$

$$K_P = K_x(RT)^{\Delta n} \qquad (4.21)$$

Temperature dependence of equilibrium constant:

From equation (4.9)

$$\frac{\Delta G^0}{T} = -R\ ln\ K_P$$

Differentiating with respect to T

$$\frac{\partial\left(\frac{\Delta G^0}{T}\right)}{\partial T} = -R\frac{d\ (\ln K_P)}{dT} \qquad (4.22)$$

From Gibbs-Helmholtz equation for standard Gibbs free energy

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

$$\Rightarrow \frac{\Delta G^0}{T^2} = \frac{\Delta H^0}{T^2} + \frac{1}{T}\frac{\partial(\Delta G^0)}{\partial T}$$

$$\Rightarrow \frac{\Delta G^0}{T^2} - \frac{1}{T}\frac{\partial(\Delta G^0)}{\partial T} = -\frac{\Delta H^0}{T^2}$$

$$\Rightarrow \Delta G^0\frac{\partial\left(\frac{1}{T}\right)}{\partial T} - \frac{1}{T}\frac{\partial(\Delta G^0)}{\partial T} = -\frac{\Delta H^0}{T^2}$$

$$\Rightarrow \frac{\partial\left(\frac{\Delta G^0}{T}\right)}{\partial T} = -\frac{\Delta H^0}{T^2} \qquad (4.23)$$

Combining equations (4.22) and (4.23),

$$\frac{d\ (\ln K_P)}{dT} = \frac{\Delta H^0}{RT^2}$$

Integrating this equations for an initial and final temperatures T_1 and T_2

$$\int_{K_P^1}^{K_P^2} d(\ln K_P) = \int_{T_1}^{T_2}\frac{\Delta H^0}{RT^2}dT$$

$$\Rightarrow ln\frac{K_P^2}{K_P^1} = \frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (4.24)$$

Here we need note that this treatment about chemical equilibrium based on concentrations, mole fractions and partial pressures is rather approximate, it is obvious that more accurate treatments would involve the activities and the fugacities instead.

W CHECK YOUR PROGRESS

Q1. What are ideal and non-ideal solutions?

Q2. In case of non-ideal solutions, why is activity necessary instead of mole fraction?

Q3. Calculate the mean ionic activity coefficient of 0.005 M $MgSO_4$ at 25°C. A = 0.509.

2 4.8 LET US SUM UP

The Raoult's law, which states partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution, differentiates between ideal and non-ideal solutions. Ideal solution obeys this law while non-ideal solution does not obey. In case of non-ideal solutions activity comes into play instead of mole fraction. In case of salt solutions, ions dissociate and hence mean ionic activity should be considered.

K 4.9 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: Ideal solution follows Raoult's law while non-ideal solutions do not follow it. Ideal solution consists of components where interactions between different components are almost same while in non-ideal solutions the interactions between different species differ from that of the same species.

Answer to Q2: In non-deal solution, the vapour pressure is replaced by fugacity because the interactions between different species differ from that of the same species.

Answer to Q3: Mean ionic activity is around 0.515.

O 4.10 FURTHER READING

- P.W. Atkins. *Physical Chemistry*. Oxford University Press.
- B.R. Puri, L.R. Sharma, Madan S. Pathania *Principles of Physical Chemistry*
- I.N. Levine *Physical Chemistry.* Mc Graw Hill (India)
- K.L. Kapoor *A Textbook of Physical Chemistry, Vol. I & II.* Mc Graw Hill (India).
- G.W. Castellan. *Physical Chemistry*. Addison-Wesley

M 4.11 MODEL QUESTIONS

Q1. Which of the solution is closest to an ideal solution, a) A solution of hexane and octane, b) A solution of hexane and chloroform, c) A solution of hexane and hexanoic acid.

Q2. Calculate the total vapour pressure a system containing 2 moles of component A and 3 moles of component B, the vapour pressures of which are 0.25 atm and 0.35 atm respectively. Consider ideal behaviour.

Q3. Calculate the mean ionic activity coefficient of 0.01 M NaCl solution at 25°C.

Q4. Calculate the ratio of equilibrium constants for a reaction of gaseous species

behaving ideally at temperatures 300 K and 350 K ($\Delta H^0 = 83.14\ kJ\ mol^{-1}$).

UNIT 5: PHASE EQUILIBRIUM CONCEPT AND THREE-COMPONENT SYSTEMS

UNIT STRUCTURE

5.1 Learning Objectives
5.2 Introduction
5.3 Thermodynamic Criteria of Phase Equilibrium
5.4 Gibbs Phase Rule
5.5 Reduced Phase Rule
5.6 Triangular Phase Diagrams
5.7 Water-Acetic Acid-Chloroform System
5.8 Ammonium Chloride-Ammonium Sulphate-Water System
5.9 Applications of Ternary Systems
5.10 Let Us Sum Up
5.11 Answers to Check Your Progress
5.12 Further Reading
5.13 Model Questions

5.1 LEARNING OBJECTIVES

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

- learn thermodynamic criterion for phase equilibria
- apply Gibbs phase rule
- understand the concepts of phase diagrams
- understand the various applications of phase diagrams

5.2 INTRODUCTION

A phase is a distinct, homogeneous part of a system which is separated from other parts of the system by certain boundary and hence is mechanically separable. Phases can be single-component or multi-component. For example, a mixture of gases in a container constitute one phase as gases are miscible and hence homogeneous. On the other hand, water and benzene don not mix. So, even if these two liquids are shaken vigorously, after some time they get separated with water settling at the bottom of the container due to high density and benzene (lower density than water) is accumulated on the top of the water. Thus, a water-benzene system constitute a two phase system or in general, immiscible liquids constitute multi-phase system. One the other hand completely miscible liquids like water and ethanol still constitute a single phase system, because such liquids from a homogeneous mixture.

5.3 THERMODYNAMIC CRITERIA OF PHASE EQUILIBRIUM

Before proceeding further with phase equilibria, we set up the thermodynamic criterion for equilibrium between phases. Let us consider a pure substance in its two phases

α and β. Suppose n_α moles of the substance is in phase $\alpha$and n_β moles is in phase β. In this case, the Gibbs free energy is a function of T, P, n_α and n_β, Thus, we can write

$$G \rightarrow G(T, P, n_\alpha, n_\beta) \qquad (5.1)$$

Note that this similar to Section 3.3 in the unit 3. Hence, we can write the differential dG

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_\alpha,n_\beta} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_\alpha,n_\beta} dP + \left(\frac{\partial G}{\partial n_\alpha}\right)_{T,P,n_\beta} dn_\alpha + \left(\frac{\partial G}{\partial n_\beta}\right)_{T,P,n_\alpha} dn_\beta \qquad (5.2)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_\alpha,n_\beta} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_\alpha,n_\beta} dP + \mu_\alpha dn_\alpha + \mu_\beta dn_\beta \qquad (5.3)$$

Where, μ_α and μ_β are the chemical potentials of the substance in α and β phases, respectively. Suppose, dn amount of the substance converts from the α to β phase at constant temperature and pressure. Then equation (5.3) becomes

$$dG = \mu_\alpha(-dn) + \mu_\beta dn \qquad (5.4)$$

Since at equilibrium $dG = 0$

$$\begin{aligned} dG &= \mu_\alpha(-dn) + \mu_\beta dn \\ \Longrightarrow 0 &= \mu_\alpha(-dn) + \mu_\beta dn \\ \Longrightarrow \mu_\alpha &= \mu_\beta \end{aligned} \qquad (5.5)$$

Equation (5.5) is the criterion for equilibrium between two phases i.e. chemical potentials of the two phases become equal. This can be generalised to arbitrary number of phases in equilibrium e.g.

$$\mu_\alpha = \mu_\beta = \mu_\gamma = \mu_\delta = \cdots\cdots$$

5.4 GIBBS PHASE RULE

The Gibbs phase rule is a simple mathematical equality connecting number of phase (P), degrees of freedoms (F) and number of components (C) at phase equilibrium. Note that one should not confuse the variable P here with pressure. The Gibbs phase rule has the form

$$F = C - P + 2 \qquad (5.6)$$

For example, at liquid water and water vapour equilibrium, the number of phases is $P = 2$ and number of component is $C = 1$ as only water is the component. Hence, number of degrees of freedom is $F = 1$. This means that the phase equilibrium is characterised by either temperature or pressure.

A caution in determining the number of components is necessary while dealing with gases. Consider the hypothetical case

$$n_A A(g) \rightleftharpoons n_B B(g)$$

Now, the partial pressures of each gas is

$$p_A = \frac{n_A}{n_A + n_B} P_{Total}$$

$$p_B = \frac{n_B}{n_A + n_B} P_{Total}$$

Hence,

$$\frac{p_A}{p_B} = \frac{n_A}{n_B}$$

Hence, the partial pressures of gases in a mixture of gases in equilibrium are related which presents another constraint relation. Hence, given the information of one component, the other component is known. If there are 3 gases, e.g.

$$n_A A(g) \rightleftharpoons n_B B(g) + n_C C(g)$$

$$p_A = \frac{n_A}{n_A + n_B + n_c} P_{Total}$$

$$p_B = \frac{n_B}{n_A + n_B + n_c} P_{Total}$$

$$p_c = \frac{n_C}{n_A + n_B + n_c} P_{Total}$$

The partial pressures of any two components are related and hence, knowing any one will automatically determine the other two. Hence, we need the information of only one component. The thumb rule is that, the number of components in a mixture of different gases always 1.

Derivation of the Gibbs phase rule:

Before deriving the Gibbs phase rule it is important to understand the concept of reduction is degrees of freedom due to constraints between variables or degrees of freedom. Consider a function $f(x, y, z)$ which has three degrees of freedom x, y and z. But suppose there is a relation (constraint) between y and z, say $y + z = k$ (k is a constant) then we need to know only either of y or z as knowing one of them fixes the other. Thus, the three dimensional function becomes two dimensional i.e. $f(x, y, z) \rightarrow f(x, y)$ or $(x, y, z) \rightarrow f(x, z)$. Essentially, the degrees of freedom is reduced from 3 to 2. If there is one more such relation between x and y or x and z, the degrees of freedom further reduces to 1. The bottom-line is, if m number of such relations between the variables for a problem with a total of l degrees of freedom, then the actual number of degrees of freedom becomes $l - m$.

Next we derive the Gibbs phase rule. Assume, there are C components whose compositions vary to give P phases named as $\alpha, \beta, \gamma, \cdots, P$. So, in each phase, the mole fractions of those C components are the degrees of freedom (variables) as the properties of each phase depends on them. We assume the following mole fractions of the components in each phase

$$\begin{gathered} Phase\ \alpha \rightarrow (x_1^\alpha, x_2^\alpha, x_3^\alpha, \cdots\cdots, x_C^\alpha) \\ Phase\ \beta \rightarrow \left(x_1^\beta, x_2^\beta, x_3^\beta, \cdots\cdots, x_C^\beta\right) \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ Phase\ P \rightarrow (x_1^P, x_2^P, x_3^P, \cdots\cdots, x_C^P) \end{gathered}$$

Thus, in there are CP degrees of freedom. Including the temperature and pressure, the total number of degrees of freedom becomes $CP + 2$. However, the sum of mole fractions in each phase must be equal to 1. Thus,

$$x_1^\alpha + x_2^\alpha + x_3^\alpha + \cdots\cdots + x_C^\alpha = 1$$

$$x_1^\beta + x_2^\beta + x_3^\beta + \cdots\cdots + x_C^\beta = 1$$
$$\vdots \qquad \vdots \qquad \vdots$$
$$\vdots \qquad \vdots \qquad \vdots$$
$$x_1^P + x_2^P + x_3^P + \cdots\cdots + x_C^P = 1$$

Thus, there are P such equations of constraints. Furthermore, the chemical potential of each component among different phases must be equal at equilibrium. Thus, for component 1, we can write

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \cdots\cdots = \mu_1^P$$

Note that there are $P-1$ equality i.e. that many equations of constraints for the component 1. Since, there are C components, the number of constraints due to equality of chemical potentials is $C(P-1)$.

Thus we have

1. Total number of degrees of freedom without counting the constraints = $CP+2$
2. Number of constraints coming from mole fraction summation = P
3. Number of constraints coming from equality of chemical potentials = $C(P-1)$

Hence, total number of constraints= $CP - C + P$

Hence the actual number of degrees of freedom is, $F = CP + 2 - (CP - C + P)$. Hence,

$$F = C - P + 2$$

which is the **Gibbs phase rule**.

5.5 REDUCED PHASE RULE

Since, experiments are normally carried out at constant pressure, it is customary to fix that variable which gives the reduced phase rule as

$$F = C - P + 1 \qquad (5.7)$$

Thus, in case of liquid water and water vapour equilibrium, if the pressure is held constant at 1atm, then according to the reduced phase rule,

$$F = 0$$

This means, the properties of the liquid-vapour equilibrium are invariant.

5.6 TRIANGULAR PHASE DIAGRAMS

Triangular phase diagram is a convenient method of expressing phase diagrams of systems containing three components. The three sides of an isosceles triangle represent the mass percentages of the components. The three vertices of the triangle represent the conditions when 100% of only one component is present.

Let us consider a hypothetical three component system with components A, B and C. The triangular phase diagram for this system is shown in the figure below. Of the triangle ΔPQR, the sides PQ, QR and RP contain the percentages of components A, B and C. The vertex P represents a condition when 100% of components A is present. Similarly, vertices Q and R represent a conditions for 100% of components B and C, respectively. The points on each of the sides of the triangle represent the percentages of the components in the system e.g. on the side PQ, the percentages of the component A are shown. For illustration, we have shown the percentages in multiples of 20. However, the percentages can be shown in arbitrarily finer resolution e.g. $0\%, 1\%, \cdots, 100\%$. Similarly, on the sides QR and RP, the percentages of the component

B and C are shown. The lines inside the triangle intersect at different points which represent different composition of the ternary mixture. Apart from the vertices, a point on any of the sides mean only two components are present. For example, points on the sides PQ, QR and RP represent systems composed of only two components components (A, B), (B, C) and (A, C), respectively.

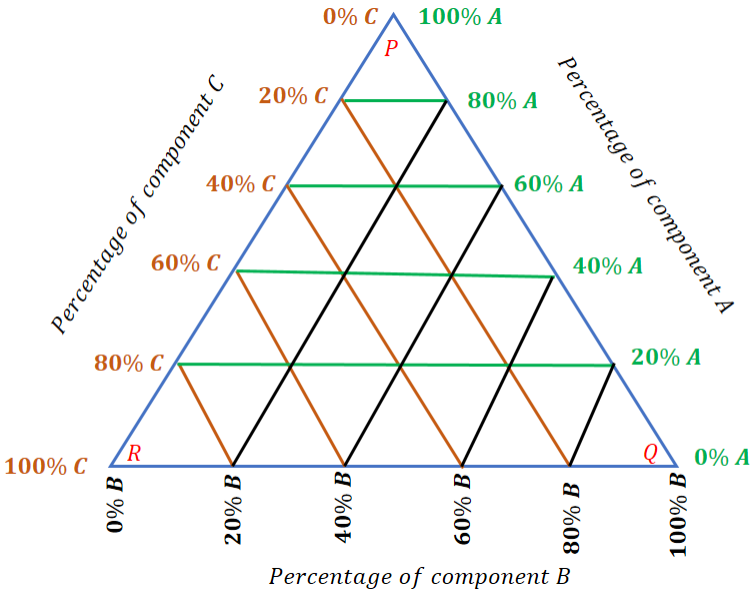


Figure 5.1: A triangular phase diagram for a hypothetical three component system

How to read triangular phase diagram:

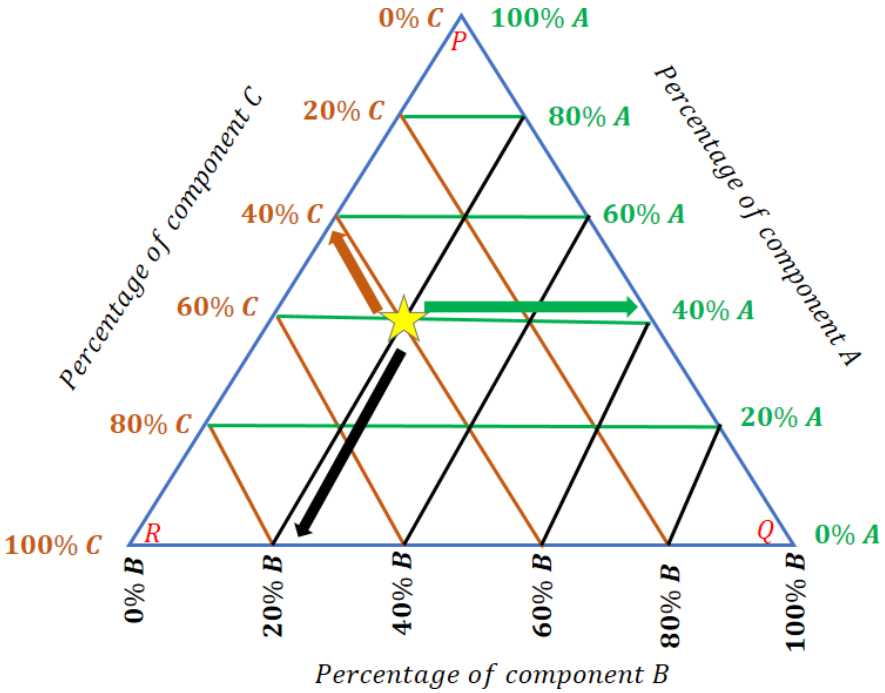


Figure 5.2: A schematic showing how to read a triangular phase diagram

The following rule of thumbs can be applied to read the composition of the three components system represented by the start:
1. Starting from the point (the star) and look at the percentage composition of component A. In the given case it is 40% as highlighted by the dark arrow.
2. Then starting from the point, look for the percentage of component B. In the given case, it is 20% as highlighted by the black coloured arrow.
3. Then starting from the point, look for the percentage of component C. In the given case, it is 40% as highlighted by the dark arrow.
So, the point highlighted by the star represents a composition $40\%\, A + 20\%\, B + 40\%\, C$. In case of any error in reading the triangular phase diagram, the percentages do not add up to 100. Also, one can start reading the phase diagram to track the composition of component B or C first. Hence the above thumb rules are not hard and fast but make the reading more convenient.

5.7 WATER-ACETIC ACID-CHLOROFORM SYSTEM

1. Water and chloroform are partially miscible with each other.
2. Chloroform will completely mix with water until a threshold ratio of percentages of the two components is achieved.
3. Water will completely mix with chloroform until a threshold ratio of percentages of the two components is achieved.
4. If chloroform is added to water beyond the threshold percentage, then water and chloroform layers will separate out. However, an amount of chloroform still remains mixed with water to maintain the threshold ratio of percentages of chloroform and water. However, now there are two layers. So water molecules (from the chloroform in water layer) move to the chloroform layer until the threshold ratio of miscibility of water in chloroform is achieved. Thus we have two layers: 1. Chloroform in water, 2. Water in chloroform.
5. Acetic acid is completely miscible with both chloroform and water. Hence, addition of acetic acid to the system in point number 4 would further mix chloroform and acetic acid i.e. more amount of water will move to the chloroform layer and vice versa.
6. If the amount of acetic acid is gradually increased, the amount of water in the chloroform layer will gradually increase. Similarly, the amount of chloroform in the water layer will gradually increase on addition of acetic acid. That means, acetic acid homogenise the water chloroform system.
7. After a critical concentration of acetic acid, no more separation between the chloroform and water layer will exist and the whole solution becomes a homogenous mixture i.e. single phase. This point is called as isothermal critical point or a plait point.

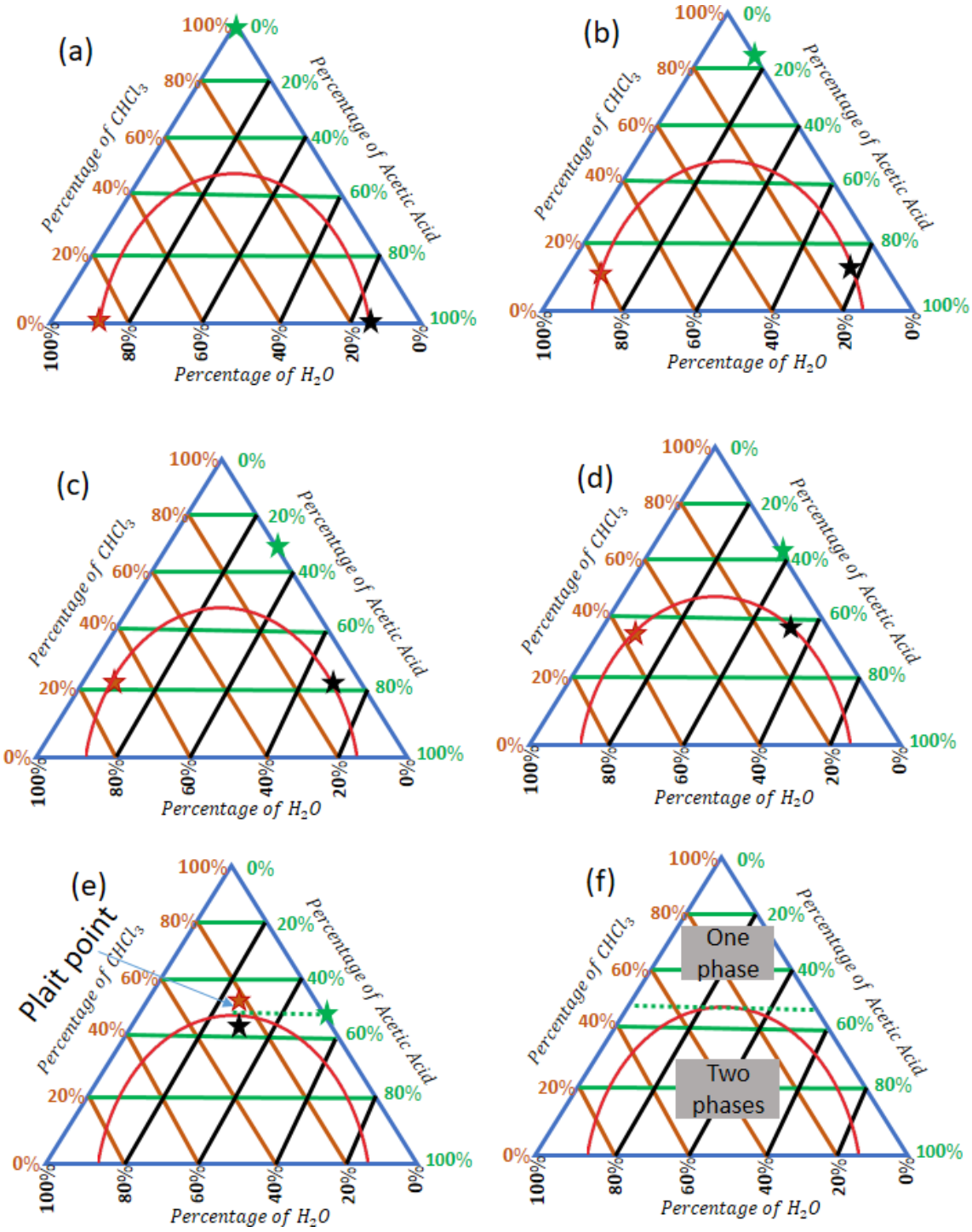


Figure 5.3: Showing different stages of increasing the concentration of acetic acid on the composition of water and chloroform

5.8 AMMONIUM CHLORIDE-AMMONIUM SULPHATE-WATER SYSTEM

The phase diagram of "$NH_4Cl + (NH_4)_2SO_4 + Water$" ternary system describes how homogeneous solution coverts into saturated solutions of either salt and both the salts

depending upon the percentages of the components. The figure below is a schematic phase diagram of the "$NH_4Cl + (NH_4)_2SO_4 + Water$ ternary system.

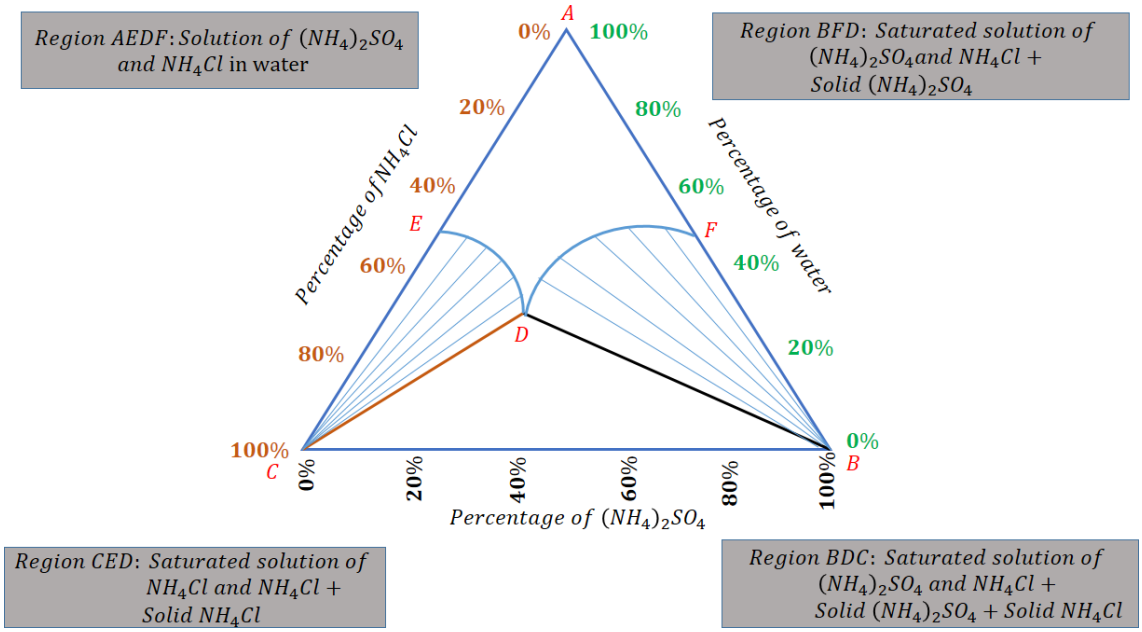


Figure 5.4: A schematic phase diagram of ammonium chloride-ammonium sulphate-water system

The phase diagram can be divided into different regions all representing different percentages of NH_4Cl, $(NH_4)_2SO_4$ and water. Various regions are described below:

1. Region AEDF: In this region, the percentages are such that both the salts are soluble in water. Hence this region represents the homogeneous solution where number of phases is only 1.

2. Region CED: In this region, the percentage of NH_4Cl is high and such that the solution becomes saturated with respect to this salt. Hence, this region represents the two phases comprising of the solution and solid NH_4Cl.

3. Region BFD: In this region, the percentage of $(NH_4)_2SO_4$ is high and such that the solution becomes saturated with respect to this salt. Hence, this region represents the two phases comprising of the solution and solid $(NH_4)_2SO_4$.

3. Region BDC: In this region, the solution becomes saturated with respect to both the salts. Hence, this region represents the solution, solid NH_4Cl and solid $(NH_4)_2SO_4$ coexist. The number of phases in this region in 3.

Along the curve ED, the saturated NH_4Cl solution is in equilibrium with the homogeneous solution of $NH_4Cl + (NH_4)_2SO_4$ in water. Similarly, along the DF curve, the saturated solution of $(NH_4)_2SO_4$ is in equilibrium with the homogeneous solution of $NH_4Cl + (NH_4)_2SO_4$ in water. At point D, all the phases are in equilibrium with each other.

5.9 APPLICATIONS OF TERNARY SYSTEMS

The ternary phase diagram has numerous applications. Here are some of the main applications of ternary systems.

1. Chemical Processing and Separation Methods:
Crystallization and Purification: As we understood in the NH_4Cl-$(NH_4)_2SO_4$-H_2O system, ternary phase diagrams play a vital role in the design of industrial crystallization processes. They help you understand the precise conditions of temperature and concentration required to separate a pure solid from a mixture. For instance, in the potash industry, phase diagrams of salt systems (such as KCl-NaCl-H_2O) are employed to purify potassium chloride from crude ore. By dissolving the mixture and then carefully evaporating water, the phase diagram helps you understand how to separate the impure NaCl first, leaving a pure KCl solution from which the desired compound can be extracted through crystallization.
Solvent Extraction (Liquid-Liquid Equilibrium): One of the most common ternary systems is when you have two non-mixable liquids (such as oil and water) and a third component (a solute) that can dissolve in both liquids. The ternary phase diagram of such a system plays a vital role in the design of solvent extraction processes.

2. Petroleum and Natural Gas Engineering:
The phenomenon of hydrocarbons in the ground is a lesson in the complexities of multi-component thermodynamics. A mixture of several hundred different hydrocarbons (methane, propane, hexane, and so on) can be analyzed using a ternary plot.
Enhanced Oil Recovery (EOR): When simple extraction is not sufficient to get the oil out, gases such as CO_2, N_2, or methane are injected into the oil field. The phase behavior of the ternary mixture Oil-Gas-Water is of prime importance. The ternary plot assists the engineer in understanding whether the injected gas will mix with the oil, making it more voluminous and less viscous, or whether it will simply bypass the oil. It also assists in understanding whether the mixture will remain in two separate phases (oil and gas) or in a single, miscible phase that can easily move towards the extraction point.
Gas Hydrate Formation: In deep sea pipelines, water and small hydrocarbon molecules (such as methane) combine to form ice-like substances called gas hydrates. These substances can clog the pipelines, leading to enormous operational difficulties and hazards. The ternary plot of Water-Methane-Other Hydrocarbons assists in understanding the pressure and temperature conditions at which these hazardous substances form, and engineers inject inhibitors like methanol or glycol to prevent it.

3. Metallurgy and Materials Science:
Alloys exist as solid solutions or mixtures of different materials because metals typically exist in this form. Ternary phase diagrams serve as essential tools for researchers who need to create innovative metallic materials.
Alloy Design and Heat Treatment: Alloy properties including strength and hardness and corrosion resistance depend on microstructure which results from the combination of material composition and thermal treatment. Ternary diagrams (e.g., Iron-Chromium-

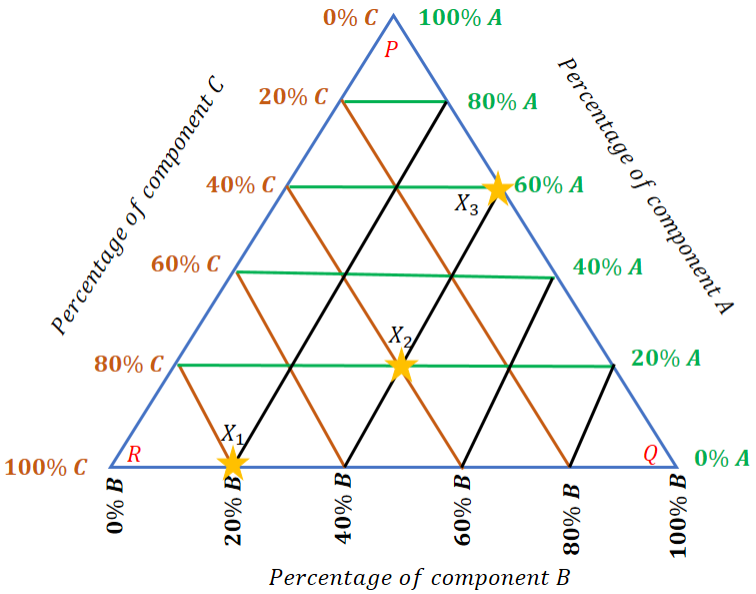
Nickel for stainless steels, Aluminum-Copper-Magnesium for high-strength aerospace alloys) tell metallurgists:
a) What phases will be present at a given composition and temperature.
b) The temperature at which the alloy will start to melt (solidus) and become fully liquid (liquidus).
The heat treatment process for the alloy requires solution treatment followed by quenching and aging to create the intended phase distribution and material characteristics.
Ceramics and Slags: Ternary oxide systems play an essential role in creating cement glass and advanced ceramic materials. The CaO-Al_2O_3-SiO_2 (Calcia-Alumina-Silica) diagram serves as the primary framework for comprehending:
Portland Cement: The diagram shows the main components that provide cement strength which includes tricalcium silicate and dicalcium silicate.
Metallurgical Slags: During the process of iron and steel production a layer of slag which consists of molten oxides floats above the molten metal to capture impurities. The CaO-FeO-SiO_2 diagram helps engineers design a slag that remains liquid at steelmaking temperatures while maintaining proper chemical composition to effectively remove sulfur and phosphorus from steel.

4. Environmental Science and Engineering:
Ternary systems are also powerful tools for understanding and remediating environmental problems.
Fate of Contaminants: The behavior of organic contaminants (like a solvent spill) in the environment can be modeled using ternary diagrams (e.g., Water-Soil-Organic Contaminant). This helps predict whether the contaminant will dissolve in groundwater, volatilize into the soil air, or remain as a separate, immobile phase.
Surfactant-Based Remediation: To clean up contaminated groundwater, engineers sometimes inject surfactants (soap-like molecules). The ternary diagram of Water-Contaminant-Surfactant is used to design a mixture that will form a microemulsion, effectively "dissolving" the trapped organic contaminant so it can be pumped out and treated.

W CHECK YOUR PROGRESS

Q1. Calculate the number of components, phases and degrees of freedom in
a) an unsaturated aqueous solution of sodium chloride
b) $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$

Q2. Identify the percentage composition of a ternary mixture of compounds at the points X_1, X_2, X_3 as represented by the stars in the triangular phase diagram below?



Q3. How ternary phase diagrams are useful in environmental science?

2 5.10 LET US SUM UP

Thermodynamics equilibrium is characterised by equal chemical potentials of a component across different phases. The Gibbs phase rule connects number of phase (P), degrees of freedoms (F) and number of components (C) at phase equilibrium and given by

$$F = C - P + 2$$

Triangular phase diagrams are used to represent compositions of ternary systems where each side the triangle acts like an axis where the percentages of the components are written. We can extract any composition as a point in the triangular phase diagram. Two examples of phase diagrams of three components systems are water-acetic acid-chloroform and ammonium chloride-ammonium sulphate-water. Acetic acid converts inhomogeneous layers of water and chloroform into a single phase after a critical concentration is reached. Depending upon the composition, homogeneous solution of ammonium chloride+ammonium sulphate in water, the saturated solutions of the individual salts and the saturated solution containing both the salts exist. These different phases so obtained remain in equilibrium with each other.

K 5.11 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: a). $C = 2$, water and sodium chloride, $P = 1$ since it is a homogeneous unsaturated solution, $F = 3$

b). $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$, the two gases give only 1 component. Hence, $C = 3$, Fe, FeO and gas, $P = 3, Fe(s)$, $FeO(s)$ and the two gases mix to give 1 phase, $F = 2$.

Answer to Q2: X_1: $20\%\ B + 80\%\ C$, X_2: $20\%\ A + 40\%\ B\ +\ 40\%\ C$, X_3: $60\%\ A + 40\%\ B$

Answer to Q.3: Ternary systems present effective solutions which help people study environmental issues and create solutions for those issues.
Fate of Contaminants: Ternary diagrams which include Water-Soil-Organic Contaminant show how organic contaminants from solvent spills behave in the environment. This helps predict whether the contaminant will dissolve in groundwater, volatilize into the soil air, or remain as a separate, immobile phase.
Surfactant-Based Remediation: Engineers use surfactants which are soap-like molecules to treat groundwater that has been contaminated. The ternary diagram of Water-Contaminant-Surfactant is used to design a mixture that will form a microemulsion, effectively "dissolving" the trapped organic contaminant so it can be pumped out and treated.

O 5.12 FURTHER READING

- P.W. Atkins. *Physical Chemistry*. Oxford University Press.
- B.R. Puri, L.R. Sharma, M.S. Pathania. *Principles of Physical Chemistry*
- I.N. Levine. *Physical Chemistry.* Mc Graw Hill (India)
- K.L. Kapoor. *A Textbook of Physical Chemistry, Vol. II & III.* Mc Graw Hill (India)

M 5.13 MODEL QUESTIONS

Q1. Calculate the number of components, phases and degrees of freedom in
a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
b) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

Q2. In the phase diagram of "$NH_4Cl + (NH_4)_2SO_4 + Water$" system, from which Region NH_4Cl will be crystalized at slightest evaporation of water?

Q3. In the triangular diagram in the section 5.6 (the first figure), identify the approximate location of the point where the components A, B and C will be in equal proportion?

Q4. Write down the utility of ternary phase diagrams in pharmaceuticals and food industries.

UNIT 6: BASIC CONCEPTS OF NON-EQUILIBRIUM THERMODYNAMICS

UNIT STRUCTURE

6.1 Learning Objectives
6.2 Introduction
6.3 The Concept of Internal Entropy Production
6.4 Generalised Forces and Generalised Flows
6.5 Linear Laws for the Non-Equilibrium Processes
6.6 Let Us Sum Up
6.7 Answers to Check Your Progress
6.8 Further Reading
6.9 Model Questions

6.1 LEARNING OBJECTIVES

After going through this unit, you will:

- learn the scope of non-equilibrium thermodynamics.
- appreciate the concept of internal entropy production in non-equilibrium irreversible processes.
- be familiar with various generalised forces that cause various non-equilibrium processes to occur, these processes manifested as various generalised flows.
- know the phenomenological linear laws relating the generalised flows with the generalised forces.
- appreciate the Onsager reciprocal relation and some other important relations regarding the coefficients in the phenomenological linear equations, and the concept of microscopic reversibility that leads to the Onsager relation.

6.2 INTRODUCTION

Non-equilibrium thermodynamics or irreversible thermodynamics, the branch of science mostly founded by Ilya Prigogine (born 1917 in Russia; was awarded Nobel Prize in Chemistry in 1977 for establishing this novel branch of science) discusses about irreversible (non-equilibrium) processes. Most physicochemical processes we experience, such as heat flow, diffusion, osmosis, chemical transformation, evaporation of liquids into air, electrical conduction, etc., are irreversible ones. In any irreversible process, such as the heat flow from a hot body to a neighbouring cold body, the entropy of the universe increases: this gives the concept of entropy production in such processes. Considering the whole region where such a process occurs as the system, the irreversible process can be considered to happen *inside* the system, so such entropy production is termed the internal entropy production.

Any such irreversible process always occurs because of some generalised forces or affinities (e.g., difference in chemical potential, difference in temperature, difference in

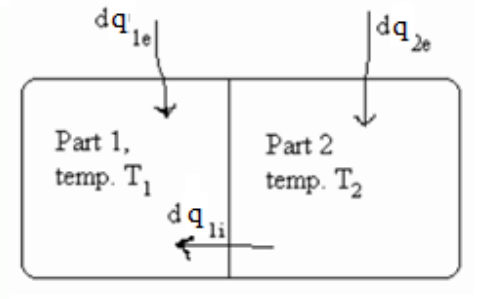
electrical potential etc.) which result in some generalised fluxes or flows (chemical reaction and diffusion, heat flow, current flow, etc.). Non-equilibrium thermodynamics considers some generalised linear relations among such flows and fluxes; and looks for the possible interrelation among the coefficients involved in those linear relations.

The concepts of non-equilibrium thermodynamics is greatly helpful in explaining the unidirectional arrow of time, and in explaining the prolonged sustenance of some highly ordered open systems such as living organisms like us. The progress of time is associated with positive values of internal entropy production – so, as entropy production must be positive, time must flow forward only. Similarly, the long sustenance of such ordered open systems is associated with a near-minimum rate of internal entropy production (as per a principle named after Prigogine himself), with the system entropy remaining practically constant but the entropy of the surroundings always increasing, thus implying continuous increase of the entropy of the universe.

6.3 THE CONCEPT OF INTERNAL ENTROPY PRODUCTION

Let us consider a system inside which an irreversible process is occurring. As the entropy change dS of the system plus the entropy change dS_{surr} of the surroundings together equals the entropy change dS_{univ} of the universe, and as from the second law of thermodynamics dS_{univ} must be positive for the irreversible process, it is clear that this increase in entropy of the universe, dS_{univ}, is the internal entropy production d_iS for the process. In non-equilibrium thermodynamics, these entropy changes are considered from another viewpoint as below:

As entropy is an extensive property, so this infinitesimal entropy change dS of the system can be expressed as a sum of two parts: (i) the entropy flow d_eS into the system from the exterior i.e., the surroundings, and (ii) the internal entropy production d_iS inside the system, such that $dS = d_eS + d_iS$. However, the said d_eS is nothing but the negative of the entropy change of the surroundings, i.e., $d_eS = -dS_{surr}$.This is because the irreversible process under consideration is considered to occur within the system only, thus the entropy change dS_{surr} in the surroundings can occur solely due to a transfer of entropy from the system towards it, which is evidently the opposite of the transfer of entropy d_eS from the surroundings to the system, thus $dS_{surr} = -d_eS$.it is obvious that the internal entropy production $d_iS = dS - d_eS = dS + dS_{surr} = dS_{univ}$,as we mentioned above. So, as per the aforesaid second law, the internal entropy production can never be negative, and for an irreversible process it has to be positive (can't be zero also).



As an illustrative example of internal entropy production in an irreversible process, let us consider a system consisting of two sub-systems 1 and 2, maintained respectively at two uniform temperatures T_1 and T_2 shown in figure. True, this is too simplified a model for situations such as mixing of hot and cold water, say before drinking warm water from a cup, as in such cases evidently there may be

many different temperatures at different parts of the cup – but science always deals with too simplified models!

Nevertheless, entropy being an extensive property, it is obvious that entropy change for the whole system $dS = dS_1 + dS_2$, where dS_1 and dS_2 are entropy changes for the two sub-systems. Let the heat absorbed by each sub-system be divided into two parts as: $\delta q_1 = \delta q_{1i} + \delta q_{1e}$ and $\delta q_2 = \delta q_{2i} + \delta q_{2e}$, where δq_{1i} is the heat absorbed by sub-system 1 from sub-system 2 (i.e., from interior of the system, hence the subscript i) and δq_{1e} is the heat absorbed by sub-system 1 from the surroundings (exterior) of the system, and similarly for δq_{2i} and δq_{2e} (clearly, $\delta q_{2i} = -\delta q_{1i}$). For this idealised process, the heat transfers may be considered as reversible. Thus we get that the entropy change for the whole system dS is: $dS = \delta q_1/T_1 + \delta q_2/T_2 = \delta q_{1e}/T_1 + \delta q_{2e}/T_2 + \delta q_{2i}\,(-1/T_1 + 1/T_2)$.

Remembering $dS = d_eS + d_iS$, it becomes obvious that the part $[\delta q_{1e}/T_1 + \delta q_{2e}/T_2]$ equals the entropy flow d_eS reversibly transferred from the surroundings to the system, so that the remaining part $[\delta q_{2i}(1/T_2 - 1/T_1)]$ is the internal entropy production d_iS arising from the irreversible heat flow inside the system; i.e., $d_iS = \delta q_{2i}\,(1/T_2 - 1/T_1)$. It can be easily seen that the internal entropy production here is always positive. One form of the second law of thermodynamics (the Clausius statement), as well as our human experience also, tells us that heat spontaneously flows from a body at a higher temperature to a body at a lower temperature, so if $T_1 > T_2$, $\delta q_{2i} > 0$, while if $T_2 > T_1$, $\delta q_{2i} < 0$. But if $T_1 > T_2$, $(1/T_2 - 1/T_1) > 0$ and so $d_iS = \delta q_{2i}\,(1/T_2 - 1/T_1) > 0$. Similarly, if $T_2 > T_1$, $(1/T_2 - 1/T_1) < 0$ and so again $d_iS = \delta q_{2i}\,(1/T_2 - 1/T_1) > 0$. Thus if there is a non-zero heat flow, $\delta q_{2i} \neq 0$ and $T_2 \neq T_1$, and so the entropy production $d_iS > 0$. [However, if $T_2 = T_1$, $\delta q_{2i} = 0$ and $(1/T_2 - 1/T_1) = 0$, so then $d_iS = 0$.] We may further note here that d_iS/dt, called the rate of internal entropy production and generally denoted as σ, is a widely used concept in non-equilibrium thermodynamics.

6.4 GENERALISED FORCES AND GENERALISED FLOWS

In unit 6.2, we came across the idea that there are various generalised forces or driving forces or affinities such as temperature difference, difference in chemical potential, etc. that acts as the cause of some generalised fluxes or flows such as heat flow, diffusion, etc., getting manifested as kinds of irreversible processes. But formally in non-equilibrium thermodynamics, we define the generalised forces and the generalised flows in a specific way, so that the rate d_iS/dt of internal entropy production either equals the product of a generalised force χ (chi) and a generalised flow J, or (if several generalised forces and generalised flows are operating simultaneously) equals the sum of the products of the generalised forces and the corresponding generalised flows. In this way, a generalised flow is defined as a time rate of a process, such as the rate of spontaneous internal heat flow $(\delta q_{2i}/dt)$, or $(\delta q_i/dt)$, between the hot and the cold parts of the system, as in the above example, evidently, $d_iS/dt = (\delta q_{2i}/dt)\,(1/T_2 - 1/T_1)$.On the other hand, the generalised force is something that arises from the difference of an intensive thermodynamic property (such as of 1/T for heat flow, or of μ/T for diffusion), that difference acting as the cause of the generalised flow. As is clear, here we have $(1/T_2 - 1/T_1)$, the difference of the inverses of the temperatures, as the actual

generalised force or affinity, not the temperature difference as we might have qualitatively thought or felt about! The following is a table of various common kinds of generalised forces and generalised flows, formally defined in such a way so that their product or products can equal the rate of internal entropy production, i.e., d_iS/dt.

Table 6.1: Various Kinds of Generalised Forces and Generalised Flows

Irreversible Process	Generalised Force χ	Generalised Flow J	d_iS/dt (= χ J)
Heat Flow	$\Delta(1/T)$	$\delta q_i/dt$	$\{\Delta(1/T)\}.\{\delta q_i/dt\}$
Diffusion	$-\Delta\mu/T$	dn_i/dt	$\{-\Delta\mu/T\}.\{dn_i/dt\}$
Chemical Reaction	A/T (= $-\Delta G/T$)	$d\xi/dt$ (= v = r V)	$\{A/T\}.\{d\xi/dt\}$
Electric Current	$-\Delta V/T$	dQ/dt (= I)	$\{-\Delta V/T\}.\{dQ/dt\}$

In all these above listed cases, just like the first illustrated case of spontaneous heat flow, we are assuming simplified model systems in which there are only two sub-systems with each part having a distinct value of the intensive property, the difference of which creates the generalised force causing the corresponding generalised flow.

Thus, in these cases about diffusion, the difference in the chemical potential μ (between the two sub-systems) divided by the system temperature T is the generalised force, while the rate of internal flow of matter, expressed as the amount of matter crossing the sub-system boundary per unit time, is the generalised flow. It is interesting to note why for the heat flow process, there is no negative sign in the expression for the generalised force χ , whereas in the other three there is one, if χ is expressed in terms of differences in the familiar intensive properties. This is because heat flows from a region of lower 1/T to one of higher 1/T (need note that where T is higher, 1/T is lower), whereas at constant temperature matter diffuses from a region of higher μ to one of lower μ, or a chemical reaction transform substances with a higher Gibbs energy G into those with a lower G, or the electric current (i.e., the time rate of flow dQ/dt of electric charge Q) flows from a region of a higher electric potential V to one with a lower V. Thus, in case of heat flow, if $1/T_2 > 1/T_1$, i.e., $\Delta(1/T) > 0$, heat flows from part 1 to part 2 making $J > 0$; but in case of diffusion, if $\mu_2/T > \mu_1/T$, i.e., $\Delta\mu/T > 0$, matter flows from part 2 to part 1 making $J < 0$.

Let us now elaborate about the entropy production during a (spontaneous) chemical reaction in more details. A chemical reaction, such as $2CO(g) + O_2(g) = 2CO_2(g)$, is expressed formally in chemical kinetics as $0 = \Sigma_i \nu_i S_i$, where ν_i are the stoichiometric coefficients of the substances S_i (i.e., the reactants and the products) in a peculiar kind of balanced chemical equation, so that for the reactants the coefficients ν_i are negative while for the products the ν_i are positive. Thus, the reaction $2CO(g) + O_2(g) = 2CO_2(g)$ is expressible as $0 = -2CO(g) - O_2(g) + 2CO_2(g)$ (thus, here the coefficients are: $\nu_{CO} = -2$, $\nu_{O2} = -1$, $\nu_{CO2} = +2$,), while the reaction $2 H_2(g) + O_2(g) = 2 H_2O(l)$ is expressible as $0 = - 2H_2(g) - O_2(g) + 2 H_2O(l)$.As the reaction progresses, the amounts (number of moles) n_i of each substance i changes: Initially, each $n_i = n_i°$ (its initial amount), but at the end of the reaction, after $|\nu_i|$ mole of a reactant consumed or a product produced

(say 2 moles of CO consumed or 2 moles of CO_2 produced), n_i would equal ($n_i^\circ + \nu_i$). So, in chemical kinetics, a parameter ξ (zeta) called the advancement of the chemical reaction is defined as: $n_i = n_i^\circ + \nu_i \xi$, where $\xi = 0$ at the beginning of the reaction while $\xi = 1$ at its end – obviously, with the progress of the reaction, ξ changes from 0 to 1. This gives that the change in amounts of substances along the reaction is: $dn_i = \nu_i\, d\xi$. The speed v of the chemical reaction is defined as $v = (1/\nu_i)\, dn_i/dt$. [Thus, for the above combustion reaction of CO, $v = (-1/2)\, dn_{CO}/dt = (-1/1)\, dn_{O2}/dt = (1/2)\, dn_{CO2}/dt$.] However, as $dn_i = \nu_i\, d\xi$, we get that speed $v = (1/\nu_i).\nu_i\, d\xi/dt$, or, $v = d\xi/dt$. [It may be noted here that the comparable and more familiar quantity, the rate r of the chemical reaction, is defined as $r = (1/\nu_i)\, d[S_i]/dt = (1/\nu_i)\, d(n_i/V)/dt$, so if the volume V of the reaction mixture remains constant, the rate r and the speed v are related as: $r = v/V$.]

Now, for the reaction mixture progressing infinitesimally along the chemical reaction, the amount of a substance i changes by dn_i, so the change in Gibbs free energy is $dG = VdP - SdT + \Sigma_i \mu_i dn_i$ (as per the familiar expression of dG for an open system), where the symbols carry their usual meanings. Now, as $G = U + PV - TS$, we have: $dG = dU + PdV + VdP - TdS - SdT$. Equating the two expressions of dG gives (do verify): $TdS = dU + PdV - \Sigma_i \mu_i dn_i$. Assuming that in the reaction no non-mechanical work is done, the work done $\delta w = -PdV$, implying that $TdS = (dU - \delta w) - \Sigma_i \mu_i dn_i = \delta q - \Sigma_i \mu_i dn_i$. This finally gives the system entropy change as $dS = \delta q/T - (1/T)\, \Sigma_i \mu_i\, dn_i$.

However, remembering that $dS = d_eS + d_iS$, we note that $\delta q/T$ is nothing but the entropy flow d_eS into the system from the surroundings, so that here the internal entropy production $d_iS = -(1/T)\, \Sigma_i \mu_i dn_i$. As $dn_i = \nu_i\, d\xi$, we get $d_iS = -(1/T)\, \Sigma_i \mu_i \nu_i\, d\xi$. So, here the rate of internal entropy production is:

$$d_iS/dt = -(1/T)\, \Sigma_i \mu_i\, \nu_i\, d\xi/dt = -(1/T)\, (\Sigma_i \mu_i\, \nu_i)\, v$$

For a reaction, $(-\Sigma_i \mu_i \nu_i)$ is a parameter that governs the direction of the reaction and is called the chemical affinity A of the reaction (related with concept of generalised force or generalised affinity). Thus if A is positive, reaction would be going in the forward direction. [It is obvious that $A = -\Delta_r G$, the Gibbs energy of reaction, as for a reaction ($\Sigma_i \mu_i \nu_i$) is nothing but $\Delta_r G$ itself: say, for $0 = -2\, CO(g) - O_2(g) + 2CO_2(g)$, $\Sigma_i \mu_i \nu_i = -2\, \mu_{CO} - \mu_{O2} + 2\mu_{CO2} = 2\mu_{CO2} - (2\, \mu_{CO} + \mu_{O2})$, which is nothing but the $\Delta_r G$ for the reaction.]

In terms of the chemical affinity A and the speed v of the chemical reaction, the rate of internal entropy production here is expressible as: $d_iS/dt = (A/T)v$, where A/T is the generalised affinity χ and J is the generalised flow. [Though A is called the affinity here, the actual generalised affinity χ is A/T here, not A itself.]

In the above discussions, we have limited ourselves to simpler situations where there is only one kind of generalised force χ, and corresponding to that there is only one kind of generalised flow J, with $d_iS/dt = \chi\, J$. But in reality, two or more pairs of generalised forces χ_k and generalised flows J_k (where k = 1, 2, ..) may coexist, and in such cases, as was hinted earlier, the rate of internal entropy production will be $d_iS/dt = \Sigma_k\, \chi_k\, J_k$. Thus, if between two parts of a system the temperature T as well as the chemical potential T are different, then difference of (1/T) and of (μ/T) will coexist, so heat flow and diffusion processes will occur simultaneously – this phenomenon is called thermodiffusion. If heat flow and matter diffusion processes are denoted respectively as

1 & 2, or as 'th' & 'm', then we'll have $d_iS/dt = \chi_1 J_1 + \chi_2 J_2$, or, $d_iS/dt = \chi_{th} J_{th} + \chi_m J_m$. We'll discuss more about such situations in sections 6.5 and 6.6, and also in Unit 7.

6.5 LINEAR LAWS FOR THE NON-EQUILIBRIUM PROCESSES

Let us now see how the generalised flows J_k depend on the generalised forces χ_k. We note that at equilibrium all J_k and χ_k are zero, so for systems not significantly far from equilibrium the generalised flows may be safely assumed to linearly depend on the generalised forces: i.e., that $J_k = \Sigma_i L_{ki} \chi_j$ (with the coefficients L_{ki} being constants). Clearly, if only one kind of generalised force χ_k (say, a difference in chemical potential) is there, then the above relation would mean $J_k = L_{kk} \chi_k$, implying that in such cases the corresponding generalised flow J_k (say, the rate of diffusion) is proportional to the generalised force χ_k (say, the ratio of the negative difference of chemical potential and the temperature) There are many examples of such linear relations in the physical sciences, such as the Fick's law for diffusion, the Fourier's law for heat flow, the Ohm's law for electric current, etc. Each of those laws linearly relates one type of generalised flow with the corresponding generalised force, giving a proportional variation of the form $J_k = L_{kk} \chi_k$. (However, these old experimental laws may not be defined in a way with their product equals the rate of internal entropy production, as is the desired norm in this relatively new branch of science). However, there are also some other experimentally discovered linear laws in the physical sciences that relates one kind of generalised flow with another kind of generalised force, such as the ones associated with Soret effect and Dufour effect that deal with simultaneous heat flow and diffusion.

As such types of laws are generalisations from observed irreversible phenomena, they are called phenomenological relations, and the coefficients L_{ki} there are called phenomenological coefficients (the word 'phenomenological' means 'of experimental origin'). The 'pure' coefficients L_{kk} stand for the relation of a generalised flow with the same type of generalised force, e.g., the coefficients for heat conductivity, electrical conductivity, diffusion etc., while the 'cross' coefficients L_{ki} with $k \neq i$ describe the interference of two irreversible flows k & i, such as thermodiffusion.

Considering only two arbitrary irreversible processes 1 & 2 happening together, we get $J_1 = L_{11} \chi_1 + L_{12} \chi_2$ and $J_2 = L_{21} \chi_1 + L_{22} \chi_2$, while $d_iS/dt = J_1 \chi_1 + J_2 \chi_2$. This gives $d_iS/dt = L_{11} \chi_1^2 + (L_{12} + L_{21}) \chi_1 \chi_2 + L_{22} \chi_2^2 > 0$, which implies that always the 'pure' coefficients L_{ii} (e.g., L_{11} and L_{22}) are all positive [e.g., if $\chi_2 = 0$, $d_iS/dt = L_{11} \chi_1^2 > 0$, implying that the pure coefficient $L_{11} > 0$], while the 'cross' coefficients L_{ki} , with $k \neq i$, (e.g., L_{12} and L_{21}) may be positive or negative.

There are some relations among the phenomenological coefficients, the most well-known among them being the Onsager reciprocal relation. Lars Onsager (born 1903 in Norway, awarded Nobel prize in 1968) has shown that for fluxes and affinities defined obeying the standard relation $d_iS/dt = \Sigma_k \chi_k J_k$, the 'cross' coefficients L_{ik} and L_{ki} (where $i \neq k$) in the relation $J_k = \Sigma_i L_{ki} \chi_k$ must be equal, i.e., $L_{ik} = L_{ki}$, and this is known as the Onsager reciprocal relation. The derivation of this relation involves complicated steps that utilises the concept of microscopic reversibility. Microscopic reversibility means the symmetry of all mechanical equations of motions of individual particles with respect to

time, i.e., that those equations are invariant for replacement of t with (–t). For example, the Newton's second law m $(d^2x/dt^2) = F_x$ is invariant for replacement of t with (–t).
Another important relation is that the *magnitude* of the 'cross' coefficient L_{ik} (with $i \neq k$) has to be less than the geometric mean $(L_{ii}\ L_{kk})^{½}$ of the two 'pure' coefficients L_{ii} and L_{kk}, i.e., that $|L_{ik}| < (L_{ii}\ L_{kk})^{½}$. To derive this relation, let us consider the (quite general) case of $(\chi_1 \neq 0,\ \chi_2 \neq 0)$ for which $L_{11}\ \chi_1^2 + (L_{12} + L_{21})\ \chi_1\ \chi_2 + L_{22}\ \chi_2^2 > 0$, obviously meaning: $L_{11}\ ß^2 + (L_{12} + L_{21})\ ß + L_{22} > 0$ where $ß = \chi_1/\chi_2$, i.e., ß is clearly a real quantity. However, this inequality also means that $L_{11}\ ß^2 + (L_{12} + L_{21})\ ß + L_{22} \neq 0$, which further means that the quadratic equation $L_{11}\ ß^2 + (L_{12} + L_{21})\ ß + L_{22} = 0$ can have no real roots (values) for ß, meaning that two roots $ß = \{-(L_{12} + L_{21}) \pm ((L_{12} + L_{21})^2 - 4\ L_{11}\ L_{22})^{½}\}/(2\ L_{11})$ of that quadratic equation can only be complex. This, however, would mean that $\{(L_{12} + L_{21})^2 - 4\ L_{11}\ L_{22}\}^{½}$ must be a purely imaginary number, i.e., that $(L_{12} + L_{21})^2 - 4\ L_{11}\ L_{22} < 0$, which means $(L_{12} + L_{21})^2 < 4\ L_{11}\ L_{22}$. Using the Onsager reciprocal relation $L_{12} = L_{21}$, this immediately gives $(2\ L_{12})^2 < 4\ L_{11}\ L_{22}$, or that $|L_{12}| < (L_{11}\ L_{22})^{½}$, implying that, in general, $|L_{ik}| < (L_{ii}\ L_{kk})^{½}$.

W CHECK YOUR PROGRESS

Q1. In non-equilibrium thermodynamics, the increase of the entropy of the universe during a spontaneous process within a system is known by a specific technical term. What is that term? Briefly justify the name of that term.

Q2. Briefly state how non-equilibrium thermodynamics helps us to explain why time can flow only in the forward direction.

Q3. For spontaneous heat flow between two parts of a system kept at different temperatures, what are the expressions of the generalised force and the generalised flow? Even though heat flows there because of difference in the temperatures, we can't take $(-\Delta T)$ as the generalised force. Why?

Q4. For a spontaneous chemical reaction occurring in a reaction mixture of constant volume V, express the rate of internal entropy production in terms of the Gibbs free energy of the reaction $\Delta_r G$, the reaction rate r and the volume V.

Q5. Prove that a 'pure' type of phenomenological coefficient L_{kk} must be positive.

2 6.6 LET US SUM UP

- Non-equilibrium thermodynamics discusses about irreversible processes such as heat flow, diffusion, osmosis, chemical reaction, electric current, etc., in which entropy of the universe increases, meaning entropy being produced.

- There are generalised forces or affinities, such as differences in inverse of temperature or in chemical potential etc., between different parts of a system, because of which a generalised flow or flux such as heat flow or diffusion occurs. The rate of entropy production equals the product of the generalised force and the generalised flow, or the sum of such products.

- It can be shown that for a chemical reaction, the generalised force is $-\Delta_r G/T$, the ratio of the negative of Gibbs energy $\Delta_r G$ of the reaction and the

temperature T, while the generalised flow is the speed of the reaction v that equals the product of the reaction rate r and the reaction-mixture volume V.

- Generally, the generalised flows J_k can be assumed, and are experimentally found, to depend on the generalised forces χ_k in a linear manner, leading to the linear phenomenological relations of the form $J_k = \Sigma_i L_{ki} \chi_k$. Several generalised forces and generalised flows may coexist in a system, involving various phenomenological coefficients L_{ki} relating them.

- The phenomenological coefficients L_{ki} are found to have some noteworthy characteristics such that: (i) the 'pure' coefficients L_{ii} are always positive, (ii) the 'cross' coefficients L_{ik} and L_{ki} (where $i \neq k$) must be equal, as per Onsager reciprocal relation, (iii) the magnitude of the 'cross' coefficient L_{ik} must be less than the geometric mean $(L_{ii} L_{kk})^{½}$ of the two 'pure' coefficients.

- Non-equilibrium thermodynamics is able to explain some interesting phenomena such as the unidirectional arrow of time, and the prolonged sustenance of highly ordered open systems such as the living organisms.

K 6.7 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: The specific technical term is internal entropy production. As during an irreversible process the entropy of the universe increases, unlike in the case of energy, so entropy gets produced here. As for such a process occurring *inside* the system, the entropy gets produced *inside* the system, so it is called internal entropy production.

Answer to Q2: As with progress of time, entropy gets produced in positive amount, and as entropy production must be positive only, so it follows that time must flow only in the forward direction.

Answer to Q3: For this system, the expressions of the generalised force χ and the generalised flow J are respectively $(1/T_2 – 1/T_1) = \Delta(1/T)$ and $(\delta q_{2i}/dt)$ or $(\delta q_i/dt)$. We can't take $(–\Delta T)$ as the generalised force, as in that case the rate of internal entropy production d_iS/dt won't then equal the product of the generalised force χ and the generalised flow J, which it must do.

Answer to Q4: Here, rate of internal entropy production $d_iS/dt = (A / T)\, v$, where chemical affinity $A = –\Delta_rG$, the reaction speed $v = r V$ and T is the reaction temperature. So, here $d_iS/dt = (–\Delta_rG / T).\, r V$.

Answer to Q5: If there exist only one kind of generalised force χ_k (i.e., $\chi_k \neq 0$), the rate of internal entropy production d_iS/dt will equal $\chi_k J_k$, where the generalised flow J_k will equal $L_{kk} \chi_k$. So, $d_iS/dt = \chi_k J_k = \chi_k L_{kk} \chi_k = L_{kk} \chi_k^2$. As $d_iS/dt > 0$, and as obviously $\chi_k^2 > 0$ (as that is a square of a real non-zero quantity χ_k), so the 'pure' coefficient L_{kk} must be positive.

O 6.8 FURTHER READING

- Prigogine, I. & Kondepudi, D. (1998). *Modern Thermodynamics: From Heat Engines to Dissipative Structures.* Wiley, UK.
- Prigogine, I. (1961). *Introduction to Thermodynamics of Irreversible Processes.* Interscience Publishers, New York. (also in archive.org, <https://archive.org/details/introductiontoth0000prig>).
- Prigogine, I. (1977). *Time, Structure and Fluctuations.* Nobel Lecture, 8th Dec 1977. Stockholm, Sweden.
- Rajaram, J. & Kuriacose, J. C. (2013) *Chemical Thermodynamics: Classical, Statistical and Irreversible.* Pearson, India.

M 6.9 MODEL QUESTIONS

Q1. Explain the concept of entropy production during an irreversible process in general. Why is this entropy production termed as internal entropy production?

Q2. Discuss how entropy gets produced for heat flow between two parts of the system kept at two different temperatures. For this system, find rate of internal entropy production as product of a generalised force and a generalised flow.

Q3. List the expressions of generalised force and generalised flow for heat flow, diffusion and electric current between two parts of a system. Briefly explain why the expression of generalised force for heat flow doesn't have a negative sign, unlike that for the other two.

Q4. How is the advancement parameter ξ for a chemical reaction defined in terms of varying amounts of the various chemical species? Discuss how the speed v of the reaction is defined in terms of ξ. How is v related to the rate r?

Q5. Starting from the relation between amount of a reactant/product species with the advancement parameter ξ for a spontaneous chemical reaction, obtain an expression for the rate of internal entropy production for the chemical reaction in terms of the chemical affinity A and the speed v of the chemical reaction. Relate its generalised affinity χ and A.

Q6. Express why and how the generalised flows can be expressed as being linearly dependent on the generalised forces. Illustrate some experimentally known examples of proportional dependence of a generalised flow on the corresponding generalised force.

Q7. Discuss the characteristics and the inter-relations among the phenomenological coefficients. Show that the magnitude of the 'cross' coefficient L_{ik} , where $i \neq k$, must be less than the geometric mean $(L_{ii}\, L_{kk})^{½}$ of the two 'pure' coefficients.

UNIT 7: COUPLED FLOWS, STATIONARY STATES AND LOCAL SUSTENANCE OF ORDER

UNIT STRUCTURE

7.1 Learning Objectives
7.2 Introduction
7.3 The Concept of Coupled Flows and Reactions
7.4 The Thermoelectric Effects
7.5 The Non-equilibrium Stationary States
7.6 Prigogine's Principle for the Stationary States
7.7 Local Sustenance of Ordered Systems
7.8 Let Us Sum Up
7.9 Answers to Check Your Progress
7.10 Further Reading
7.11 Model Questions

7.1 LEARNING OBJECTIVES

After going through this unit, you will:

- appreciate the concept of coupled flows, including that of coupled reactions.
- learn about the experimentally observed thermoelectric effects representing some coupled flow phenomena, and the inter-relations between their coefficients arising from the Onsager's reciprocal relations.
- appreciate the concept of non-equilibrium stationary states arising in various forms - heat flow, flow of matter, mixing chambers, multi-step chemical reactions and living bodies.
- perceive the Prigogine's principle of minimum entropy production for the non-equilibrium stationary states and learn to verify it for selected systems.
- comprehend the prolonged sustenance of highly ordered systems such as living organisms, in apparent violation of the second law of thermodynamics.

7.2 INTRODUCTION

As we learnt in Unit 6, several generalised forces and their corresponding generalised flows simultaneously coexist in many cases, with each force influencing the various flows. Such simultaneous, mutually interacting, flows are described as coupled flows. Several chemical reactions may also simultaneously occur and influence one another, as is common in a living body, and such reactions are called coupled reactions. Such coupled flows and coupled reactions are of special interest theoretically and practically, in various fields such as physics, engineering, chemistry and biology. For example, these make possible the ordered growth and healthy sustenance of the living beings, even though they are living and thriving in a universe where breaking down of order is the general norm. Some experimentally observed thermoelectric effects, such as the

Seebeck and the Peltier effects, represents coupled flow phenomena that got widely investigated in physics, and so it is worthwhile to have an overview of those here.

All around us, we come across systems, open ones such as a pond or an adult frog, which are in apparent equilibrium with the system properties (e.g., water level or mass) remaining almost constant, but actually remaining so with two or more flows (such as moderate rainfall and atmospheric evaporation, or feeding and excretion) counteracting each other or one another in their effects. In chemical engineering also, in case of continuous-process manufacturing such as of H_2SO_4 from reaction of SO_3 and H_2O, we find that the reaction mixture may always contain fixed amounts of the reactants and products at constant temperature and pressure, but there is no equilibrium here, but rather constant entry of the reactants and removal of the products. Such a system is said to be in a non-equilibrium stationary state. In such a stationary state, entropy keeps getting produced continuously, but at a constant rate, and that constant rate is the minimum rate – this phenomenon is explained by the Prigogine's principle of minimum entropy production. For some simple systems of this sort, we can even easily prove that the said rate is actually a minimum.

And, as was mentioned in Unit 6, the prolonged sustenance of a highly ordered open system, such as a living body, is associated with the Prigogine's principle, with the system entropy remaining practically constant but the entropy of the surroundings always increasing, thus not actually violating the second law of thermodynamics about the inevitable nature of continuous increase of the entropy of the universe.

7.3 THE CONCEPT OF COUPLED FLOWS AND REACTIONS

In many situations, a generalised irreversible flow described in non-equilibrium thermodynamics (such as heat flow, diffusion, or electrical conduction, etc.) exists not singly, but several of them simultaneously exist together in the same system. In such cases, there are also several corresponding generalised forces coexisting, with one generalised force influencing not only its corresponding generalised flow, but other flows as well. Such a phenomenon is called coupled flows. In a coupled flow situation, each flow (e.g., heat flow) gets influenced by not only the generalised force of its own type (e.g., difference in inverse of temperature) but also the other generalised forces, such as difference in chemical potential or in electrical potential. Assuming the linear phenomenological relations, the dependence of a flow (say, the k-th one) on these forces χ_j is given by the linear relation $J_k = \Sigma_i L_{ki} \chi_j$, where the 'cross' coefficients L_{ki} remain related by the Onsager reciprocal relation, $L_{ki} = L_{ik}$. Concept of coupled flows are utilised to explain coupled reaction-transport systems in biology, energy conversions in fuel cells and thermoelectric generators, and coupled multiphase-substance flow (CMF) models for particle migration and heat flow within porous media in geotechnical engineering.

An interesting pair of coupled flow situation is the heat flow and material diffusion occurring simultaneously under the influence of difference in concentration (thus, in chemical potential) and/or of difference in temperature (thus, in the inverse of temperature). If was found that a difference in concentration among different parts of a

system creates a heat flow among these parts, and it can be significant for gas mixtures. This phenomenon is called the Dufour effect. Similarly, a difference in temperature among different parts of a system containing a mixture of lighter and heavier particles causes the components of the mixture to move differently among the parts, with the lighter particles moving to the hotter parts and the heavier particles moving to the colder parts. This phenomenon is called the Soret effect. Another pair of coupled flows is about the experimentally well-known and technologically utilised thermal effect of electrical currents and the electrical effect of temperature differences, together known as the thermoelectric effects, which will be elaborated in the next unit.

Because of the dependence on the other generalised forces, sometimes it happens that a generalised flow may even occur in a direction opposite to its own generalised force, i.e., a flow J_k may be of opposite sign to its force χ_k , implying that their product $(\chi_k J_k) < 0$, even though the overall rate of entropy production, $d_iS/dt = \Sigma_i (\chi_j J_i)$, remains positive (as that must remain positive!). This can, of course, happen if the magnitude(s) of the other generalised force(s) χ_j other than χ_k is/are large enough, and its/their contribution $L_{ki} \chi_j$ to J_k, as per the relation $J_k = \Sigma_i L_{ki} \chi_j$, is/are of opposite sign to the contribution $L_{kk} \chi_k$ from the own generalised force χ_k itself.

One special kind of a coupled flow situation is the simultaneous occurrence of several chemical reactions, with chemical affinity A_i of each influencing the speeds of all of those, as per the same linear relations $J_k = \Sigma_i L_{ki} \chi_j$, where $\chi_j = A_i /T$. As mentioned earlier, such reactions are called coupled reactions, and in case of coupled reactions there are striking, obvious examples of some reactions occurring in opposite direction to their own generalised force. Thus, biosynthetic reactions forming complex, highly ordered proteins from amino acids are strongly non-spontaneous ones, if these are to occur alone. However, coupled with the quite spontaneous hydrolysis reactions of ATP (Adenosine Triphosphate) and GTP (Guanosine Triphosphate) occurring simultaneously, such non-spontaneous biosynthetic reactions can easily occur. The mathematical relations governing such coupled reactions can be illustrated as below:

For a single chemical reaction occurring alone, we have, $d_iS/dt = (A/T)\, v > 0$, where A is its chemical affinity, v is its speed and T is the system temperature. For a pair of two coupled reactions 1 and 2, we have, $d_iS/dt = (A_1/T)\, v_1 + (A_2/T)\, v_2 > 0$, or that, $d_iS/dt = (A_1v_1 + A_2v_2)/T > 0$. Thus, it may occur that for one reaction, say reaction 1, $A_1 v_1 < 0$ (thus, that reaction may proceed in a direction opposite to its own affinity A_1), if for the other reaction the product $A_2 v_2$ is sufficiently positive, so that $(A_1v_1 + A_2v_2) > 0$. This is the guiding relation for coupled reactions, that the sum $\Sigma_i (A_i v_i) > 0$ for the various coupled reactions i, even though for one particular reaction k out of them, $A_k v_k < 0$.

7.4 THE THERMOELECTRIC EFFECTS

The thermoelectric effects deal with the interrelations between heat flow and electric conduction in some electrical conductor systems (e.g., in the thermoelectric devices). From the viewpoint of non-equilibrium thermodynamics, the thermoelectric effects arise from the coupled dependence of the thermal flow (heat flow) and electrical flow (current) on the generalised thermal force (difference of inverse of temperature) and

the generalised electrical force (difference of electrical potential), generally between the two junctions of two different conductors joined together (the Seebeck and the Peltier effects), though there is also the Thomson effect dealing with a kind of thermal flow (heat generation or absorption) associated with current flowing through one conductor having a temperature gradient along its direction of current. However, the effects are varyingly formulated (as detailed below) in forms of interrelations among the two generalised forces (in case of Seebeck effect) or among the two generalised flows (in case of Peltier effect), etc., thus differing from the formal forms of linear phenomenological relations found in non-equilibrium thermodynamics, formulated strictly between the generalised forces χ_i on one hand and the generalised flows J_i on the other. Various thermoelectric effects are as in Table 7.1.

Table 7.1: Various Thermoelectric Effects

Thermoelectric Effect	Cause	Effect	Approx. Relation
Seebeck Effect	Temp. Diff. ΔT	Electr. Pot. Diff. ΔV	$\Delta V \approx S_{AB}\, \Delta T$
Peltier Effect	Electric Current I	Heat Flow $\delta q/dt$	$\delta q/dt = \Pi_{AB}\, I$
Thomson Effect	Electric Current I & Temp. Grad. dT/dx	Heat Production $\delta q/dt$	$\delta q/dt = \mu\, J\, dT/dx$ (where $J = I/A$)

Seebeck Effect:

It deals with the development of an EMF (i.e., a potential difference), called the thermoelectric EMF, created by the presence of a temperature difference between two junctions (**Figure 7.1**) of two different conductors (made of conducting materials A and B) joined together at two ends (here the right and the left ends, kept at two different temperatures). This arrangement is called a thermocouple, which is generally used to measure temperatures within various kinds of devices, sometimes even for a useful conversion of heat energy to electrical one.

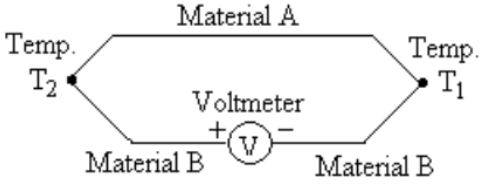


Figure 7.1: A Thermocouple

The Seebeck effect arises because the applied temperature difference causes the charge carriers of electricity (i.e., the mobile electrons or the mobile holes – a hole meaning a lack of an electron) present in the materials to diffuse from the hot region (i.e., hot junction) towards the cold region, similar to what gas molecules would do. Mobile charge carriers moving towards the cold junction region leave behind their oppositely charged and immobile ions at the hot junction region, thus giving rise to the thermoelectric EMF.

As per the Seebeck effect, the potential difference ΔV {i.e., $V(T_2) - V(T_1)$} generated between the two junctions maintained at two different temperatures T_1 and T_2 (so that $T_2 > T_1$) is given by the following approximate relation (where S_A and S_B are the

Seebeck coefficients of the conducting materials A and B respectively, whereas $S_{AB} = S_A - S_B$ is the *Seebeck coefficient* of the thermocouple):

$$\Delta V \approx S_{AB}\Delta T, or\ \Delta V \approx (S_A - S_B)\Delta T$$

Peltier Effect:

It deals with the thermal consequence (i.e., cooling/heating effect) of an electrical current flowing through a junction of two different conducting materials, as in the case of the two junctions within the aforementioned thermocouple. When a current I is made to flow through the circuit in the said device, heat would be absorbed at one junction (called *thermoelectric cooling* or *Peltier cooling*), while heat would be evolved (with a rate of equal magnitude) at the other junction – thus, there is a heat flow from one junction to the other. Peltier effect is utilised in *thermoelectric heat pumps* or *Peltier coolers*, which are solid-state cooling devices transferring heat from one side (the cooler side) of the device to the other side.

The Peltier effect is measured by the *rate of Peltier cooling,* which is defined as the time rate of heat absorbed (i.e., δq/dt) at one junction; this rate is proportional to the current I that flows through it (it is considered as flowing from material A towards material B), as:

$$\delta q/dt = (\Pi_A - \Pi_B)\, I = \Pi_{AB}\, I$$

Where Π_{AB} is the Peltier coefficient of the thermocouple, whereas Π_A & Π_B are the Peltier coefficients of the conducting materials A and B respectively, with $\Pi_{AB} = \Pi_A - \Pi_B$.

The Seebeck and the Peltier coefficients for a thermocouple are interrelated as per the simple relation $\Pi_{AB} = T\, S_{AB}$, which arises because of the Onsager reciprocal relation existing between two coupled flows that are inherently associated with these two effects. These effects represent irreversible cross-phenomena between thermal and electrical driving forces and flows: Seebeck effect is about the electrical effect of thermal driving force, whereas Peltier effect is about the thermal effect of electrical driving force. However, as was mentioned, these effects are expressed in forms differing from the formal forms of linear phenomenological relations used in non-equilibrium thermodynamics. So the Seebeck and the Peltier coefficients, S_{AB} and Π_{AB}, are not exactly equal (unlike the exactly equal cross-coefficients L_{ki} and L_{ik} in the Onsager reciprocal relation) but are rather proportional to each other with 1/T or T as the proportionality constant, as is obvious from the above relation $\Pi_{AB} = T\, S_{AB}$. (We may also note that for each conducting material, $\Pi_A = T\, S_A$ and $\Pi_B = T\, S_B$, so that subtraction of the second from the first gives $\Pi_{AB} = T\, S_{AB}$).

Thomson Effect:

This effect discusses the thermal (i.e., heating/cooling) effect of an electric current passing through *one* conducting material having a temperature gradient along the direction of the current. If dT/dx is the temperature gradient along the direction of current through the conducting wire, then the heat production (δq/dt) per unit time (expressed as per unit volume of the conducting material) due to the Thomson effect is given as: $\delta q/dt = -\mu\, J\, dT/dx$. Here μ is the Thomson coefficient and J = I/A is the current density (i.e., electric current I divided by the cross-sectional area A). Thus we see that if the temperature increases along the direction of the current, the temperature

gradient dT/dx is positive and so δq/dt will be negative (i.e., cooling effect will be observed) for a material having a positive value of the Thomson coefficient, as is the case with copper. However for iron, this coefficient is negative.

7.5 THE NON-EQUILIBRIUM STATIONARY STATES

As was mentioned in **Section 7.2**, in a system experiencing a non-equilibrium stationary state, such as in a continuous-process reaction chamber (**Figure 7.2**) of a chemical factory, the thermodynamic properties of the system such the mass, the amounts of the various substances, the internal energy, the enthalpy, etc. remain constant, i.e., these do not change with time. However, we might even have different parts of such a system with different intensive property values such as being at different temperatures or pressures, say with inlet part being cooler and outlet part hotter due to an exothermic reaction occurring there, but even in such a case, for a true stationary state, a given part of the system such as the outlet will have a definite temperature and pressure that do not change with time! But, such a system is not at all at equilibrium (let us remember that at equilibrium, no net change happens); rather, an irreversible process is obviously going on there, such as a spontaneous chemical reaction (e.g., the formation of H_2SO_4 from SO_3 and H_2O) occurring in the reaction chamber of the factory. So, rather justifiably, such a system is said to be in a *non-equilibrium stationary state*. In such a stationary state, even though one (or more) irreversible process keeps occurring, the system properties can remain invariant because there are several flows of matter and energy, or at least only of energy, between the system and the surroundings, and these flows together with the generalised irreversible flows in the system counteract one another, resulting in time-invariant values of the thermodynamic properties inside the system. Thus, in this example, reactants come in, the irreversible reaction occurs, and the product goes away, these three flows counteracting the effects of one another within the system.

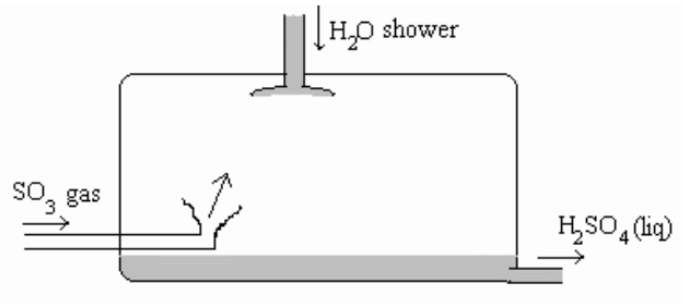


Figure 7.2: Steady State in a Reaction Chamber

There are deceptively similar parallelisms between the non-equilibrium stationary state (sometimes also called steady states) and equilibrium. Just as matter kept in an isolated or effectively isolated closed system (e.g., mixture of ethyl acetate and dilute sulphuric acid) tends to spontaneously move towards attaining equilibrium (e.g., the hydrolysis-esterification equilibrium, with constant final concentrations of ethyl acetate, water, sulphuric acid, ethanol and acetic acid), just similarly matter in an open or a closed system (e.g., the aforementioned reaction chamber, or a closed bottle in a garbage dump) subject to an constant external flow (e.g., insertion of the reactants into the inlet at a constant rate, or heat flow at constant rate from sunshine on its exposed part) tends to spontaneously move towards attaining a non-equilibrium stationary state (e.g., with invariant amounts of the reactants and products inside, or an invariant

temperature distribution among the different parts). Secondly, after attaining either equilibrium, or a non-equilibrium stationary state, as was already mentioned above, the thermodynamic properties inside the system just similarly become time-invariant.

7.6 PRIGOGINE'S PRINCIPLE FOR THE STATIONARY STATES

For a non-equilibrium stationary state not far from the equilibrium, there is a principle discovered by Ilya Prigogine, which states that the rate of internal entropy production is a minimum for such a stationary state. This principle is called the *Prigogine's Principle of Minimum Entropy Production*. This principle means that after a small deviation or fluctuation is made to occur around the stationary state (e.g., by manually withdrawing some extra amount of product from a continuous reaction chamber), the rate σ (i.e., d_iS/dt) of entropy production will be more than the fixed value of this rate for the stationary state, and then it can only decrease with time (i.e., its time derivative dσ/dt would be negative), so that the stationary state with the minimum rate of entropy production will be re-attained. On the other hand, while in the stationary state, the time derivative dσ/dt of the rate σ of entropy production is clearly zero, as the rate $\sigma = d_iS/dt$ itself is obviously constant for the clearly invariant stationary state. Thus, dσ/dt is negative for small deviation from the stationary state, while at the stationary state itself, dσ/dt is zero. So, the time derivative of dσ/dt, i.e., $d^2\sigma/dt^2$, is positive at the stationary state. Thus, we find that such stationary states are stable states (i.e., automatically or spontaneously re-attainable ones), with the first derivative of d_iS/dt zero, and the second derivative positive – i.e., with d_iS/dt being a minimum. This is the said Prigogine's principle.

To better understand this principle, and also to mathematically derive it for a specific situation, let us consider a closed system containing a pure gas and having two chambers separated by a small hole (or a capillary), while the two chambers are being maintained at two different constant temperatures T_1 and T_2 (using a heating burner below one chamber and cooling pipes around the other chamber, as in **Figure 7.3**). Here we see that there is a heat flow J_h corresponding to the heat-transport affinity χ_h (equal to the difference of inverse temperature) maintained at a constant value $\Delta(1/T)$, whereas there also arise an affinity $\chi_m = -\Delta(\mu/T)$ corresponding to matter transport. Because of the existence of stationary state, there would be no net matter flow, and so J_m equals zero, though χ_m is non-zero. [We may note here that as the system is closed, not isolated, so heat can flow into one part of the system and move away from the other part, so inside the system also, the heat flow J_h can be non-zero in the stationary state. However, as in this closed system matter can't come in or move out of the system, so inside the system also,

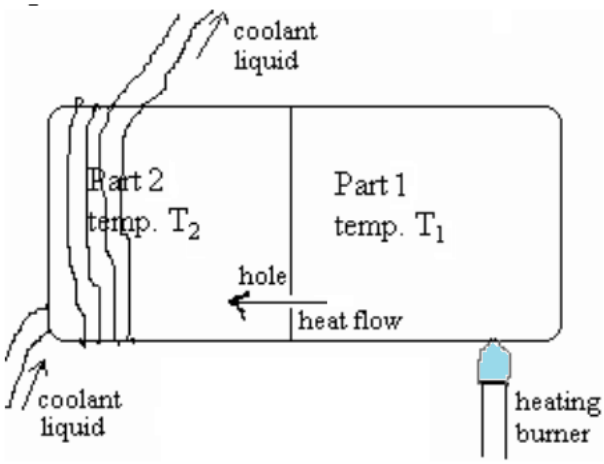


Figure 7.3: Heat Flow in a Closed System

in the stationary state, the matter flow J_m must be zero.]

As the system was assumed to be not far from equilibrium, the phenomenological linear relations are valid which give:

$J_h = L_{hh}\,\chi_h + L_{hm}\,\chi_m$, $J_m = L_{mh}\,\chi_h + L_{mm}\,\chi_m$, where $d_iS/dt = J_h\,\chi_h + J_m\,\chi_m > 0$.

From Onsager's reciprocal relation, we get $L_{hm} = L_{mh}$, so we finally get:

Rate of internal entropy production, $\sigma = d_iS/dt = L_{hh}\,\chi_h^2 + 2\,L_{mh}\,\chi_m\,\chi_h + L_{mm}\,\chi_m^2$

Now, we may note that there are only two generalised forces, namely χ_h and χ_m, in this system, and $\sigma = d_iS/dt$ will depend only on them. However, in this stationary state, clearly the two temperatures T_1 and T_2 remain constant (will be automatically so, if heated and cooled at constant rates), so, $\chi_h = \Delta(1/T) = (1/T_2 - 1/T_1)$ remains at a constant value. So, d_iS/dt actually depends only on (or, in other words, it is a function only of) χ_m , the lone variable specifying the process.

So, differentiating $\sigma = d_iS/dt$ with respect to that variable χ_m , we get:

$d\sigma/d\chi_m = 2\,L_{mh}\,\chi_h + 2\,L_{mm}\,\chi_m = 2(L_{mh}\,\chi_h + L_{mm}\,\chi_m)$.

But as $J_m = L_{mh}\,\chi_h + L_{mm}\,\chi_m$ and as we know that J_m is zero here, so the first derivative of d_iS/dt, $d\sigma/d\chi_m = 2\,J_m = 0$. Thus, as that first derivative is zero, so $\sigma = d_iS/dt$ is either a maximum or a minimum. As it couldn't have been a maximum, as it is always a finite positive quantity, so we find that the rate of internal entropy production (d_iS/dt) is a minimum in this stationary state, thus verifying the said Prigogine's principle.

7.7 LOCAL SUSTENANCE OF ORDERED SYSTEMS

Non-equilibrium thermodynamics is particularly successful in explaining the prolonged sustenance of ordered open systems, including the highly ordered biological living systems such as ourselves, thriving for rather long periods of years and decades, amidst the all-pervading natural tendency in the universe of continual increase of disorder associated with the second-law of thermodynamics. This paradoxical issue is explained by considering the development of stationary states in various kinds of open systems, starting from non-living systems such as the continuous-process reaction chambers and ponds, to the complex living bodies. An isolated system can't show such a long persistence of a highly ordered state that brims with activities such as physical processes and bio-chemical reactions, as it would have violated the second law. However, the open system in such a stationary state continually undergoes some spontaneous thermodynamic processes in which entropy is continually produced, or in other words, disorder is being created. However, unlike the case of an isolated system, here the produced entropy is not remaining inside the system but rather is being continually expelled outside into the surroundings (along with the high-entropy reaction products, such as carbon dioxide and water, moving out into the surroundings, and also as heat moving out). Thus, the inside of such a system (say, the inside of a living body) can remain particularly low-entropy (i.e., highly ordered) for an extremely long period such as several decades, though at the expense of a regular increase of entropy at its surroundings.

W CHECK YOUR PROGRESS

Q1. What are coupled flows? Mention any two applications of coupled flows.

Q2. What is meant by Dufour effect? To observe this effect, does it become necessary to have two non-zero generalised forces exist simultaneously?

Q3. How can the otherwise non-spontaneous biosynthetic reactions forming complex, highly ordered proteins from amino acids occur in living bodies?

Q4. How are the Seebeck and the Peltier coefficients of a thermocouple related? What is the theoretical basis behind this relation?

Q5. Why can the Thomson effect in thermoelectric effects also be regarded as a 'cross flow' kind of phenomena?

Q6. How can the amounts of the reactants and products inside a continuous process reaction chamber remain constant, even though reactions are going on?

Q7. As per the Prigogine's principle, for a non-equilibrium stationary state not far from the equilibrium, what are the signs of σ and $d^2\sigma/dt^2$ at the stationary state, where σ is the rate of entropy production? What is the value of dσ/dt there?

Q8. For a non-equilibrium stationary state in a system, what happens to the entropy produced within the system? Does it remain there itself?

2 7.8 LET US SUM UP

- In many situations, two or more generalised irreversible flows (e.g., heat flow, diffusion, etc.) coexist together, along with their corresponding generalised forces. Such a phenomenon is called coupled flows. Examples are Soret effect and Dufour effect about interaction of heat flow and diffusion.

- Coupled reactions involving several chemical reactions occurring together are also important coupled flows phenomena, which occurs in living bodies whereby highly non-spontaneous reactions such as biosynthetic reactions can happen by virtue of being coupled with some spontaneous reactions.

- The thermoelectric effects such as Seebeck, Peltier and Thomson effects, well investigated in physics and involving commonplace applications such as thermocouples and Peltier coolers, also involve irreversible coupled flows. The simple relation between the Seebeck and Peltier coefficients arises from the Onsager reciprocal relation in non-equilibrium thermodynamics.

- In many situations, a non-equilibrium stationary state arise in some open or even some closed systems, where the system properties such as amounts of matter, internal energy, enthalpy, etc., remain invariant with time, so that the inside of the system may deceptively feel like being in equilibrium. However, one or more irreversible flow(s), such as spontaneous chemical reactions, continuously occur there at a constant rate, so it is not at all in equilibrium.

- As per the Prigogine's principle of minimum entropy production, valid for a non-equilibrium stationary state not far from the equilibrium, the rate of internal entropy production is a minimum in such a stationary state. Such a stationary state is also a stable state which automatically gets re-attained after occurrence of any small fluctuation or deviation away from it.

- Some highly ordered open systems, such as the living bodies, have a prolonged sustenance ranging up to many years, by virtue of being in practically a non-equilibrium stationary state. Here the system maintains its ordered state with its entropy remaining practically constant, but with the entropy of the surroundings continuously increasing due to the irreversible processes occurring within the system, with the entropy produced inside continually getting transferred to the surroundings.

K 7.9 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: In many cases, two or more generalised forces and their corresponding generalised flows coexist simultaneously, with each force influencing the various flows. Such simultaneous and mutually interacting flows are called coupled flows.
Two applications of coupled flows are: thermoelectric effect and electro-osmosis.

Answer to Q2: If a difference in concentration exists among different parts of a system, it causes a heat flow among these parts, and it can be significant for gas mixtures. This phenomenon is called the **Dufour effect**. No, to observe this effect, it is not necessary to have two non-zero generalised forces exist simultaneously. It would be observed if there is a difference in concentration among parts of a system, even though there is no difference in temperature among the parts.

Answer to Q3: Biosynthetic reactions forming complex, highly ordered proteins from amino acids, even though non-spontaneous otherwise, can occur by being coupled with the spontaneous hydrolysis reactions of ATP and GTP occurring simultaneously.

Answer to Q4: The Seebeck coefficient S_{AB} and the Peltier coefficient Π_{AB} of a thermocouple are related as $\Pi_{AB} = T\, S_{AB}$. This relation arises because of the Onsager reciprocal relation existing between two coupled flows that are theoretically associated with these two effects. However, as these effects are not formulated as per rules of non-equilibrium thermodynamics, the two coefficients are not being equal, but rather proportional involving the temperature T.

Answer to Q5: Yes, the Thomson effect can be regarded as a 'cross flow' kind of phenomenon, as it involves production of heat due to a electric current flowing along a conductor having a temperature gradient, because heat production is not a generalised flow directly associated with a generalised force involving electrical conduction.

Answer to Q6: This happens because there the reactants move in, the products move out, while the chemical reaction(s) inside consumes the reactants and produces the

products, thereby all these three kinds of flows counteracting the effects of one another within the system.

Answer to Q7: The signs of σ and $d^2\sigma/dt^2$ at the stationary state are, respectively, positive (a constant) and negative. The value of dσ/dt there is 0 (as σ is a constant).

Answer to Q8: For a non-equilibrium stationary state in a system, the entropy produced within the system does not remain there; it goes out into the surroundings, along with the high-entropy reaction products moving out, and with the heat released into the surroundings.

O 7.10 FURTHER READING

- Prigogine, I. & Kondepudi, D. (1998). *Modern Thermodynamics: From Heat Engines to Dissipative Structures.* Wiley, UK.
- Prigogine, I. (1961). *Introduction to Thermodynamics of Irreversible Processes.* Interscience Publishers, New York. (also in archive.org, <https://archive.org/details/introductiontoth0000prig>).
- Prigogine, I. (1977). *Time, Structure and Fluctuations.* Nobel Lecture, 8th Dec 1977. Stockholm, Sweden.
- Rajaram, J. & Kuriacose, J. C. (2013). *Chemical Thermodynamics: Classical, Statistical and Irreversible.* Pearson, India.
- Rastogi, R. P. (2007). *Introduction to Non-equilibrium Physical Chemistry*, Elsevier Science.

M 7.12 MODEL QUESTIONS

Q1. Discuss the phenomenological linear relations, the specific Onsager relation and the expression for entropy production that a coupled flow situation involving two generalised forces χ_1 and χ_2 need obey. Here, under what condition can the flow J_1 have a sign opposite to the sign of χ_1? Can both J_1 and J_2 here have their signs respectively opposite to the signs of χ_1 and χ_2?

Q2. What kind of particles of matter should be there in a system where we can easily observe some peculiar flow behaviour of matter related to differences in temperatures within the system?

Q3. Explain the concept of coupled reactions. Why are coupled reactions very significant in biological systems?

Q4. Briefly discuss the technological applications of the thermoelectric effects.

Q5. Discuss the similarity and the difference between a system in equilibrium and another system in a non-equilibrium stationary state.

Q6. Show that for a closed system heated at one part and cooled at the other part at constant heating/cooling rates, with the two parts remaining at fixed temperatures, the rate of internal entropy production is indeed a minimum.

Q7. Discuss how an adult animal is visualised as an open thermodynamic system lying approximately in a non-equilibrium stationary state, and how this rough model helps explain the long sustenance of its highly ordered living body, even

though the disorder of the universe must increase as per the second law of thermodynamics.

UNIT 8: INTRODUCTION TO POLYMER CHEMISTRY

UNIT STRUCTURE

8.1 Learning Objectives
8.2 Introduction
8.3 Introduction to Polymers
8.4 Monomers and Repeat Units
    8.4.1 Monomers
    8.4.2 Repeat Units
8.5 Degree of Polymerisation
8.6 Classification of Polymers
    8.6.1 On the basis of origin
    8.6.2 On the basis of Chain Structures
    8.6.3 On the basis of behaviour on heating
    8.6.4 On the basis of Mechanical Properties
    8.6.5 On the basis of Type of Monomers
8.7 Speciality Polymers
8.8 Let Us Sum Up
8.9 Answers to Check Your Progress
8.10 Further Reading
8.11 Model Questions

8.1 LEARNING OBJECTIVES

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

- define polymers and explain their importance in daily life and industry
- distinguish between monomers and repeat units
- understand and calculate the degree of polymerisation
- classify polymers into linear, branched, and network polymers with examples
- differentiate between natural and synthetic polymers
- differentiate between thermoplastics and thermosetting polymers
- classify polymers according to their mechanical properties as plastics, elastomers, and fibres, and explain their key features and examples.

8.2 INTRODUCTION

The development of human civilisation has always been closely linked to the materials available at different stages of history. Distinct eras such as the Stone Age and Iron Age reflect how transformative certain materials were in shaping tools, infrastructure, and social progress. As human needs evolved from basic survival requirements such as food, shelter, and protection to advanced technological demands so did the complexity of materials, leading to the development of metals, ceramics, composites, and synthetic materials.

Among modern materials, polymers occupy a central position in the contemporary life.

Their presence is so integrated into daily activities that they often go unnoticed. From household items and clothing to medical devices and electronic components, polymer-based materials contribute significantly to comfort, convenience, and technological advancement.

8.3 INTRODUCTION TO POLYMERS

The word “polymer” originates from Greek, where “poly” means many and “meros” means parts, indicating substances composed of repeating structural units. Chemically, polymers are macromolecules formed by the covalent bonding of numerous small molecules known as monomers. Their physical and chemical properties depend largely on molecular architecture, chain length, and intermolecular interactions.

Due to their lightweight nature, chemical resistance, durability, and design flexibility, polymers are extensively applied in sectors such as packaging, construction, healthcare, transportation, and aerospace engineering. Common polymeric materials encountered in everyday life include plastics, elastomers, synthetic fibers, adhesives, and protective coatings.

8.4 MONOMERS AND REPEAT UNITS

8.4.1 Monomers

A monomer is a small molecule with relatively low molecular weight that has the ability to chemically bond with other molecules of the same or different type to form a large molecule known as a polymer. These molecules possess reactive sites such as functional groups (–OH, –COOH, $–NH_3$, etc.) or unsaturation at carbon–carbon bonds (C=C or C≡C), which allow them to participate in polymerization reactions.

During polymerization, a large number of monomer molecules repeatedly link together through covalent bonding, producing long chains or three-dimensional network structures called polymers. Some of the vinyl monomers and their resultant polymers are listed in **Table 8.1**.

Table 8.1: Vinyl monomers and their corresponding polymers

Monomer	**Polymer Formed**
Ethene (C_2H_4)	Polyethylene (PE)
Propene (C_3H_6)	Polypropylene (PP)
Vinyl chloride (CH_2=CHCl)	Polyvinyl chloride (PVC)
Styrene (C_6H_5CH=CH_2)	Polystyrene (PS)
Tetrafluoroethene (CF_2=CF_2)	Polytetrafluoroethylene (PTFE, Teflon)
Methyl methacrylate	Polymethyl methacrylate (PMMA)
Acrylonitrile	Polyacrylonitrile (PAN)
Butadiene	Polybutadiene
Isoprene	Polyisoprene (Natural rubber)

The molecular structure of a monomer greatly influences the properties of the polymer formed. Characteristics such as mechanical strength, elasticity, heat resistance, and

chemical stability depend largely on the arrangement of atoms and functional groups present in the original monomer.

Polyfunctional monomers forming Condensation Polymers

Some polymers are produced from two similar or different monomers through condensation reactions, where small molecules such as water, alcohol, HCl, etc. are eliminated during polymer formation. A few polyfunctional monomers and their resultant polymers are listed in **Table 8.2**.

Table 8.2: Condensation polymers and their parent monomers:

Monomer	**Polymer Formed**
Hexamethylenediamine + Adipic acid	Nylon-6,6
Ethylene glycol + Terephthalic acid	Polyethylene terephthalate (PET)
Phenol + Formaldehyde	Bakelite
Hydroxyacids	Polyester
Hydroxyisocyanate	Polyurethane
Aminoacids	Polyamide (Protein)

8.4.2 Repeat Units

A repeat unit is the basic structural segment that appears repeatedly along the polymer chain. It is derived from the monomer after the polymerization reaction has occurred. Hence, the monomer is the original small molecule before reaction whereas the repeat unit is the structural fragment that actually constitutes the polymer backbone.

In addition polymerization, unsaturated bonds (e.g. double bond) present in the monomer open up and rearrange to form single bonds that connect repeating segments.

Table 8.3: Repeat units of few addition polymers:

Monomer (Name & Structure)	**Polymer (Name & Structure)**	**Repeat Unit Structure**
Ethene (Ethylene) $CH_2=CH_2$	Polyethylene (PE) $(–CH_2–CH_2–)_n$	$–CH_2–CH_2–$
Propene (Propylene) $CH_2=CH–CH_3$	Polypropylene (PP) $(–CH_2–CH(CH_3)–)_n$	$–CH_2–CH(CH_3)–$
Vinyl chloride $CH_2=CHCl$	Polyvinyl chloride (PVC) $(–CH_2–CHCl–)_n$	$–CH_2–CHCl–$
Styrene $C_6H_5–CH=CH_2$	Polystyrene (PS) $(–CH_2–CH(C_6H_5)–)_n$	$–CH_2–CH(C_6H_5)–$
Tetrafluoroethylene $CF_2=CF_2$	Polytetrafluoroethylene (PTFE) $(–CF_2–CF_2–)_n$	$–CF_2–CF_2–$
Acrylonitrile $CH_2=CH–CN$	Polyacrylonitrile (PAN) $(–CH_2–CH(CN)–)_n$	$–CH_2–CH(CN)–$
Vinyl acetate $CH_2=CH–OCOCH_3$	Polyvinyl acetate (PVAc) $(–CH_2–CH(OCOCH_3)–)_n$	$–CH_2–CH(OCOCH_3)–$
Methyl methacrylate	Polymethyl methacrylate (PMMA)	$–CH_2–$

$CH_2=C(CH_3)COOCH_3$	$(–CH_2–C(CH_3)(COOCH_3)–)_n$	$C(CH_3)(COOCH_3)–$
Chloroprene $CH_2=CCl–CH=CH_2$	Neoprene (Polychloroprene) $(–CH_2–CCl=CH–CH_2–)_n$	$–CH_2–CCl=CH–CH_2–$

In condensation polymerization, the repeat unit is formed after the removal of small molecules such as water, HCl, NH_3, methanol etc.

Table 8.4: Repeat units of few condensation polymers:

Monomer (Name & Structure)	**Polymer (Name & Structure)**	**Repeat Unit Structure**
Hexamethylenediamine + Adipic acid $H_2N–(CH_2)_6–NH_2$ + $HOOC–(CH_2)_4–COOH$	Nylon-6,6 $(–NH–(CH_2)_6–NH–CO–(CH_2)_4–CO–)_n$	$–NH–(CH_2)_6–NH–CO–(CH_2)_4–CO–$
Caprolactam cyclic amide	Nylon-6 $(–NH–(CH_2)_5–CO–)_n$	$–NH–(CH_2)_5–CO–$
Ethylene glycol + Terephthalic acid $HO–CH_2–CH_2–OH$ + $HOOC–C_6H_4–COOH$	Polyethylene terephthalate (PET) $(–O–CH_2–CH_2–O–CO–C_6H_4–CO–)_n$	$–O–CH_2–CH_2–O–CO–C_6H_4–CO–$
Phenol+ Formaldehyde C_6H_5OH + HCHO	Bakelite (Phenol-formaldehyde) cross-linked polymer	$–C_6H_4–CH_2–$
Urea + Formaldehyde NH_2CONH_2 + HCHO	Urea-formaldehyde resin network polymer	$–NH–CO–NH–CH_2–$
Melamine+ Formaldehyde $C_3N_3(NH_2)_3$ + HCHO	Melamine-formaldehyde resin cross-linked polymer	$–NH–CH_2–$

Note: Some polymers like Bakelite and Buna-S are copolymers or network polymers, so their structures are more complex than simple linear repeat units as shown in the **Table 8.4**.

8.5 DEGREE OF POLYMERISATION

The number of repeat units in a given polymer chain is called the degree of polymerization of the polymer. If the polymer chain contains 'n' number of repeat units with molecular weight of each repeat unit is m_s, the molecular weight of the polymer will be nm_s; n values can range from 1 to ∞.

$$\text{Degree of Polymerization} = \frac{\text{Molecular mass of polymer}}{\text{Molecular mass of repeat unit}}$$

In a polymer sample, the degree of polymerization varies over a wide range because polymerization reaction is a statistical process in which the chain growth occurs to a different extent in different chains. Thus, it would be necessary to define **average degree of polymerization ($\bar{X}_n$)** of a polymer in a sample.

$$\text{Average Degree of polymerization, } \bar{X}_n = \frac{\bar{M}_n}{m_s}$$

$$\text{Or,} \qquad \bar{X}_w = \frac{\bar{M}_w}{m_s}$$

where, $\bar{M}_n$ and $\bar{M}_w$ are the number average and weight average molecular weight of a polymer sample respectively. For example,

If average molecular mass of polymer = 42,00,000 g/mol
Molecular mass of repeat unit = 28 g/mol
Then,

$$\text{average degree of polymerization} = \frac{4200000}{28} = 150000$$

Degree of polymerisation is an important parameter that determines the molecular weight and many physical properties of polymers. A higher degree of polymerisation generally leads to increased mechanical strength, higher melting point, higher boiling point and greater viscosity of the polymers formed.
Polymers with low degrees of polymerization are often brittle or waxy, while those with high degree of polymerization exhibit toughness and elasticity. Control of the degree of polymerization (i.e. molecular weight) during polymer synthesis is therefore critical for tailoring materials for specific applications.

8.6 CLASSIFICATION OF POLYMERS

Polymers can be classified in various ways such as based on their origin, structure, behaviour on heating and mechanical properties.

8.6.1 Classification of Polymers based on their origin

Polymers can be classified based on their origin (source) into three main types:

(i) **Natural Polymers**: - Polymers that occur naturally in plants, animals, or microorganisms are called natural polymers or biopolymers. They are formed by biological processes. Examples are- Cellulose, Starch, Natural rubber, Proteins, Silk, Wool, etc.

(ii) **Semi-Synthetic Polymers**: - Polymers obtained by chemical modification of natural polymers to improve their properties are called semi-synthetic polymers. Examples are- Cellulose acetate, Cellulose nitrate (nitrocellulose), Rayon, Vulcanized rubber, etc.

(iii) **Synthetic Polymers**: - Polymers that are artificially synthesized from monomers through chemical reactions in laboratories or industries are called synthetic polymers. Examples are- Polyethylene (PE), Polypropylene (PP), Polyvinyl chloride (PVC), Polystyrene (PS), Nylon, Bakelite, etc.

8.6.2 Classification of Polymers based on structure

Based on structure of their molecular chain polymers can be classified into three main types:

(i) **Linear Polymers**: - In linear polymers the monomer units are joined end to end in single long chains. These chains are closely packed and have high density, tensile strength, and melting point. Examples are-

Polyethylene (PE); $-\left[\boldsymbol{CH_2{-}CH_2}\right]_n-$

Polypropylene (PP); $-\left[\boldsymbol{CH_2{-}CH(CH_3)}\right]_n-$

Polyvinyl chloride (PVC); $-\left[\boldsymbol{CH_2{-}CH(Cl)}\right]_n-$

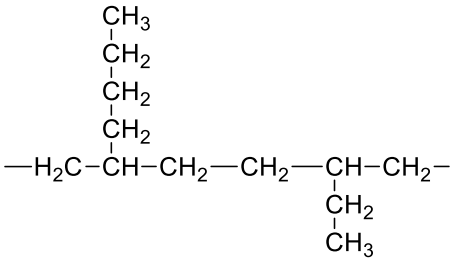
Polystyrene (PS); $-\left[\boldsymbol{CH_2{-}CH(C_6H_5)}\right]_n-$

Polyacrylonitrile (PAN); $-\left[\boldsymbol{CH_2{-}CH(CN)}\right]_n-$

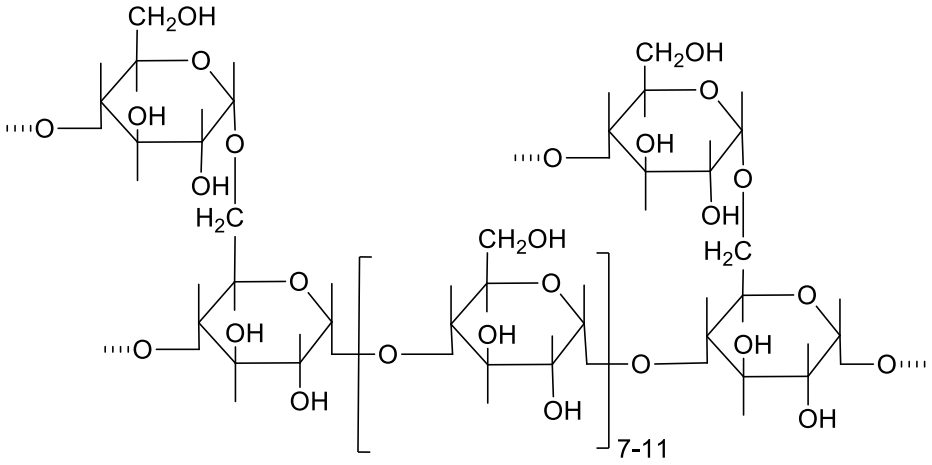
Nylon-6,6 ; $-\left[\boldsymbol{NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO}\right]_n-$

Polyethylene terephthalate; $-\left[\boldsymbol{O{-}CH_2{-}CH_2{-}O{-}CO{-}C_6H_4{-}CO}\right]_n-$
(PET / Terylene)

(ii) **Branched Polymers**: In branched polymers the main chain has side chains or branches of varying lengths. These polymers are less closely packed, have lower density, and are softer. For examples; Low-density polyethylene (LDPE), Glycogen, Amylopectin, etc.

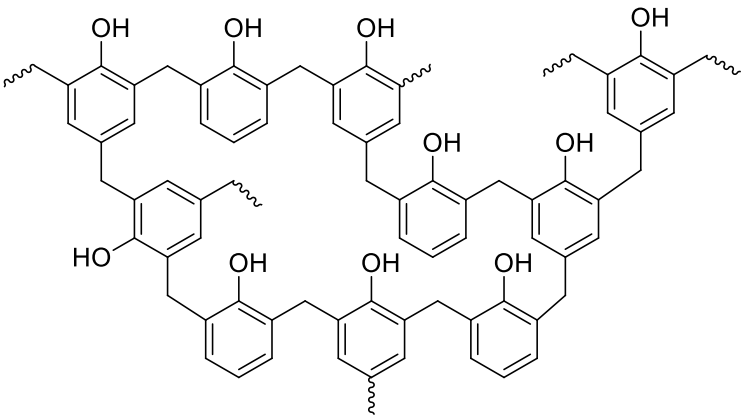


Structure of Low-density polyethylene (LDPE)

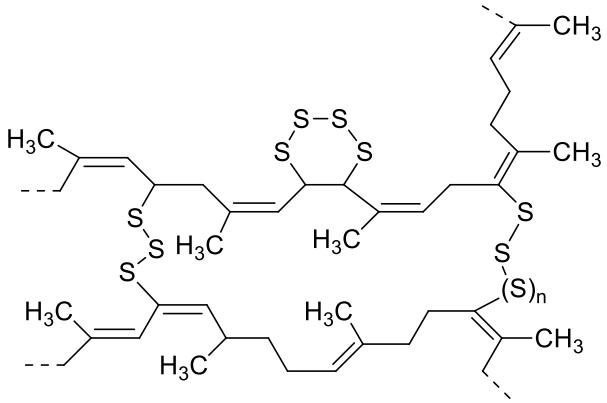


Structure of Glycogen

(iii) **Cross-linked (Network) Polymers**: The polymer chains are interconnected by covalent bonds forming a three-dimensional network resulting a Cross-linked (Network) Polymer. These polymers are hard, rigid, and insoluble. Examples are Bakelite, Melamine, Vulcanized rubber, Phenol-formaldehyde resin, etc.



Structure of Bakelite



Structure of Vulcanised rubber

8.6.3 Classification of Polymers based their behaviour on heating

Polymers can be classified based on their behavior on heating into two main types: thermoplastics and thermosetting polymers.

(i) **Thermoplastics:** Thermoplastics are polymers which soften when heated and harden when cooled. This process is reversible, so they can be reshaped and remoulded many times. They generally have linear or slightly branched structures. Examples are- Polyethylene (PE), Polypropylene (PP), Polyvinyl chloride (PVC), Polystyrene (PS), Nylon, etc.

(ii) **Thermosetting Polymers**: Polymers that harden permanently when heated due to formation of cross-linked three-dimensional networks are called thermosetting polymers. Once set, they cannot be remelted or reshaped. Examples are- Bakelite, Melamine-formaldehyde, Urea-formaldehyde, Epoxy resins, etc.

Table 8.5: **Distinction between Thermoplastics and Thermosetting Polymers**

Property	Thermoplastics	Thermosetting Polymers
Behavior on heating	Soften on heating and harden on cooling	Harden permanently when heated
Structure	Linear or branched	Highly cross-linked network
Recyclability	Can be remoulded and recycled	Cannot be remoulded
Examples	PE, PVC, PS, Nylon	Bakelite, Melamine, Epoxy

8.6.4 Classification of Polymers Based on Mechanical Properties

Polymers, whether natural or synthetic, can be classified into **plastics, elastomers, and fibres** on the basis of their mechanical properties and the strength of intermolecular forces present between their polymer chains. The nature of these intermolecular forces largely determines the flexibility, elasticity, and strength of the polymer materials.

(i) **Plastics:** Plastics are polymers that can be easily moulded into different shapes when heated and subjected to pressure. They were originally developed as substitutes for materials such as wood and metals due to their versatility and ease of processing.

In plastics, the intermolecular forces between polymer chains are moderate, allowing the materials to be either rigid or flexible depending on their molecular structure. Because of this property, plastics can be shaped, moulded, and fabricated into a wide range of useful products. Most plastics are synthetic in origin and are produced through chemical processes. Although some natural materials may show plastic-like behaviour, they are generally less durable and have more limited applications compared to synthetic plastics. Common examples of plastics include polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), and Bakelite.

(ii) **Elastomers (Rubbers)**: Elastomers, commonly known as rubbers, are polymers that exhibit high elasticity. These materials can be stretched considerably and return to their original shape when the applied force is removed. This property arises because elastomers possess weak intermolecular forces between polymer chains along with a small degree of cross-linking. The cross-links prevent the chains from sliding permanently past one another, allowing the material to regain its original form after

deformation. Due to this structure, elastomers are soft, flexible, and highly elastic, making them suitable for applications such as tyres, seals, and elastic bands. Examples of elastomers include natural rubber, Buna-S, Buna-N, and neoprene.

(iii) **Fibres**: Fibres are polymers that may be woven into long, thin, and strong filaments with high tensile strength. In these materials, the polymer chains are highly oriented and closely packed, resulting in strong intermolecular forces between them. Because of this arrangement, fibres exhibit high strength, stiffness, and resistance to stretching, making them ideal for the manufacture of textiles, ropes, and industrial materials. Fibres may be natural or synthetic. Natural fibres, such as cotton, wool, silk, and jute, are obtained from plant or animal sources. They are generally breathable, comfortable, and biodegradable. In contrast, synthetic fibres, such as polyester, nylon, and acrylic, are produced through chemical processes. These fibres typically possess greater strength, durability, and resistance to moisture, although they may be less breathable and may contribute to microplastic pollution in the environment.

8.6.5 Classification of Polymers Based on the Type of Monomers

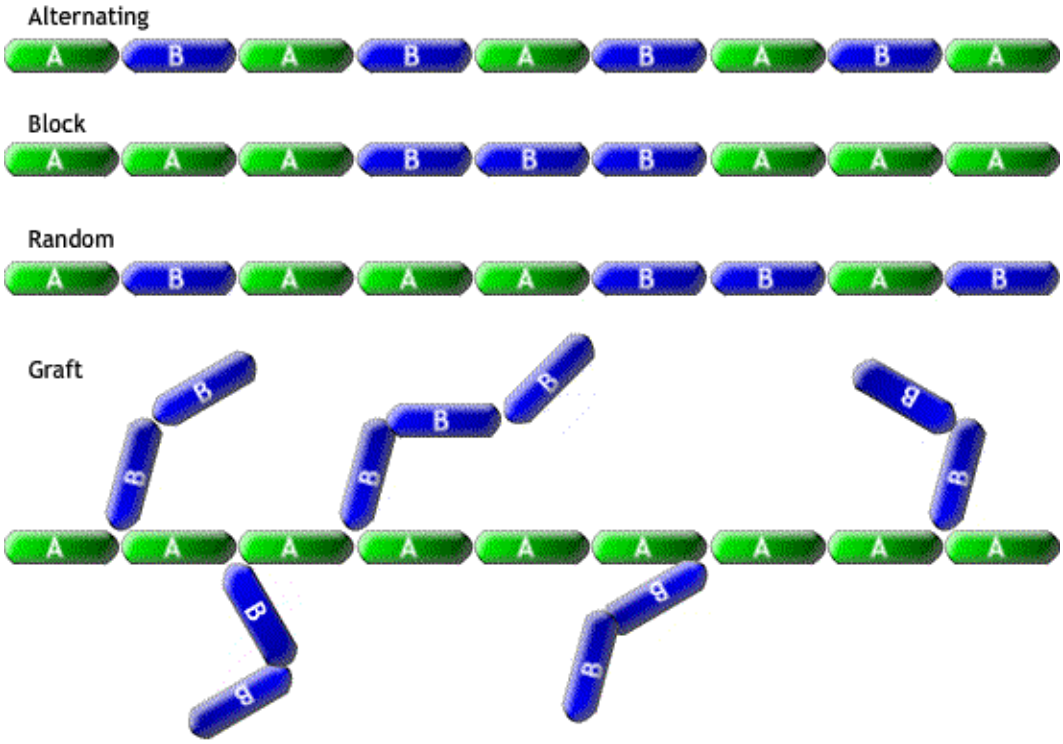
Polymers can also be classified according to the number and type of monomer units that participate in the polymerization process. Based on this criterion, polymers are broadly divided into homopolymers and copolymers.

(i) **Homopolymers**: A homopolymer is a polymer formed from only one type of monomer. During polymerization, the same monomer unit repeats many times to form a long chain macromolecule. Because the repeating unit is identical throughout the polymer chain, homopolymers usually have uniform chemical composition and structure.

Homopolymers are generally produced through addition polymerization or condensation polymerization, depending on the nature of the monomer involved. These polymers often exhibit consistent physical and chemical properties due to the presence of identical repeating units. Examples of homopolymers are- Polyethylene, Polypropylene, Polyvinyl chloride, Polystyrene. In these polymers, the repeating unit derived from a single monomer is repeated throughout the entire chain.

(ii) **Copolymers:** A copolymer is a polymer that contains two or more different types of monomers in its structure. In this case, different monomer molecules combine during polymerization to form a polymer chain containing more than one type of repeating unit.

The presence of different monomers allows chemists to modify and improve the properties of polymers, such as strength, flexibility, thermal stability, and chemical resistance. Copolymers can be arranged in several ways along the chain, such as random, alternating, block, or graft copolymers.



Common examples of copolymers are Nylon-6,6, Styrene-butadiene rubber (SBR), Dacron (Terylene or PET) etc.

8.7 SPECIALITY POLYMERS

Speciality polymers are advanced polymeric materials designed to exhibit specific and enhanced properties for particular applications. In recent years, several emerging areas of speciality polymers have gained significant attention due to their unique functionalities and wide technological applications. Some of the speciality polymers are discussed below.

(i) **Conducting Polymers:** Conducting polymers are a group of polymers that exhibit the unusual ability to conduct electrical current, a property not normally associated with traditional polymeric materials. This behaviour arises due to the presence of alternating single and double bonds along the polymer chain, which allows electrons to move more freely through the structure. These materials combine the lightweight and flexible nature of polymers with electrical properties similar to those of semiconductors. Typical examples include polyaniline, polypyrrole, and polythiophene. Because of these characteristics, conducting polymers are increasingly used in electronic components, sensors, rechargeable batteries, antistatic coatings, and flexible electronic devices.

(ii) **Stimuli-Responsive Polymers:** Stimuli-responsive polymers, often referred to as smart polymers, are materials capable of altering their physical or chemical characteristics when exposed to certain environmental changes. External factors such as temperature, pH, light, electric fields, or magnetic fields can trigger these changes. In response to such stimuli, the

polymer may undergo variations in solubility, volume, shape, or mechanical strength. These reversible transformations make these polymers particularly useful in advanced technologies. They are widely applied in controlled drug delivery systems, biosensors, self-healing materials, and adaptive coatings.

(iii) **Degradable Polymers:** Degradable polymers are specially designed polymeric materials that can break down into smaller, less complex molecules through natural processes. Their degradation may occur through chemical reactions such as hydrolysis, exposure to environmental factors like sunlight and oxygen, or through the action of microorganisms. The development of degradable polymers is important for addressing environmental concerns associated with long-lasting plastic waste. In addition to eco-friendly packaging, these polymers are also used in the biomedical field for applications such as surgical sutures, temporary implants, and drug delivery systems, where gradual degradation within the body is desirable.

(iv) **Hydrogels**: Hydrogels are cross-linked polymer networks that have a strong affinity for water and are capable of absorbing and retaining large quantities of it. Even after absorbing significant amounts of water, the network structure prevents the material from dissolving. This unique combination of high water content and structural stability gives hydrogels a soft and elastic nature that closely resembles biological tissues. Due to these properties, hydrogels have become highly valuable in medical and pharmaceutical applications. They are commonly used in contact lenses, wound dressings, drug delivery systems, and tissue engineering.

(v) **Functional Polymers:** Functional polymers are specially engineered macromolecules whose chemical structures contain particular functional groups or molecular segments that provide them with desired properties. By carefully selecting monomers and designing the polymer architecture, scientists can create materials that exhibit unique behaviours such as electrical conductivity, catalytic ability, responsiveness to external stimuli, and compatibility with biological systems. Because of these characteristics, functional polymers are often regarded as smart materials.

Functional polymers find wide applications in several advanced fields including electronics, energy systems, medicine, and environmental technology. They are used in biomedical materials such as contact lenses, dental resins, and artificial organs including synthetic skin, kidneys, and blood-related components. In addition, functional polymers are employed in fire-resistant materials, sensing devices, stimuli-responsive systems, separation membranes, and protective anticorrosive coatings. Their versatility and tunable properties make them important materials for modern technological and healthcare applications.

(vi) **Biomimetic Polymers**: Biomimetic polymers are synthetic materials developed to imitate the structures, functions, or behaviours found in natural biological systems. Nature provides numerous examples of highly efficient materials and processes, and biomimetic polymers attempt to replicate these features in artificial systems. By copying biological designs, researchers can create materials that interact more effectively with living tissues or perform complex functions. Such polymers are widely

investigated for use in biomedical engineering, artificial organs, tissue scaffolds, drug delivery technologies, and other medical applications where compatibility with biological environments is essential.

(vii) **Shape Memory Polymers**: Shape memory polymers belong to a class of intelligent materials that can recover their original form after being temporarily deformed. These polymers can be programmed into a specific temporary shape and will return to their initial configuration when exposed to an appropriate external trigger such as heat, light, or moisture. This property results from the unique arrangement of their molecular structure, which allows the material to store and release mechanical energy. Because of their light weight, flexibility, and ease of processing, shape memory polymers are increasingly used in medical devices, aerospace structures, deployable systems, and smart textiles.

W CHECK YOUR PROGRESS

Q1. How are polymers classified based on their origin?
Q2. What are linear polymers? Give one example.
Q3. Name two examples of speciality polymers.
Q4. Discuss how the molecular structure of monomers influences the physical and chemical properties of the resulting polymer.
Q5. Why do elastomers exhibit high elasticity? Explain on the basis of their molecular structure.
Q6. Differentiate between homopolymers and copolymers.
Q7. Describe the concept of speciality polymers and discuss any two of their modern applications.
Q8. Explain the importance of degradable polymers in addressing environmental challenges associated with plastic waste.

2 8.8 LET US SUM UP

- This unit presents the basic principles of polymer chemistry and highlights the significance of polymers in everyday life and industrial applications. Polymers are large molecules formed when many small molecules called monomers join together through chemical reactions.
- The repeating structural segments within a polymer chain are known as repeat units. The degree of polymerisation represents the number of repeat units in a polymer and strongly influences its molecular weight and physical properties.
- Polymers can be classified in several ways. According to their origin, they may be natural, semi-synthetic, or synthetic. Based on molecular structure, polymers are grouped as linear, branched, or cross-linked polymers. With respect to thermal behaviour, they are divided into thermoplastics, which soften on heating, and thermosetting polymers, which become permanently hard.
- Depending on mechanical properties, polymers are categorized as plastics, elastomers, and fibres. They can also be classified as homopolymers or copolymers depending on the number of monomers involved in their formation.

- The unit also introduces speciality polymers, which are advanced materials designed for specific functions. Examples include conducting polymers, stimuli-responsive polymers, degradable polymers, hydrogels, functional polymers, biomimetic polymers, and shape-memory polymers, many of which are used in modern technologies such as electronics, medicine, and environmental applications.

K 8.9 ANSWERS TO CHECK YOUR PROGRESS

Answers to Q1: Natural polymers, semi-synthetic polymers, and synthetic polymers.

Answers to Q2: Polymers in which monomer units are connected in long straight chains are called linear polymers; example: polyethylene

Answers to Q3: Conducting polymers, hydrogels, shape-memory polymers, or stimuli-responsive polymers are examples of speciality polymers.

Answers to Q4: A monomer's functional groups, side chains, and bonding arrangement affect the polymers flexibility, thermal stability, and intermolecular forces.

Answers to Q5: Elastomers exhibit high elasticity because their flexible polymer chains, weak intermolecular forces and limited cross-linking allows stretching but restore the original shape when the stress is removed.

Answers to Q6: Homopolymers contain one type of monomer, whereas copolymers contain two or more different monomers arranged as random, alternating, block, or graft structures.

Answers to Q7: Speciality polymers are materials designed with specific functional properties such as conductivity, responsiveness, or biodegradability. Two modern applications are biomedical applications and energy storage devices.

Answers to Q8: Degradable polymers help to address plastic-waste problems because they break down through hydrolysis, sunlight, or microbial action and reduce long-term accumulation of plastics in the environment.

O 8.10 FURTHER READING

- Billmeyer, F. W., Jr. (1984). *Textbook of polymer science* (3rd ed.). New York: John Wiley & Sons.
- Misra, G. S. (1993). *Introduction to polymer chemistry*. New Delhi: Wiley Eastern Limited.
- Gowariker, V. R., Viswanathan, N. V., & Sreedhar, J. (1986). *Polymer science*. New Delhi: New Age International Publishers.
- K.L. Kapoor. A Textbook of Physical Chemistry, Vol. *V*. Mc Graw Hill (India).

M 8.11 MODEL QUESTIONS

Q1. Define polymers and explain the difference between monomers and repeat units with suitable examples.
Q2. What is meant by the degree of polymerisation? Explain how it influences the physical properties of polymers.
Q3. Classify polymers based on their origin and give examples for each category.
Q4. Describe the different types of polymer chain structures. Explain linear, branched, and cross-linked polymers with examples.
Q5. Differentiate between thermoplastic and thermosetting polymers with respect to structure, behaviour on heating, and examples.
Q6. Explain the classification of polymers based on their mechanical properties as plastics, elastomers, and fibres, and mention one example of each.

UNIT 9: AVERAGE MOLECULAR WEIGHTS OF POLYMERS AND THEIR DETERMINATION

UNIT STRUCTURE

9.1 Learning Objectives
9.2 Introduction
9.3 Average molecular weight of polymers
  9.3.1 Number average molecular weight
  9.3.2 Weight average molecular weight
9.4 Polydispersity Index
9.5 Determination of molecular weight of polymers
  9.5.1 Viscometric method
  9.5.2 Osmometric method
  9.5.3 Light scattering method
  9.5.4 Size exclusion chromatography method
9.6 Let Us Sum Up
9.7 Answers to Check Your Progress
9.8 Further Reading
9.9 Model Questions

9.1 LEARNING OBJECTIVES

After studying this unit, you will be able to:

- explain the concept of average molecular weight in polymers.
- describe the concept of molecular weight distribution in polymer samples.
- define and derive the expressions for number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$).
- understand the concept and importance of the Polydispersity Index (PI) in polymer characterization.
- classify the methods used for molecular weight determination of polymers into absolute and relative methods.
- describe the principles and procedures of Viscometric, Osmometric, Light Scattering, and Size Exclusion Chromatography methods.

9.2 INTRODUCTION

Polymers are macromolecules formed by the repeated linkage of small units known as monomers. Unlike ordinary small molecules, polymer molecules do not all have the same size or molecular mass. Because, during the polymerization process, chains grow to different lengths depending on reaction conditions and termination steps. As a result, a polymer sample usually contains a mixture of molecules with varying chain lengths and therefore different molecular masses.

Because of this variation, it is not possible to assign a single, fixed molecular mass to a polymer. Instead, polymer chemists describe the molecular mass in terms of **average**

molecular weights. These averages represent the overall molecular characteristics of the polymer sample. The distribution of molecular masses present in a polymer is referred to as the **molecular weight distribution**.

Determining the molecular mass of polymers is very important because it strongly influences many of their physical and mechanical properties such as strength, viscosity, elasticity, melting behaviour, and processing characteristics. In practice, different types of averages are used to represent polymer molecular mass. These averages provide useful information about the size distribution of polymer chains and help in understanding the behaviour and applications of polymeric materials.

9.3 AVERAGE MOLECULAR WEIGHT OF POLYMERS

Unlike small molecules, polymers do not possess a single, definite molecular mass. A typical polymer sample contains a large number of macromolecules that have the same chemical composition but differ in the length of their chains. Because the chain length varies from molecule to molecule, the molecular masses of the individual polymer molecules are also different. As a result, a polymer sample is considered **polydisperse**, meaning it consists of molecules with a distribution of molecular weights rather than a single value.

For this reason, it is necessary to express the molecular mass of polymers in terms of **average molecular weights** instead of a single molecular mass. Several averaging methods are used in polymer chemistry, but the two most widely used and experimentally measurable averages are the number-average molecular weight and the weight-average molecular weight.

9.3.1 Number Average Molecular Weight ($\bar{M}_n$)

The **number-average molecular weight ($\bar{M}_n$)** is calculated by considering the number of molecules present at each molecular weight. In this method, each polymer molecule contributes equally regardless of its size.

The number average molecular weight is defined as the total mass of the dispersed material divided by the total number of molecules present. If n_1, n_2, ……. represent the number of molecules having masses m_1, m_2, …….; then-

$$\bar{M}_n = \frac{n_1 m_1 + n_2 m_2 + n_3 m_3 + \ldots\ldots\ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots\ldots\ldots} = \frac{\sum n_i m_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i}$$

Number average molecular weight can be correlative with polymer colligative properties, e.g. Osmotic pressure. Techniques such as osmometry and end-group analysis are commonly used to determine the number average molecular weight.

9.3.2 Weight Average Molecular Weight ($\bar{M}_w$)

The **weight-average molecular weight** takes into account the relative mass contribution of each polymer molecule in the sample. The Weight Average Molecular Weight takes into account that the larger molecules contribute a much higher amount

of the molecular mass of the polymer sample. Thus, in this case, larger and heavier molecules have a greater influence on the average value than smaller molecules. For a polymer sample having $n_1, n_2, \ldots\ldots$ number of molecules of masses $m_1, m_2, \ldots\ldots$

Total weight of the polymer sample $= W = \sum n_i m_i$

Weight of the fraction-1 = $w_1 = n_1 m_1$

Weight fraction of the fraction-1= $\frac{n_1 m_1}{\sum n_i m_i}$

Molecular weight contribution by the fraction-1= $\frac{n_1 m_1}{\sum n_i m_i} m_1 = \frac{n_1 {m_1}^2}{\sum n_i m_i}$

The weight Average Molecular Weight of the whole sample is given by-

$$\bar{M}_w = \frac{n_1 {m_1}^2}{\sum n_i m_i} + \frac{n_2 {m_2}^2}{\sum n_i m_i} + \frac{n_3 {m_3}^2}{\sum n_i m_i} + \ldots\ldots\ldots = \frac{\sum n_i {m_i}^2}{\sum n_i m_i} = \frac{\sum w_i m_i}{\sum w_i}$$

$$\bar{M}_w = \frac{n_1 {m_1}^2 + n_2 {m_2}^2 + n_3 {m_3}^2 + n_3 {m_3}^2 + \ldots\ldots\ldots}{\sum n_i m_i} = \frac{\sum n_i {m_i}^2}{\sum n_i m_i}$$

Weight-average molecular weight may be correlated with properties such as melt viscosity. Experimental methods such as light scattering and ultracentrifugation are often used to determine the weight-average molecular weight.

Note: Another type of average molecular weight used in polymer science is the **z-average molecular weight** ($\bar{M}_z$). It gives greater emphasis to the heavier polymer molecules present in a sample and is mathematically expressed as:

$$\bar{M}_z = \frac{n_1 {m_1}^3}{\sum n_i {m_i}^2} + \frac{n_2 {m_2}^3}{\sum n_i {m_i}^2} + \frac{n_3 {m_3}^3}{\sum n_i {m_i}^2} + \ldots\ldots\ldots = \frac{\sum n_i {m_i}^3}{\sum n_i {m_i}^2} = \frac{\sum w_i {m_i}^2}{\sum w_i m_i}$$

where n_i represents the number of molecules having molecular mass m_i, and w_i represents the weight of fraction of molecules with mass m_i.
The **z-average molecular weight** is particularly useful because it is strongly influenced by the presence of high-molecular-weight chains. Therefore, it is often related to mechanical properties of polymers, such as **toughness and strength**, which depend significantly on the larger polymer molecules present in the material.

Measurement of viscosity of dilute solutions of a polymer sample gives **viscosity average molecular weight** ($\bar{M}_{vis}$) which is nearly equal to weight average molecular weight; i.e. $\bar{M}_{vis} \approx \bar{M}_w$. For most polydisperse polymer sample $\bar{M}_z > \bar{M}_w > \bar{M}_n$ as shown in the distribution of molecular weight in a typical polymer sample (**Figure 9.1**).

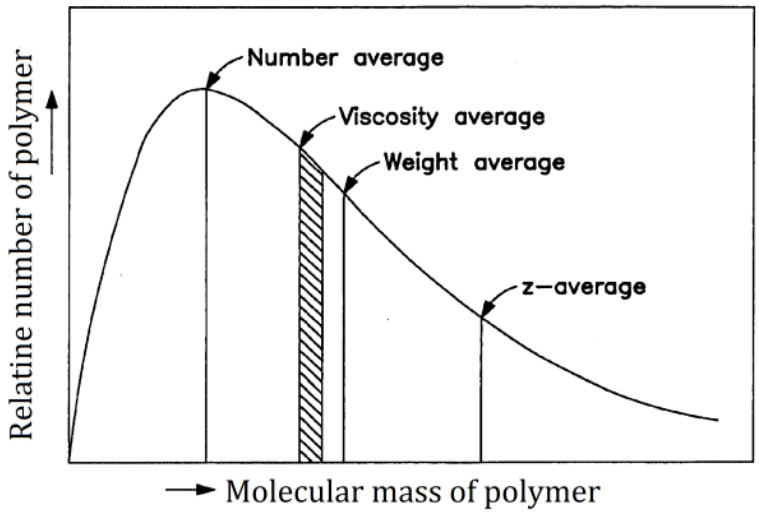


Figure 9.1: Distribution of molecular weight in a typical polymer sample

9.4 POLYDISPERSITY INDEX

Since heavier molecules contribute more strongly in the weight-average calculation, the value of weight average molecular weight is almost always higher than the number average molecular weight (i.e. $\bar{M}_w \geq \bar{M}_n$) for most polymer samples. The ratio of weight average molecular weight to the number average molecular weight is called polydispersity index.

Polydispersity index $(PI) = \frac{\bar{M}_w}{\bar{M}_n} \geq 1$

If all the polymer chains are equal in length (i.e. each molecule has same molecular weight) then the sample will consider as perfectly homogeneous having PI = 1. Polydispersity index is a very important parameter and it gives an idea of lowest and highest molecular weight species as well as the distribution pattern of the intermediate molecular weight species. A value close to 1 indicates a narrow distribution of molecular weights, whereas larger values indicate a broader distribution (**Figure 9.2**). Various processing properties of polymers are affected by the molecular weight distribution. For example, the melt viscosity, surface gloss, toughness and optical properties of polyolefins decrease when molecular weight distribution increases.

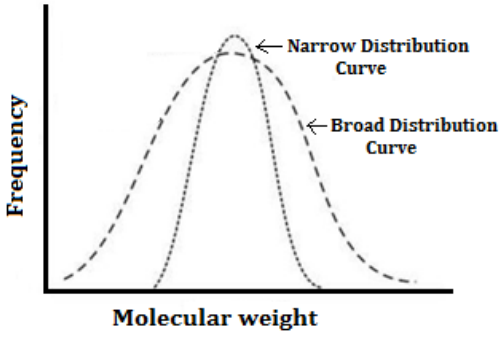


Figure 9.2: Typical molecular weight distribution curves for two polymers samples

9.5 DETERMINATION OF MOLECULAR WEIGHT OF POLYMERS

The molecular weight of polymers can be determined using several experimental techniques. These methods are broadly classified into absolute methods and relative methods.

1. Absolute Methods:

Absolute (or primary) methods directly determine the molecular weight of polymers without the need for calibration using standard samples. Absolute methods are time consuming, often require expensive apparatus and difficult to carry out. Some important absolute techniques are listed below:

(a) **Methods Based on Colligative Properties:**

These techniques depend on the effect of dissolved polymer molecules on the properties of the solvent. They are particularly useful for determining the number-average molecular weight ($\bar{M}_n$) of polymer sample. The common approaches include:

(i) **Osmometry:** Either Vapour Phase Osmometry or Membrane Osmometry

(ii) **Cryoscopy:** In this technique, molecular weight of polymer samples is determined by measuring the depression of freezing point of the solvent.

(iii) **Ebulliometry:** Analogous to Cryoscopy, this method is based on the elevation of boiling point of the solvent.

(b) End-Group Analysis:

In this technique, the number of terminal functional groups present in polymer chains is measured. From this information, the number average molecular weight ($\bar{M}_n$) can be calculated.

(c) Light Scattering Method:

This method measures the intensity of light scattered by polymer molecules in solution and is commonly used to determine the weight-average molecular weight ($\bar{M}_w$).

(d) Mass Spectrometry:

Advanced mass spectrometric techniques can be used to determine the molecular weight ($\bar{M}_w$) of relatively low-molecular-weight polymers with high accuracy.

(e) **Ultra-centrifugation**:

High-speed centrifugation is used to study the sedimentation behavior of polymer molecules. Two important approaches are Sedimentation Velocity Method and Sedimentation Equilibrium Method. This technique primarily used to obtain weight-average molecular weight ($\bar{M}_w$) or the z-average molecular weight ($\bar{M}_z$) of polymers.

2. Relative Methods

Relative methods estimate molecular weight by comparing the properties of polymer solutions with standard of known molecular weight. Thus, the relative or secondary methods give the comparisons between the molecular weights of different polymers and must be calibrated by reference that has been studied by one of the absolute/primary methods. They are fast, simple and accurate. The examples of such methods are viscometry and Gel Permeation Chromatography.

In **viscometry method**, viscosity of dilute solutions of a polymer sample are determine and from which the viscosity-average molecular weight ($\bar{M}_{vis}$) can be obtained. For many polymers, this value is close to the weight-average molecular weight, i.e. $\bar{M}_{vis} \approx \bar{M}_w$.

Gel Permeation Chromatography (GPC) is a **fractionation method** that separate polymer molecules according to their size or molecular weight and provide information about the complete molecular weight distribution.
Gel Permeation Chromatography is also known as **size-exclusion chromatography**. This technique separates polymer molecules based on their hydrodynamic volume (size) rather than absolute molecular weight, requiring calibration with known standards (usually polystyrene of known molecular weight) to determine molecular weight distributions. It provides detailed information about the entire molecular weight distribution of the polymer sample. Hence, both $\bar{M}_n$ & $\bar{M}_w$ are obtainable from this method.
In this unit, we will discuss the Membrane Osmometric, Viscometric, Light scattering and size exclusion chromatography methods only.

9.5.1 Viscometric Method

It is simple method for the determination of molecular weight of polymers. The presence of macromolecules raises the viscosity of the solvent due to their long chains, large hydrodynamic volumes, and complex structures which create significant internal friction and restrict the flow by large molecules.

If η be the viscosity of the polymer solution,η_0 is the viscosity of the pure solvent, t be the time required to flow for a fixed volume of solution from mark '*a*' to '*b*' in the viscometer (**Figure 9.3**) and t_0 be time required to flow by the same volume of solvent, then,

$$\frac{\eta}{\eta_0} = \frac{t}{t_0}$$

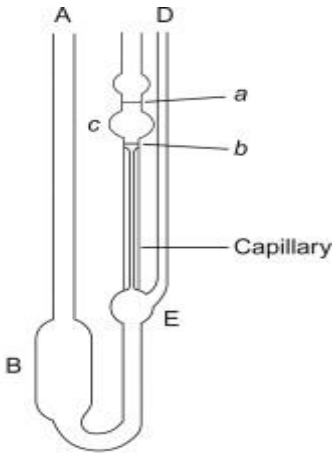


Figure 9.3: Ubbelohde Viscometer

International Union of Pure and Applied Chemistry (IUPAC) suggested the following terminology for viscosities of solutions;

(i) Relative viscosity: $\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$

(ii) Specific viscosity: $\eta_{sp} = \eta_{rel} - 1 = \frac{\eta}{\eta_0} - 1 = \frac{t-t_0}{t_0}$

(iii) Reduced viscosity: $\eta_{red} = \frac{\eta_{sp}}{c} = \frac{\eta_{rel}-1}{c}$

where, c is the concentration of the polymer solution in g/100ml.

(iv) Intrinsic viscosity: $[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right)$

According to Staundinger, the intrinsic viscosity (or, viscosity number or Staudinger Index) of a polymer solution is related to its molecular weight by the following equation, known as Mark-Honwink equation or Staundinger equation.

$$[\eta] = K(\bar{M}_{vis})^a \qquad (9.1)$$

Where, '*K*' and '*a*' are constants for a specific polymer in a specific solvent. Thus, knowing the values of '*a*' and '*K*', the viscosity average molar mass of the unknown polymer sample can be determined from intrinsic viscosity measurements using equation (9.1).

Determination of intrinsic viscosity $[\eta]$:

A series of solutions of different concentrations of the unknown polymer sample are prepared in a suitable solvent. For each solution reduced viscosity, η_{red} (i.e. $\frac{\eta_{sp}}{c}$) is to be calculated and is plotted against concentration as shown in **Figure 9.4**, using Huggins equation (9.2) . The intercept of the η_{red} vs concentration, 'c' plot gives the value of intrinsic viscosity $[\eta]$.

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \qquad (9.2)$$

k_H = Huggins coefficient (a constant relating to the hydrodynamic interaction of polymer chains)

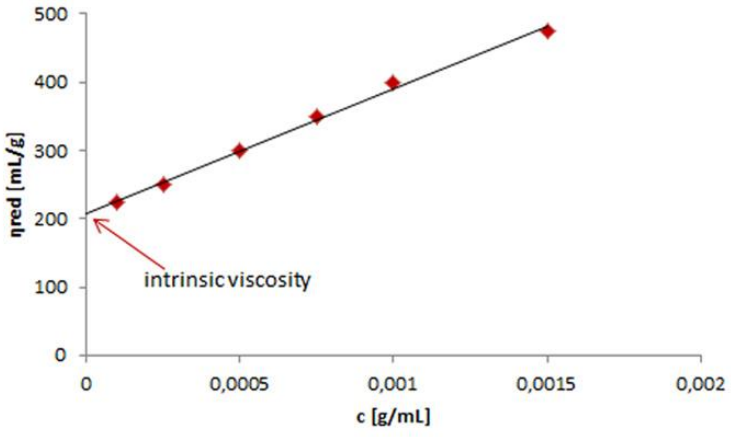


Figure 9.4: A typical plot of η_{red} against concentration for computing intrinsic viscosity

Determination of *K* and *a*: On taking logarithms of equation (9.1), we have

$$log[\eta] = log\, K + a\, log\, M \qquad (9.3)$$

The value of '*K*' and '*a*' can be determined by measuring the intrinsic viscosity of a series of sample of a given polymer, the molecular weight of which is known from some of the methods discussed above. The value of $log[\eta]$ are plotted against $log\, M$, which according to equation (9.3) will be a straight line. The intercept will be equal to $log\, K$ and the slope will be equal to '*a*'.

9.5.2 Membrane Osmometric Method

The membrane osmometer apparatus basically measures osmotic pressure of polymer solutions of known concentration, say 1 g dl^{-1}. The van't Hoff law forms the basis for the determination of number average molecular weight, $\bar{M}_n$ of a polymer sample. Following equation gives the relationship between osmotic pressure, π of polymer solution to $\bar{M}_n$ of the polymer.

$$\frac{\pi}{c} = RT\left[\frac{1}{M} + B_2 c\right] \qquad (9.4)$$

Where, π is the osmotic pressure of the polymer solution of concentration '*c'* and 'B_2' is the second virial coefficient.

Derivation of the equation:

If π is the osmotic pressure of a solution in which x_1 is the mole fraction of the solvent, then the condition for equilibrium for the chemical potential of the solvent on both side of the membrane gives-

$$RT\, ln\, \gamma_1\, x_1 + \pi \bar{V}_1 = 0 \qquad (9.5)$$

Where, $\gamma_1$is the activity coefficient of the solvent and $\bar{V}_1$ is the partial molar volume of the solvent in the solution. In case of very dilute solution, $\gamma_1 \rightarrow 1$ and $\bar{V}_1 \rightarrow {V_1}^0$, where ${V_1}^0$ is the molar volume of the pure solvent. If x_2 be the mole fraction of the polymer then, for dilute solution-

$$\pi {V_1}^0 = RT\, ln\, x_1$$
$$\pi {V_1}^0 = RT\, ln(1 - x_2)$$
$$\pi {V_1}^0 = RT(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \ldots\ldots\ldots) \qquad (9.6)$$

For polymer solution of concentration '*c'*, x_2 is given by-

$$x_2 = \frac{c/M}{1/{V_1}^0 + c/M} \approx \frac{{V_1}^0 c}{M} \quad \text{(For dilute solution)}$$

Where, M is the molar mass of the polymer.

Substituting the value of x_2 in equation (9.5) we have,

$$\frac{\pi}{c} = \frac{RT}{M}\left[1 + \frac{1}{2}\left(\frac{{V_1}^0}{M}\right)c + \frac{1}{3}\left(\frac{{V_1}^0}{M}\right)^2 c^2 + \ldots\ldots\ldots)\right]$$

$$\frac{\pi}{c} = \frac{RT}{M}[1 + A_2c + A_3c^2 + \ldots\ldots\ldots)] \qquad (9.7)$$

This equation is often written in the form-

$$\frac{\pi}{c} = RT\left[\frac{1}{M} + B_2c + B_3c^2 + \ldots\ldots\ldots)\right] \qquad (9.8)$$

Where, B_2, B_3, ... are the second, third, etc., virial coefficients. The equation (9.8) is the **van't Hoff equation**. The quantity $\frac{\pi}{c}$ is called **reduced osmotic pressure**. Since the higher virial coefficients are very small and we can neglect the third term.

$$\frac{\pi}{c} = RT\left[\frac{1}{M} + B_2c\right] \qquad (9.4)$$

$$\lim_{c\to 0}\left(\frac{\pi}{c}\right) = \frac{RT}{M}$$

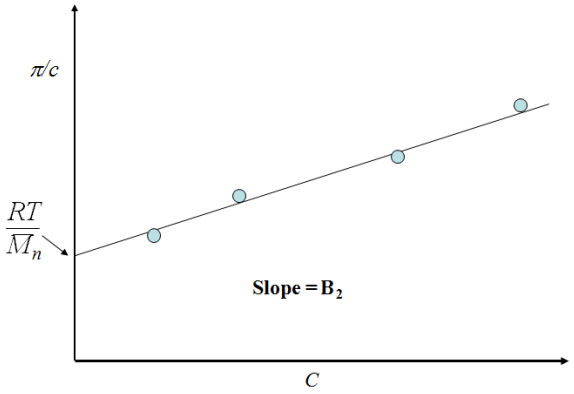


Figure 9.5: A typical plot of $\frac{\pi}{c}$ versus concentration for computing molar mass.

A plot of $\frac{\pi}{c}$ versus '*c*', extrapolated to $= 0$, gives a straight line with intercept $\frac{RT}{M}$; so, from the intercept molar mass of the polymer can be calculated.

9.5.3 Light Scattering Method

The light scattering method is an important absolute technique used to determine the weight-average molecular weight $(\bar{M}_w)$ of polymers in dilute solution. The method is based on the scattering of light when it passes through a solution containing polymer molecules.

Principle:

When a beam of monochromatic light passes through a polymer solution, the polymer molecules scatter the incident light in different directions. This scattering occurs because polymer molecules have a different refractive index compared with the surrounding solvent. The intensity of scattered light depends on:

(i) Molecular weight of the polymer

(ii) Concentration of the polymer solution

(iii) Wavelength of incident light

(iv) Difference in refractive index between solvent and solution

(v) Angle at which the scattered light is observed

Larger polymer molecules scatter **more intense light** than smaller molecules. By measuring the intensity of scattered light at different polymer concentrations and angles, the **molecular weight of the polymer** can be calculated.

For dilute polymer solutions, the intensity of scattered light is described by the **Rayleigh scattering equation**:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} + 2B_2c + 3B_3c^2 + \cdots$$

where:

c = concentration of polymer solution (gml^{-1})

R_θ = Rayleigh ratio or excess scattering intensity at angle θ

$\bar{M}_w$ = weight-average molecular weight of the polymer

$B_2 \; and \; B_3$ = second and third virial coefficient

K = optical constant depending on wavelength and refractive index

The optical constant K is given by-

$$K = \frac{4\pi^2 n_0^2}{N_A \lambda^4}\left(\frac{dn}{dc}\right)^2$$

where:

n_0= refractive index of solvent

N_A= Avogadro's number

λ = wavelength of incident light in vacuum

$\frac{dn}{dc}$ = refractive index increment of solution, i.e., the change of refractive index with concentration.

The Rayleigh ratio R_θ is given by-

$$R_\theta = \frac{i_\theta r^2}{I_0 V}$$

Where, i_θ is the intensity of scattered light per unit volume V of the scattering material which is observed at a distance r and at an angle θ with reference to the incident beam, and I_0 is the intensity of the incident beam.

For **very dilute solutions**, higher order terms become negligible and the equation simplifies to

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} + 2B_2c$$

This is called the **Debye equation.** A plot of $\frac{Kc}{R_\theta}$ versus concentration c (known as a **Debye plot**) is constructed. Extrapolation of the plot to **zero concentration** gives the intercept $1/\bar{M}_w$, from which the **weight-average molecular weight** is obtained.

At zero concentration:

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{\bar{M}_w}$$

Thus,

$$\bar{M}_w = \frac{1}{\text{intercept}}$$

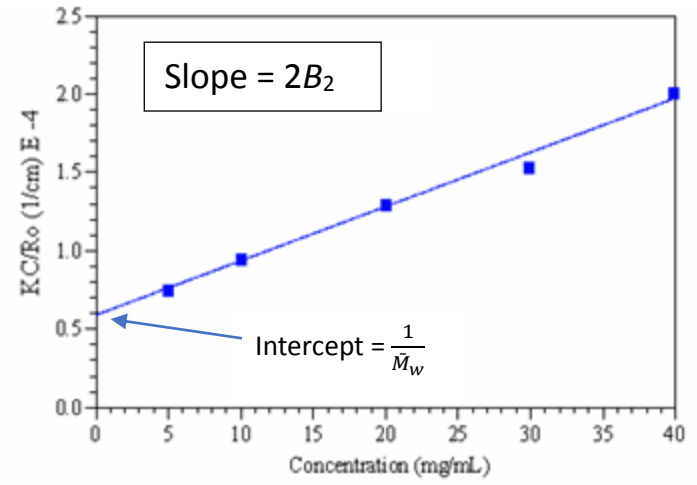


Figure 9.6: A typical Debye Plot

Experimental Procedure:

A dilute solution of the polymer is prepared in a suitable solvent. A beam of monochromatic light (usually from a laser source) is passed through the solution. The intensity of scattered light, i_θ is measured at different angles using a light scattering photometer. Measurements are taken for several polymer concentrations. Thus, the Rayleigh ratio R_θ is calculated. Then, refractive index of solvent and solutions are measured from which the optical constant K is computed. A plot of Kc/R_θversus concentration c (known as a Debye plot) is constructed. The extrapolation of which to zero concentration gives the intercept $1/\bar{M}_w$, from which the weight-average molecular weight is obtained.

Angular Dependence (Particle Size Effect)

When monochromatic light passes through a dilute polymer solution, the polymer molecules scatter the light. For very small molecules, scattering is independent of the

observation angle. However, for large polymer molecules, different parts of the molecule scatter light with different phases, causing interference of scattered waves (**Figure 9.7**).

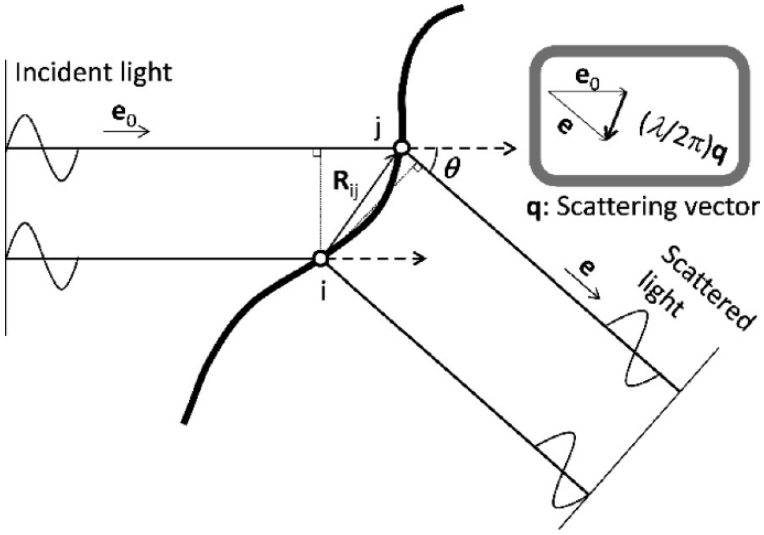


Figure 9.7: Light scattering by different parts of a large polymer molecule and the scattered light cause interference

Therefore, the intensity of scattered beam varies with the scattering angle θ. By analysing this angular dependence, both the weight-average molecular weight and the molecular size of the polymer can be determined.

For bigger polymer molecules R_θ varies with the scattering angle θ and the Debye equation gets modified as-

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w P(\theta)} + 2B_2 c$$

Where,

$$\frac{1}{P(\theta)} = 1 + \left(\frac{16\pi^2}{3\lambda^2}\right) < R_g^2 > \sin^2\left(\frac{\theta}{2}\right)$$

$< R_g^2 >$ = mean square radius of gyration of polymer molecule

$P(\theta)$= particle scattering factor

Therefore, the modified Debye equation can be written in three forms as-

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{\bar{M}_w} + \left(\frac{16\pi^2}{3\lambda^2 \bar{M}_w}\right) < R_g^2 > \sin^2\left(\frac{\theta}{2}\right)$$

$$\left(\frac{Kc}{R_\theta}\right)_{\theta\to 0} = \frac{1}{\bar{M}_w} + 2Bc$$

$$\left(\frac{Kc}{R_\theta}\right)_{c,\theta\to 0} = \frac{1}{\bar{M}_w}$$

In Zimm's plot, he adopted a double extrapolation of the plot of $\frac{Kc}{R_\theta}$ versus $\sin^2\left(\frac{\theta}{2}\right) + kc$ (where, k is an arbitrary constant) to both zero angle of scattering ($\theta = 0$) and zero concentration ($c = 0$), when $P(\theta) = 1$ and $Bc = 0$. The ordinate intercept will then give the value of $\frac{1}{\bar{M}_w}$ as shown in the **Figure 9.8**.

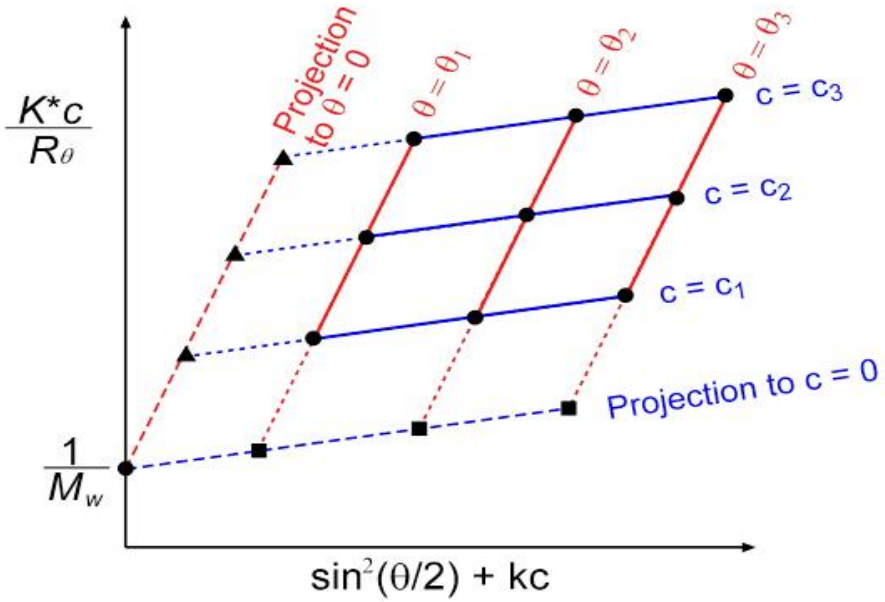


Figure 9.8: A typical Zimm plot

9.5.4 Size Exclusion Chromatography Method

Size Exclusion Chromatography (SEC) is an important chromatographic technique used to determine the molecular weight distribution and molecular weight $(\bar{M}_w \; and \; \bar{M}_w)$ and polydispersity index of polymers. It separates polymer molecules according to their hydrodynamic volume (molecular size) rather than chemical interactions with the stationary phase.

Two types of Size Exclusion Chromatography (SEC) are-

(i) **Gel Permeation Chromatography (GPC)**: This technique uses hydrophobic gel (e.g., polystyrene-divinylbenzene) and **organic solvents** to analyze synthetic polymers that are soluble in organic solvents.

(ii) **Gel Filtration Chromatography (GFC)**: This technique uses hydrophilic gel (e.g., dextran, agarose) and **aqueous solvents** (buffers) to separate water-soluble molecules, such as proteins or biological polymers.

Both GPC and GFC uses same principle. The separation in SEC is based on the ability of polymer molecules to penetrate into the pores of a porous stationary phase. The column is packed with porous polymer or silica beads having pores of different sizes. Large molecules cannot enter the pores travel through the void spaces between beads and therefore pass quickly through the column. Medium-sized molecules enter some pores and travel more slowly. Small molecules penetrate most pores and therefore

take the longest time to elute. Thus, elution order is from largest molecules to smallest molecules as shown in **Figure 9.9**.

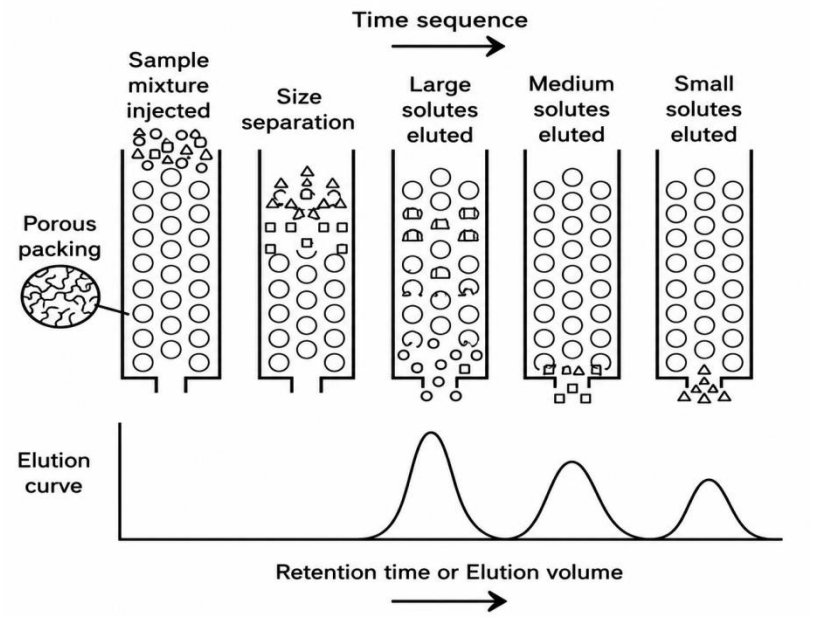


Figure 9.9: Mechanism of size exclusion chromatography

The following volume parameters are used to describe SEC behaviour.

(i) **Void Volume (V_o):** The volume outside the gel particles where large molecules travel is called void volume.

(ii) **Pore volume (V_p):** Volume inside the pores/gel of the stationary phase is called pore volume.

(iii) **Total Permeation Volume (V_t):** Total volume inside the column is the total permeation volume. Therefore -

$$V_t = V_o + V_p$$

(iv) **Elution Volume (V_e):** The volume of mobile phase required to elute a solute from the column is called elution volume.

(v) **Distribution Coefficient:** The fraction of pore volume accessible to a molecule is represented by the distribution coefficient K_d.

$$K_d = \frac{V_e - V_o}{V_t - V_o}$$

Values of K_d range between 0 and 1. $K_d = 0$ for very large molecules which are completely excluded from the pores. $K_d = 1$ for very small molecule which fully enters the pores.

Large molecules that cannot enter pores elute out of the column when a solvent volume V_o elutes out after the injection of the sample. The smallest molecules which permeate the maximum volume of the pores elute out at a volume of $V_t = V_o + V_p$. The intermediate size molecules elute between V_o and $V_t = V_o + V_p$. Hence the elution volume directly gives an estimation of the molecular size. However, we need not to compute the values of V_o and V_p. In polymer analysis, a calibration curve is prepared using standard polymers of known molecular weight. A set of standard polymers with known molecular weights (usually narrow molecular weight distribution) is first

analyzed under the same chromatographic conditions. After preparin solutions of standard polymers having known molecular weights, we have to inject each standard separately into the SEC column and measure the elution volume **(V_e)** for each standard. Then a graph is plotted between $\log M$ versus elution volume, V_e. The plot of log M vs. V_e is typically **linear (Figure 9.10)** because it follows the following relationship.

$$\log M = a - bV_e$$

Where,

M= molecular weight of polymer

V_e= elution volume

a and b = constants obtained from the calibration line.

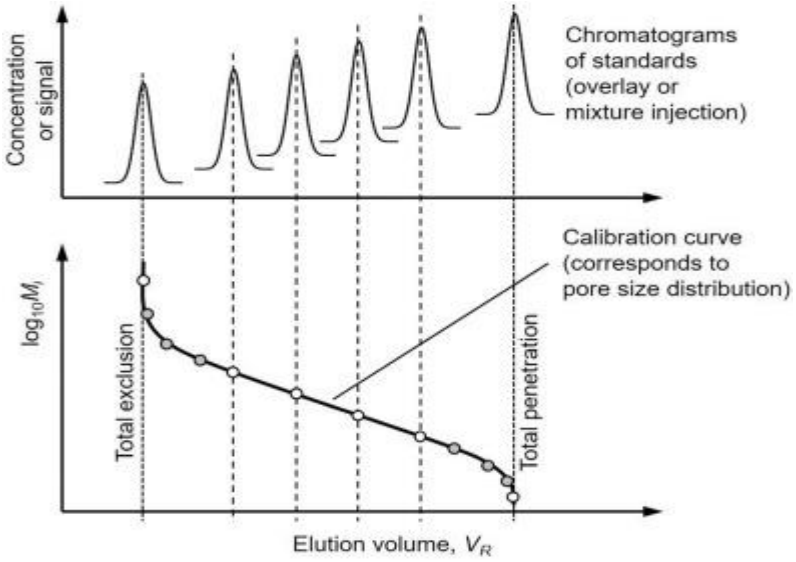


Figure 9.10: A typical calibration curve in SEC

After constructing the calibration curve, the **unknown polymer sample** is introduced into the column of SEC. Inside the column, the polymer molecules are separated into several fractions according to their molecular size. As these fractions elute from the column, they appear as individual peaks in the chromatogram. The elution volume $V_e$corresponding to each peak is carefully measured.

To determine the molecular weight of a particular fraction, its elution volume $V_e$is first located on the **x-axis** of the calibration curve. From this point, a vertical line is drawn until it intersects the calibration curve. Then a horizontal line is extended from the point of intersection to the **y-axis**, where the corresponding value of $\log M$is obtained. By converting this value to M, the molecular weight of the polymer fraction can be determined. Consequently, molecular weight distribution of the polymer sample is calculated. This allows determination of number average molecular weight, Weight average molecular weight and polydispersity index by using the following equations.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$PI = \frac{\bar{M}_w}{\bar{M}_n}$$

W CHECK YOUR PROGRESS

Q1. Why polymer samples do not have a single definite molecular mass.
Q2. Explain the concept of number-average molecular weight ($\bar{M}_n$). How it is mathematically expressed?
Q3. Describe the weight-average molecular weight ($\bar{M}_w$). How does it differ from number-average molecular weight?
Q4. What is the formula of z-average molecular weight ($\bar{M}_z$)?
Q5. In a sample there are 50 polymer molecules of molecular weight 100, 200 molecules molecular weight 1000 and 100 polymer molecules of molecular weight 10000. Calculate number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$).
Q6. Two polymers of molecular weight 10000 and 100000 are mixed together in equal parts by weight, determine the number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$)
Q7. Define the polydispersity index (PI). What information about a polymer sample can be obtained from its PI value?
Q8. Classify the different methods used for determining the molecular weight of polymers with examples.
Q9. Explain the basic principle of the viscometric method for determining the molecular weight of polymers. What is intrinsic viscosity and how is it related to molecular weight?

2 9.6 LET US SUM UP

- Unlike small molecules, polymer chains are not uniform in length, and therefore a polymer sample contains molecules with different molecular masses. Because of this variation, a single molecular weight cannot represent the entire polymer sample. Instead, polymer molecular mass is expressed in terms of average molecular weights and molecular weight distribution.
- The two most commonly used averages are the number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$). The number-average molecular weight is calculated by considering the number of molecules of each size, giving equal importance to every molecule. In contrast, the weight-average molecular weight takes into account the mass contribution of each molecule, giving greater weightage to larger polymer chains. Other averages such as z-average molecular weight ($\bar{M}_z$) and viscosity-average molecular weight ($\bar{M}_{vis}$) are also used in polymer science, with larger molecules influencing these averages more strongly.

- The Polydispersity Index (PI) is defined as the ratio of weight-average molecular weight to number-average molecular weight ($PI = \frac{\bar{M}_w}{\bar{M}_n}$). It provides information about the breadth of molecular weight distribution in a polymer sample. A value close to 1 indicates a narrow distribution, whereas higher values indicate a broader distribution. Molecular weight distribution significantly affects polymer properties such as viscosity, toughness, and processing behavior.
- Several experimental techniques are used to determine polymer molecular weight. These methods are broadly divided into absolute methods and relative methods. Absolute methods include techniques based on colligative properties (osmometry, cryoscopy, ebulliometry), end-group analysis, light scattering, mass spectrometry, and ultracentrifugation. Relative methods, such as viscometry and size exclusion chromatography (SEC), estimate molecular weight by comparing polymer properties with calibrated standards.

K 9.7 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: Polymer chains are of different lengths, leading to molecules with different molecular masses.

Answer to Q2: Number-average molecular weight ($\bar{M}_n$) is the average molecular weight of all polymer molecules in a sample. Mathematically, $\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$

Answer to Q3: $\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$

In this case, heavier molecules contribute more strongly to the average. The formula includes squared molecular mass terms and so larger molecules dominate the value.

Answer to Q4: $\bar{M}_z = \frac{\sum n_i {m_i}^3}{\sum n_i {m_i}^2}$

Answer to Q5: $\bar{M}_n = \frac{50\times100+200\times1000+100\times10000}{50+200+100} = 3442.8$

$$\bar{M}_w = \frac{50 \times 10000 + 200 \times 1000000 + 100 \times 100000000}{50 \times 100 + 200 \times 1000 + 100 \times 10000} = 8465.15$$

Answer to Q6: $\bar{M}_n = \frac{10\times10000+1\times100000}{1+10} = 18181.8$

$$\bar{M}_w = \frac{10 \times 10^8 + 1 \times 10^{10}}{10 \times 10000 + 1 \times 100000} = 55{,}000$$

Answer to Q7: Polydispersity index (PI) is the ratio of two molecular weight averages, i.e., $PI = \frac{\bar{M}_w}{\bar{M}_n}$

PI = 1 means all polymer chains are of equal length and narrow distribution of molecular weight. Larger PI values indicate broader molecular weight distribution.

Answer to Q8: The methods for determining the molecular weight of polymers are classified into absolute methods and relative methods. **Absolute methods** determine molecular weight directly without calibration, while **relative methods** require comparison with standards. Examples include osmometry, light scattering, viscometry, and gel permeation chromatography.

Answer to Q9: Polymer molecules increase the viscosity of a solvent. Intrinsic viscosity is obtained by extrapolating reduced viscosity to zero concentration and is related to molecular weight through the Mark-Houwink equation.

O 9.8 FURTHER READING

- Billmeyer, F. W., Jr. (1984). *Textbook of polymer science* (3rd ed.). New York: John Wiley & Sons.
- Misra, G. S. (1993). *Introduction to polymer chemistry*. New Delhi: Wiley Eastern Limited.
- Gowariker, V. R., Viswanathan, N. V., & Sreedhar, J. (1986). *Polymer science*. New Delhi: New Age International Publishers.

M 9.9 MODEL QUESTIONS

Q1. Equal numbers of two polymer molecules of molecular weight 10000 and 100000 are mixed together; determine the number-average molecular weight $(\bar{M}_n)$ and weight-average molecular weight $(\bar{M}_w)$.

Q2. Derive the mathematical expression for the number-average molecular weight $(\bar{M}_n)$ of a polymer sample and explain how it is related to colligative properties such as osmotic pressure.

Q3. Discuss the principle of light scattering in polymer solutions. Derive the Debye equation and explain how a Debye plot can be used to determine the weight-average molecular weight of polymers.

Q4. Explain the working principle of Size Exclusion Chromatography (SEC).

Q5. Describe how calibration curves are prepared in SEC technique and how number-average molecular weight and weight-average molecular weight are obtained from chromatographic data.

Q6. Explain the viscometric method for determining the molecular weight of polymers.

UNIT 10: AVERAGE DIMENSION OF POLYMER CHAINS IN SOLUTIONS

UNIT STRUCTURE

10.1 Learning Objectives
10.2 Introduction
10.3 Chain Configuration of Macromolecules in Solutions
10.4 Root Mean Square (RMS) End-to-End Distance $\langle R^2 \rangle^{1/2}$ and Radius of Gyration
10.5 Random Flight Model and Chain Stiffness Concept of Polymer Chains
10.5.1 Random Flight Model of Polymer Chains
10.5.2 Chain Stiffness Concept of Polymer Chains
10.6 Short-Range and Long-Range Effects in Polymer Chains
10.6.1 Short-Range Effects
10.6.2 Long-Range Effects
10.7 Average Dimensions of Polymer Chains
10.8 Concept of Theta (θ) Solvent
10.9 Let Us Sum Up
10.10 Answers to Check Your Progress
10.11 Further Reading
10.12 Model Questions

10.1 LEARNING OBJECTIVES

After going through this unit you will be able to:

- understand the concept of configuration of macromolecules in solution
- define and calculate root mean square end-to-end distance $\langle R^2 \rangle^{1/2}$ and radius of gyration (R_g)
- explain the concept of random flight model and chain stiffness
- differentiate between short-range and long-range interactions
- explain the concept of average dimensions of polymer chains
- discuss the significance of a theta (θ) solvent

10.2 INTRODUCTION

In continuation with the previous unit, where we have discussed about determination of molecular weight here you will study about average size of polymer chain in solution. When macromolecules especially polymers are dissolved in a solvent, their long-chain nature continuously changes its shapes. These polymer chains are not rigid; instead, they continuously change their conformation due to thermal motion. The shapes or configurations adopted by polymer molecules in solutions depends on various factors such as temperature, solvent quality, and intermolecular interactions between polymer chain and solvent molecules.

Understanding these configurations of polymer chains, especially **average size** and **shape** in solution, is essential for explaining several important polymer properties such

as viscosity, solubility, elasticity, and diffusion. Since individual polymer molecules cannot be described by a single fixed shape, statistical methods are employed to describe their average dimensions.

This unit introduces the **statistical models** which are used to describe polymer chain dimensions in solution. It explains important models such as the random flight model, and discusses key parameters including the root mean square end-to-end distance and radius of gyration. The influence of chain stiffness, short-range and long-range interactions, and solvent quality on polymer configuration, including the concept of a theta (**θ**) solvent, on polymer configuration is also explained.

10.3 CHAIN CONFIGURATION OF MACROMOLECULES IN SOLUTIONS

A polymer molecule consists of a large number of covalently bonded repeat or repeating units. Instead of remaining straight, the polymer chain bends, twists, and folds on itself**.** This is because the bonds in the chain can rotate freely, and the surrounding solvent molecules are constantly colliding with the polymer molecule. *Chain configuration* of macromolecules in solutions refers to the spatial arrangement (three-dimensional) of polymer chain segments, generally adopting a disordered, flexible "**random coil**" conformation due to bond rotations.

Important features of polymer chains in solution are as follows:

i. Polymer chains are coiled, not straight
ii. Chain conformation changes continuously due to Brownian motion (chain is always moving).
iii. The observed shape is always an average over many conformations

Various factors that affects chain configuration are chain flexibility (free rotation around C-C bonds increases flexibility), solvent quality (good solvent expanded coil & poor solvent contracted coil), temperature (increase in temperature increases molecular motion and thus the size of polymer chain), interactions (intra and intermolecular), and steric hindrance (due to bulky groups).

Thus, in solution polymer chains are not rigid but highly flexible due to solvent interactions, temperature, concentration, and adopt a large number of possible conformations due to rotation around single bonds.

Since a polymer chain is never stationary, describing its size using ordinary length measurements is not very useful. So, we use statistical averages to describe the dimensions of polymer chains in solution.

Two important parameters used for this purpose are; Root mean square (RMS) end-to-end distance and Radius of gyration.

10.4 ROOT MEAN SQUARE END-TO-END DISTANCE $\langle R^2 \rangle^{1/2}$ AND RADIUS OF GYRATION (R_g)

The distance between two ends of a polymer chain is called end-to-end distance (R). However, this distance keeps on changing as chain changes its shape. To get rid of this problem, we calculate average Square of the end-to-end distance.

The Average and Root Mean Square (RMS) end-to-end distance for an ideal polymer chain consisting of *N* segments each of length *l* is given by:

$$< R^2 >= Nl^2$$

$$\sqrt{< R^2 >} = l\sqrt{N}$$

Where,
N = number of segments and
l = length of each segment
It represents the average spatial size of a polymer chain and it gives us a measure of the overall size of the polymer chain in solution, even though the actual shape keeps changing.

Radius of Gyration:
The radius of gyration (R_g) is another important measure of polymer size. While the end-to-end distance considers only the two ends of the chain, the radius of gyration takes into consideration of all parts of the polymer molecule.
For a freely jointed chain, the relationship between radius of gyration and RMS end-to-end distance is:

$$\mathrm{R_g} = \sqrt{\frac{\langle \mathrm{R^2} \rangle}{6}}$$

R_g provides a better measure of compactness of polymers. It is defined as the average distance of all segments of the monomer from the center of mass of the polymer chain. Mathematically, it is written as:

$$\mathrm{R_g^2} = \frac{1}{N}\sum < (\boldsymbol{r}_i - r_{cm})^2 >$$

Where,

N = number of monomer units
$\mathbf{r}_i$ = position of the i^{th} monomer
$\mathbf{r}_{cm}$ = position of the center of mass
⟨ ⟩ denotes a configurational average

W CHECK YOUR PROGRESS

Q1. What do you mean by chain configuration of a polymer in solutions?
Q2. Write various factors that affect chain configuration of polymers in solution.
Q3. Explain how root mean square end to end distance $\langle R^2 \rangle^{1/2}$ helps in measuring dimension of a polymer?

10.5 RANDOM FLIGHT MODEL AND CHAIN STIFFNESS CONCEPT OF POLYMER CHAINS

In the previous sections, we have studied that polymer chains in solution are **not rigid**. Instead, they are long, flexible molecules whose shape keeps changing because of thermal motion. To understand and *quantify* this flexibility, we use simple statistical

models. One of the important models among them is the Random Flight Model and chain stiffness, which tells us how flexible or rigid a polymer chain actually is. The Random Flight Model and the concept of chain stiffness are fundamental pillars in polymer which describe the conformation, size, and physical behavior of polymer chains in solution.

10.5.1 Random Flight Model of polymer chains

Imagine a polymer chain made up of a large number of small segments joined end to end. Each segment can rotate freely around the single bonds. Because of this free rotation, the direction of each segment is random with respect to the previous one.
Assumptions of the Random flight model of polymer chain are:

- The polymer chain consists of **N** identical segments, each of length *l*.
- Each segment is free to orient in any direction, independent of the others.
- There are no interactions between distant (non-bonded) segments of the chain.
- Bond angles and bond lengths remain fixed, but bond rotation is free.

According to this model, the polymer chain behaves like a three-dimensional *random walk*, similar to a 'drunken person's walk' and is the simplest statistical model used to describe polymer chains.

10.5.2 Chain Stiffness Concept of Polymer Chains

Real polymer chains are not perfectly flexible. Although rotation about single bonds is possible, it is often restricted due to structural and intermolecular factors. The resistance offered by a polymer chain to bending is known as **chain stiffness.** Chain stiffness is an important concept because it governs the conformation, size, and physical properties of polymer chains in solution and in the melt. It directly affects important material properties such as elastic modulus, glass transition temperature (T_g), melt viscosity, and mechanical strength.
Chain stiffness arises mainly due to restrictions on bond rotation and molecular structure. The important factors responsible for stiffness are:

(a). Nature of chemical bonds:
Fixed bond angles and partial double-bond character restrict free rotation.

(b). Bulky side groups:
Large substituents attached to the backbone hinder rotation due to steric effects.

(c). Presence of double bonds or aromatic rings:
Double bonds and aromatic rings introduce rigidity because of planarity and limited rotational freedom.

(d). Intramolecular and intermolecular interactions:
Hydrogen bonding, dipole-dipole interactions, and π–π interactions further increase stiffness.

Effect of chain stiffness on chain conformation:
As chain stiffness increases, the polymer chain becomes less flexible and deviates from an ideal random coil. Consequently, the polymer chain adopts a less coiled and more extended conformation, the root mean square end-to-end distance increases and the chain behaves more like a semi-rigid molecule. Thus, for polymers of the same

molecular weight, a stiffer chain occupies a larger spatial dimension than a flexible one. This increase in chain dimension significantly affects solution properties such as viscosity and hydrodynamic volume.

W CHECK YOUR PROGRESS

Q4. State the main assumptions of the random flight model.
Q5. How does chain stiffness affect polymer chain dimensions?

10.6 SHORT-RANGE AND LONG-RANGE EFFECTS IN POLYMER CHAINS

In a polymer chains, the conformation and dimensions are influenced not only by the connectivity of the chain but also by **interactions** between different parts of the chain. These interactions are broadly classified into *short-range effects* and *long-range effects*. Both play a crucial role in determining the actual size and shape of polymer molecules in solution and hence effects influence the **average dimensions** of polymer chains in solution.

10.6.1 Short-Range Effects

It arises due to interactions between neighboring or closely connected segments of the polymer chain which mainly originates from the chemical structure of the polymer backbone and operates a small number of bonds.
Short-range effects are caused by:

(i). Fixed bond lengths and bond angles.
(ii). Restricted rotation around single bonds.
(iii). Presence of bulky side group.
(iv). Partial double-bond character in the backbone.

Because of these factors, the orientation of one bond influences the orientation of the next few bonds along the chain. Due to short-range effects; the polymer chain deviates from the ideal freely jointed chain model, the chain becomes stiffer and less flexible, the average end-to-end distance of the chain increases, and chain stiffness is introduced even in the absence of solvent effects. Hence, Short-range effects are therefore responsible for the intrinsic stiffness of polymer chains.

10.6.2 Long-Range Effects

Long-range effects arise due to interactions between segments of the polymer chain that are far apart along the backbone but close in space. These effects become significant in polymer solutions.
Long-range effects mainly result from:

(i). Excluded volume interactions (two segments cannot occupy the same space)
(ii). Polymer-solvent interactions
(iii). Polymer-polymer interactions

(iv). Electrostatic interactions in charged polymers

These interactions depend strongly on nature of solvent and temperature**.**

Consequences of long-range effects:

(i). The polymer chain expands beyond the dimensions predicted by the random flight model

(ii). The chain adopts a swollen coil conformation in good solvents

(iii). The end-to-end distance and radius of gyration increase

(iv). Chain dimensions become solvent-dependent

Short-Range Effects	Long-Range Effects
• Operate over a few bond lengths	• Occur between distant segments of the chain through space
• Include bond angle restrictions and steric hindrance	• Include excluded volume effects
• Affect local chain flexibility	• Cause expansion of polymer coil in good solvents

10.7 AVERAGE DIMENSIONS OF POLYMER CHAINS

In solution, a polymer chain is not fixed in shape. Because of continuous thermal motion, the chain keeps changing its conformation. At any instant, the chain may look stretched, coiled, or somewhere in between the two forms. Therefore, instead of talking about a single length or size, we describe polymer chains using **average** dimensions obtained from statistical considerations.

These average dimensions help us to understand how large a polymer molecule is in solution and how its size depends on factors like chain length, flexibility, nature of solvent, and temperature**.**

The average dimension in polymer chain refers to the statistical size of a polymer coil in solution, expressed using the Root mean square end-to-end distance and Radius of gyration as discussed earlier in section **10.4** of this unit.

The average dimensions of polymer chains depend on several factors:

(i). Degree of polymerization:

As the number of repeating units in a polymer chain increases, the chain length increases. Consequently, polymer chains with a higher degree of polymerization possess larger average dimensions (i.e. larger chains have larger average dimensions).

(ii). Chain stiffness:

Stiffer polymer chains offer greater resistance to bending and therefore occupy more space in solution. As a result, they exhibit larger average dimensions compared to more flexible chains.

(iii). Nature of solvent:

Nature of solvent or solvent quality plays a significant role in determining the size of polymer chains in solution. In a good solvent (highly solubilizing), polymer-solvent interactions dominate, results in expanded polymer coil. In a poor solvent (poorly solubilizing), polymer-polymer interactions dominate, resulting in a contracted coil.

However, in a theta (**θ**) solvent, attractive and repulsive interactions are balanced, and thus polymer chain behaves like an ideal random coil.
(iv).Temperature:
A change in temperature can cause expansion or contraction of the polymer chain, thereby affecting its average dimensions.

10.8 CONCEPT OF THETA (θ) SOLVENT

When a polymer is dissolved in a solvent, the final shape and size of the polymer chain depend on how the polymer segments interact with the solvent molecules. To understand this clearly, scientists introduced the idea of a **theta** (**θ**) solvent, which acts as a *reference condition* for polymer solutions. Now, let us understand what is a Theta (θ) Solvent?
A theta solvent is a special solvent in which the polymer-solvent interactions exactly balance the polymer-polymer interactions; as a result the polymer chain behaves as if no net interactions are acting between its chains or segments. Therefore, a theta solvent serves as a reference state for understanding the true dimensions of polymer chains in solution.

W CHECK YOUR PROGRESS

Q6. Distinguish between short-range and long-range effects in polymer chains? (Any three).
Q7. What is a theta (θ) solvent?

2 10.9 LET US SUM UP

- In this unit, we discussed the configuration and average dimensions of polymer chains in solution. Polymer chains are flexible macromolecules that continuously change their shapes due to thermal motion. Therefore, their size cannot be described by a fixed length and is instead expressed using statistical averages.
- The **root mean square (RMS) end-to-end distance** $\langle R^2 \rangle^{1/2}$ and the **radius of gyration** (R_g) are important parameters used to describe the average size of polymer chains in solution. The **random flight model** explains the polymer chain as a three-dimensional random walk with freely rotating segments.
- Real polymer chains exhibit **chain stiffness**, which arises due to restricted bond rotation, bulky side groups, and intermolecular interactions. Polymer chain dimensions are also influenced by short-range effects (bond angle restrictions and steric hindrance) and long-range effects (polymer-solvent and excluded volume interactions).
- Finally, the **average dimensions** of polymer chains depend on factors such as degree of polymerization, chain stiffness, nature of solvent or solvent quality, and temperature. The concept of a **theta** (θ) solvent represents a special condition where polymer-polymer and polymer-solvent interactions balance, causing the polymer chain to behave like an ideal random coil.

K 10.10 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: Chain configuration of macromolecules in solutions refers to the spatial arrangement (three-dimensional) of polymer chain segments, generally adopting a disordered, flexible "random coil" conformation due to bond rotations. In solution, polymer chains are not rigid and due to thermal motion the long chain continuously changes its shape by rotation around single bonds. As a result, a polymer molecule may appear coiled, partially extended, or stretched at different moments.

Answer to Q2: The various factors that affects chain configuration of a polymer in solution are as follows:

(a). Temperature:
Increase in temperature enhances thermal motion of polymer segments, leading to greater flexibility and expansion of the polymer coil.

(b). Nature of the solvent:
In a *good solvent*, polymer-solvent interactions are strong, causing the chain to expand. In a *poor solvent*, polymer-polymer interactions dominate, leading to a contracted.

(c). Polymer-solvent interactions:
Strong attractive interactions between polymer and solvent molecules promote enlargement of the polymer chain, whereas weak interactions result in shrinking of the chain.

(d). Molecular weight of the polymer:
Higher molecular weight polymers have longer chains, which generally adopt larger and more complex configurations in solution.

(e). Chain stiffness:
Rigid or semi-rigid polymer chains show more extended configurations, while flexible chains form coiled structures.

(f). Steric hindrance:
Short-range effects arise from bond angles and restricted rotations, while long-range effects are due to excluded volume and segment–segment interactions, both of which influence chain shape.

Answer to Q3: When we talk about the size of a polymer chain in solution, we cannot use a fixed length because the chain is constantly changing its shape due to thermal motion. Thus, we use statistical measures to describe the dimensions of polymer chains in solution; Root mean square end-to-end distance and Radius of gyration. The Root mean square end-to-end distance ($\langle R^2 \rangle^{1/2}$) is distance between two ends of a polymer chain is called end-to-end distance (R). However, this distance keeps on changing as chain changes its shape. To get rid of this problem, we calculate average Square of the end-to-end distance.

The Average and Root Mean Square (RMS) end-to-end distance for an ideal polymer chain consisting of *N* segments each of length *l* is given by:

$$< R^2 >= Nl^2$$

$$\sqrt{< R^2 >} = l\sqrt{N}$$

$\langle R^2 \rangle^{1/2}$ represents the average spatial size extension of a polymer chain. It also gives us an idea to measure the overall size of the polymer chain in solution when two ends are separated, even though the actual shape keeps changing.

Answer to Q4: The main assumptions of Random flight model are:

(i). Polymer chain consists of a large number of segments
(ii). Each segment is connected to the next by a flexible joint.
(iii). Bond angles and bond lengths remain fixed, but bond rotation is free.
(iv). The direction of each segment is independent of the directions of all other segments. Hence, the chain performs a random walk in space.
(v). Chain has no stiffness the model assumes the polymer has no rigidity; it can bend freely at each joint.

Answer to Q5: Chain stiffness refers to the resistance of a polymer backbone to bending or rotation about its bonds. Increased chain stiffness leads to a more extended chain conformation and larger average dimensions such as end-to-end distance and radius of gyration.

Answer to Q6:

Short-Range Effects	Long-Range Effects
• Arise due to interactions between neighboring bonds or segments along the polymer backbone. • Include bond angle restrictions and steric hindrance • Affect local chain stiffness.	• Arise due to interactions between segments far apart along the chain but close in space. • Include excluded volume effects and polymer-solvent interactions. • Affect whole polymer chain expansion or contraction in solution.

Answer to Q7: A theta solvent is a solvent in which polymer-polymer and polymer-solvent interactions exactly balanced, resulting in ideal chain behavior.

O 10.11 FURTHER READING

- B.R. Puri, L.R. Sharma, Madan S. Pathania- Principles of Physical Chemistry
- F. W. Billmeyer-Textbook of Polymer Science
- K. L. Kapoor- A Textbook of Physical Chemistry
- Cowie & Arrighi- Polymers: Chemistry and Physics of Modern Materials

M 10.12 MODEL QUESTIONS

Q1. Describe the chain configuration of macromolecules in solution
Q2. Explain root mean square end-to-end distance and radius of gyration as measures of polymer size in solution.
Q3. Explain the concept of chain stiffness in polymers.

Q4. Explain the influence of short-range and long-range effects in polymer chains and write any two distinguishing features between them.

Q5. What is the importance of theta solvent in polymer science?

UNIT 11: POLYMERIZATION REACTIONS

UNIT STRUCTURE

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11.2 Introduction
11.3 Condensation Polymerisation
- 11.3.1 Condensation and Polycondensation
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  - 11.3.3.3 Degree of Polymerisation
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11.4 Addition Polymerisation
- 11.4.1 Free Radical Polymerisation
  - 11.4.1.1 Production of free radical and Cage effect
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  - 11.4.1.4 Chain Transfer reactions
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11.5 Coordination Polymerisation
11.6 Copolymerisation
11.7 Let Us Sum UP
11.8 Answers to Check Your Progress
11.9 Further Reading
11.10 Model Questions

11.1 LEARNING OBJECTIVES

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

- explain the concept of polymerisation reactions.
- distinguish between chain polymerisation and step polymerisation.
- describe the basic principles of cationic, anionic, and coordination chain polymerisation.
- understand the concept of ring-scission (ring-opening) step polymerisation.
- explain the kinetics of free radical chain polymerisation.
- describe the kinetics of step polymerisation.

- understand the fundamentals of copolymerisation, its kinetics & mechanism and reactivity ratios governing copolymer composition.

11.2 INTRODUCTION

Polymerisation is a chemical reaction in which small, reactive molecules known as **monomers** join together to form large molecules with very high molecular mass called **polymers**. In this process, the monomer units are repeatedly linked through **covalent bonds**, producing long chains or network structures containing repeating structural units.

Polymerisation reactions play a vital role in the production of many synthetic materials such as plastics, rubbers, and fibres, as well as in the formation of important biological macromolecules. These reactions enable monomers to assemble into long chains, making it possible to manufacture materials with desirable properties such as **strength, flexibility, durability, and chemical resistance**, which are essential for a wide range of industrial and technological applications.

Polymerisation reactions are generally classified into two major categories:

1. **Step-growth polymerisation** (Condensation polymerisation)
2. **Chain-growth polymerisation** (Addition polymerisation)

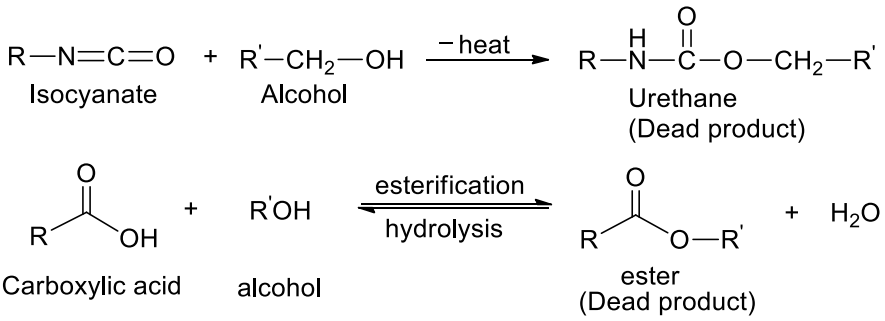
These two types differ mainly in their reaction mechanism, growth pattern, and molecular weight development.

11.3 CONDENSATION POLYMERISATION

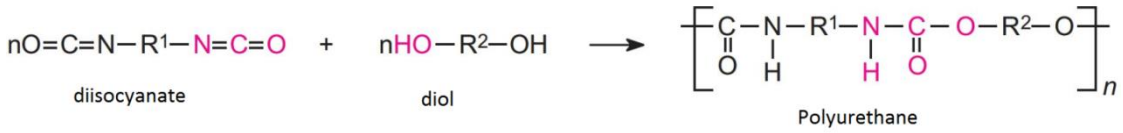
Condensation polymerization may be defined as an intermolecular reaction between bifunctional or polyfunctional molecules (called monomer) avoiding the formation of ring or cyclic structure and in a manner that makes the process functionally capable of proceeding towards infinity. The main criterion for polycondensation to take place is that the monomers should at least bifunctional. Thus, condensation polymerization is a process of formation of polymers from polyfunctional monomers of organic molecules with or without the elimination of small molecules such as water, HCl, NH_3 etc. Condensation polymerisation is also known as step-reaction or Step-growth polymerization.

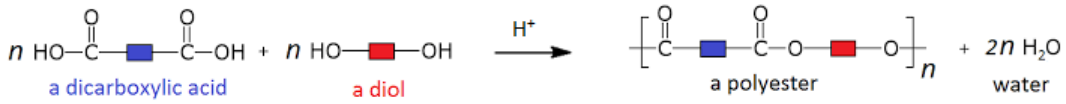
11.3.1 Condensation and Polycondensation Reactions

When a condensation reaction occurs between two **monofunctional molecules**, each molecule possesses only one reactive functional group. During the reaction, these functional groups combine and form a single stable product, after which no further reaction can take place because no additional reactive sites remain. e.g.



In contrast, when condensation reactions involve **bifunctional or polyfunctional** molecules, each molecule contains at least two reactive functional groups. After the initial reaction, unreacted functional groups are still present at the ends of the molecules, allowing further reactions with other molecules. This repeated linking of molecules produces long chain macromolecules, and the overall process is known as **polycondensation polymerization**. e.g.,

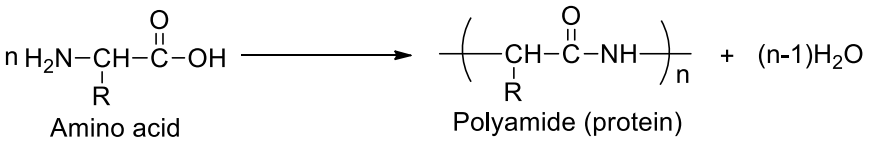


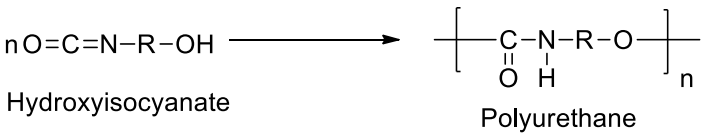


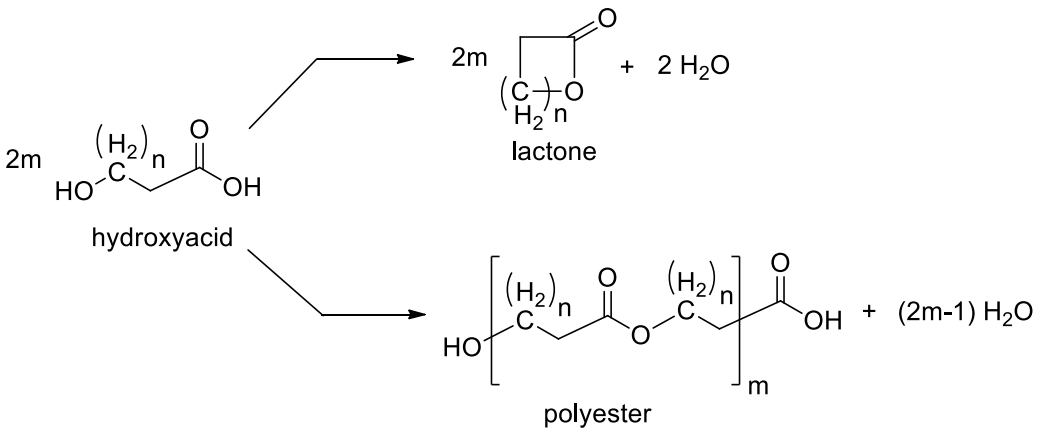
The polymers formed still contain both the functional (reactive) groups at its chain end and hence are active, not dead.

11.3.2 Self-Polycondensation Reactions

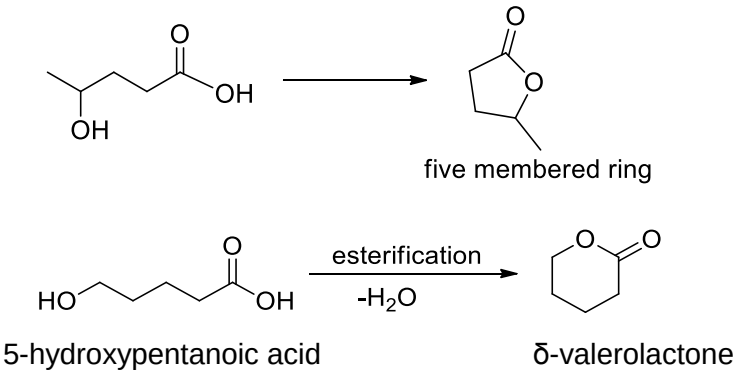
When both reactive functional groups are present within the same monomer molecule, the monomers can react with one another through these groups. As the reaction proceeds, the molecules join together in a **head-to-tail sequence**, forming long chains. This type of process is known as **self-polycondensation**, where identical monomers link repeatedly to produce a polymer. e.g.







From the above example, it is evident that for polymerization to take place lactone (ring/cyclic structure) formation must be avoided. The possibility of **ring formation** depends on the size of the ring and its stability. Rings with 3-4 members are unstable; but 5, 6 & 7 membered rings are stable and thus they form lactones. Again 8-11 membered chains form linear polymers but from 12 onwards they may form lactones because there is a possibility of approaching the two functional groups present in the same structure.



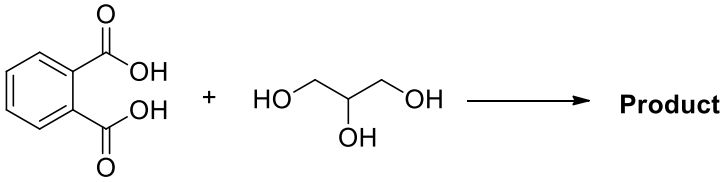
When both functional groups are present within the same monomer molecule, the reaction generally proceeds more efficiently and results in a higher polymer yield. In contrast, when two different monomers are involved, it is difficult to maintain the exact **1:1 molar ratio** required for effective polymer formation. Any imbalance in the ratio limits chain growth, which can lead to polymers with lower molecular weight and reduced product quality.

Some important type of condensation polymers are Polyesters, Polyamides, Polyethers, Polyurethanes, Phenol-formaldehyde resins, Urea-formaldehyde, Malamide formaldehyde, Polysiloxanes, etc.

11.3.3 Terminology in Polycondensation Reactions

11.3.3.1 Average Functionality

The number of reactive groups in a monomer molecule is called functionality. Average functionality is the average number of functional groups per molecule when the reactive monomer molecules are in stoichiometric equivalence. For a polycondensation to occur the average functionality must be at least 2. e.g. for the polycondensation reaction between phthalic acid and glycerol-



Bifunctional **Trifunctional**

2 **3** ← **functionality**

3 **2** ← **required molecular ratio**

Average functionality,

$$f_{av.} = \frac{(2 \times 3) + (3 \times 2)}{3 + 2} = \frac{12}{5} = 2.4$$

11.3.3.2 Extent of Reaction

Extent of reaction at any time 't' is the ratio of the number of functional groups reacted during the time 't' to the total number of functional groups present initially.

$$\text{Extent of reaction} = \frac{\text{number of functional groups reacted during the time 't'}}{\text{total number of functional groups present initially}}$$

e.g. "extent of reaction at any time 't' is 0.80" means the reaction is 80% completed. If N_0 is the initial number of reactive groups and N is the number of unreacted groups remaining at time 't', then-

$$\text{Extent of reaction, p} = \frac{N_0 - N}{N_0}$$

11.3.3.3 Degree of Polymerization

As discussed in unit-8, the average degree of polymerisation is defined as-

$$\bar{X}_n = \frac{\bar{M}_n}{m_s}$$

$$\text{Or,} \qquad \bar{X}_w = \frac{\bar{M}_w}{m_s}$$

As the polymerization reaction proceeds, more and more monomer molecules are consumed and larger chains are formed. Hence the average degree of polymerization can be define as-

$$\bar{X}_n = \frac{\text{Initial numbers of monomer molecules}}{\text{No. of monomer molecules at time 't'}} = \frac{N_0}{N}$$

11.3.4 Carother's Equation

Carother's equation gives the relationship between average functionality, extent of reaction and degree of polymerization.

Let, N_0 be the total numbers of reacting molecules initially present giving an average functionality for the system as 'f'. The reacted functional groups are also assumed to be present in stoichiometric equivalence. Let, N be the no. of molecules present at time 't' when the extent of reaction is 'p'. Total numbers of monomer molecules lost (reacted) during time 't' is equal to $N_0 - N$. For each molecule lost, number of functional groups lost is 2. So, the total number of functional groups lost during time 't' will be $2(N_0 - N)$. The total number of functional groups present initially was $N_0 f$. Therefore, the extent of reaction can be written as-

$$\text{Extent of reaction, p} = \frac{\text{number of functional groups reacted during the time 't'}}{\text{total number of functional groups present initially}}$$

$$p = \frac{2(N_0 - N)}{N_0 f}$$

$$or,\ \text{p} = \frac{2}{f}\left(1 - \frac{N}{N_0}\right) \qquad (11.1)$$

Since the average degree of polymerization is define as-

$$\bar{\text{X}}_n = \frac{\text{Initial numbers of monomer molecules}}{\text{No. of monomer molecules at time 't'}} = \frac{N_0}{N}$$

Therefore, the equation (11.1) can be written as-

$$p = \frac{2}{f}\left(1 - \frac{1}{\bar{X}_n}\right) \qquad (11.2)$$

Equation (11.2) is known as **Carother's equation**.

For a bifunctional system, $f = 2$, then,

$$p = \left(1 - \frac{1}{\bar{X}_n}\right)$$

Or,

$$\bar{X}_n = \left(\frac{1}{1-p}\right) \qquad (11.3)$$

Thus, from equation (11.3), when $p = 1$, $\bar{X}_n = \infty$; but short of complete reaction, $\bar{X}_n$ is always finite.

If the molecular weight of the repeat unit is m_s, the average molecular weight of the polymer system is given by-

$$\bar{M}_n = \bar{X}_n . m_s = \left(\frac{m_s}{1-p}\right) \qquad (11.4)$$

11.3.4.1 Gel Point

At critical extent of reaction, when $\bar{X}_n \rightarrow \infty$, equation (11.2) becomes as-

$$p_c = \frac{2}{f} \qquad (11.5)$$

Which is called the **gel point** and at gel point one observes the visible formation of a gel or insoluble polymer fraction. Therefore, gel point is the critical extent of reaction p_c, at which gelation / cross-linking would commence, i.e., at which $\bar{X}_n$ would first assume a value of infinity.

Example-1: For a typical bifunctional system, $f = 2$, theoretically gel point occur when $p_c = 1$, i.e. the reaction is 100% complete.

Example-2: For a polycondensation reaction between bifunctional and trifunctional monomer, $f = 2.4$, therefore, $p_c = \frac{2}{2.4} = 0.83$. Thus, at the point of theoretical extent of reaction 0.83 i.e. when the reaction is 83% complete, the polymer formed in the polycondensation reaction gets cross-linked and hence turns into an insoluble, infusible gelled mass. Technically, the reaction should not be allowed to proceed beyond this point otherwise the product would be unusable one. Infact, it is advisable to arrest the reaction 10-15% earlier in p_c to avoid damage of the reaction kettle and to collect good quality product.

11.3.4.2 Limitation of the Carother's equation

Two limitations of the Carother's equation are-

(i) The Carother's equation is applicable to polycondensation reaction only. It losses significance in the context of addition reaction.

(ii) Practically gelation starts even at earlier stages than predicted by the Carother's equation.
Reasons: (a) Practically gellation starts even at earlier stages than predicted by the Carother's equation because of the uncontrolled local conditions in the hot viscous reaction mass. (b) During the derivation of the Carother's equation, we have used the term average degree of polymerization, $\bar{X}_n$ .It implies that there are polymer chains shorter as well as longer than $\bar{X}_n$. The chains (living) greater than $\bar{X}_n$ get cross-linked before the theoretical gel point.

11.3.5 Control of molecular weight in Polycondensation Reaction

As the polycondensation reactions are quite rapid and go to completion, a polymer with very high molecular weight will be formed. Very high molecular weight polymers are difficult to process and hence it is necessary to limit the molecular weight. The molecular weight can be controlled by (i) Adopting a stoichiometric imbalance and (ii) Addition of monofunctional compound.

(i) **Control of molecular weight by adopting a stoichiometric imbalance:** (Quantitative effect of stoichiometric imbalance on maximum attainable molecular weight)

The molecular weight of polycondensation product can be controlled by striking a calculated stoichiometric imbalance of the two types of reactive functional groups.

Let us consider a bifunctional system having monomer of the A-A & B-B types and giving the number of 'A' and 'B' functional groups as $N_A \; and \; N_B$ respectively such that $\frac{N_A}{N_B} = r$, where $r \leq 1$, i.e. 'B' groups are presence in molar excess, if there is stoichiometric imbalance. Then, the degree of polymerization is given by-

$$\bar{X}_n = \frac{N_0}{N} = \frac{1+r}{1+r-2rp}$$

Case-I: When there is no stoichiometric imbalance, r = 1, i.e., equimolar mixture,

$$\bar{X}_n = \frac{1}{1-p}$$

Case II: When extent of conversion if 1, i.e., 100% completion, then

$$\bar{X}_n = \frac{1+r}{1-r}$$

e.g. if 'B' is 1% in excess, then, $r = \frac{100}{101}$. Therefore,

$$\bar{X}_n = \frac{1+\frac{100}{101}}{1-\frac{100}{101}} = 201$$

(ii) Control of molecular weight by addition of monofunctional compound: Suppose the initial concentrations of monomers taken are exactly equal but the reaction mixture contains some monofunctional compounds. It would decrease the degree of polymerization. If the fraction of monofunctional compound is r_1, then

$$\bar{X}_n = \frac{1+r_1}{1+r_1-p}$$

W CHECK YOUR PROGRESS

Q1. In the polymerization of hexamethylenediamine and adipic acid, a 2% excess of adipic acid is present; Calculate the degree of polymerization of the polymer formed for 98% conversion.

Q2. In the polymerization of ω-hydroxycaproic acid, HO-$(CH_2)_5$-COOH, a 2% monofunctional impurity is present; calculate the degree of polymerization of the polymer formed for 98% conversion.

11.3.6 Kinetics of Condensation Polymerization

The kinetics of step growth polymerization can be simplified by the assumption of Flory. According to Flory, "*All functional groups can be considered as being equally reactive irrespective of the chain length*".
Let us study the kinetics of polyesterification reaction which may occur in two ways *viz* (i) Self-catalysed polyesterification and (ii) acid (mineral) catalysed polyesterification.

(i) **Self-Catalysed Polyesterification:** Let us consider the reaction between a dicarboxylic acid and a diol to form a polymer. This reaction is prone to catalysed by `mineral acids but in absence of an added mineral acid, the reactant '–COOH' acts as a catalyst. For each step reaction can be written as-

$$-COOH \quad + \quad -OH \quad \xrightarrow{-COOH(Catalyst)} \quad -COO- \quad + \quad H_2O$$

A second '–COOH' group from the reactants acts as a catalyst. The rate of the reaction can be written as-

$$-\frac{d[-COOH]}{dt} = k[-COOH]^2[-OH]$$

Here, k is the rate constant of the reaction. If equimolar concentration of the '–COOH' and '–OH' group is present and their concentration being C, then

$$-\frac{dC}{dt} = kC^3$$
$$-\frac{dC}{C^3} = kdt$$

On integration,

$$2kt = \frac{1}{C^2} - \text{constant} \quad \text{---------- (a)}$$

If $C = C_0$ at $t = 0$, where C_0 being the initial concentration of each kind of functional group and p is the extent of reaction then,

$$C = C_0(1-p) \text{----------(b)}$$

Combining equations (a) and (b) we get-

$$2C_0^2kt = \frac{1}{(1-p)^2} - \text{constant} \quad \text{---------- (c)}$$

But, $\bar{X}_n = \frac{1}{1-p}$; Therefore,

$$2C_0^2kt = \bar{X}_n{}^2 - \text{constant} \text{----------(d)}$$

Equations (c) and (d) implies that the plot of $\frac{1}{(1-p)^2}$ or $\bar{X}_n{}^2$ against 't' gives a straight line.

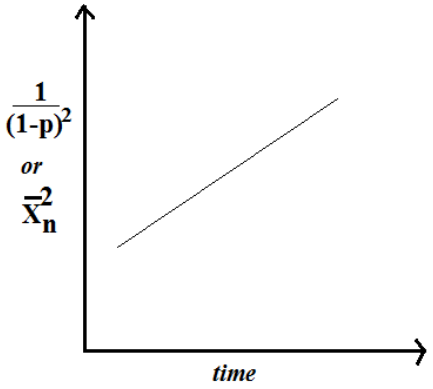


Figure 11.1: $\bar{X}_n{}^2$ versus time plot for self-catalysed polyesterification

The kinetics was verified by (i) Diethylene glycol with adipic acid at various temperatures and (ii) Diethylene glycol with Caproic acid

(ii) Polyesterification using strong acid as catalyst:

In the case of an added catalyst the rate of reaction is proportional to the hydroxyl, carboxyl and the catalyst concentration and is written as,

$$-\frac{dC}{dt} = kC_{cat}C^2$$

Since the catalyst concentration is constant,

$$-\frac{dC}{dt} = k^{\#}C^2$$

On integration, the following expressions are obtained

$$k^{\#}t = \frac{1}{C} - \text{constant}$$

Putting the value of $C = C_0(1-p)$, we get, -

$$C_0k^{\#}t = \frac{1}{(1-p)} - \text{constant} \text{ ----------}(e)$$

$$C_0k^{\#}t = \bar{X}_n - \text{constant----------(f)}$$

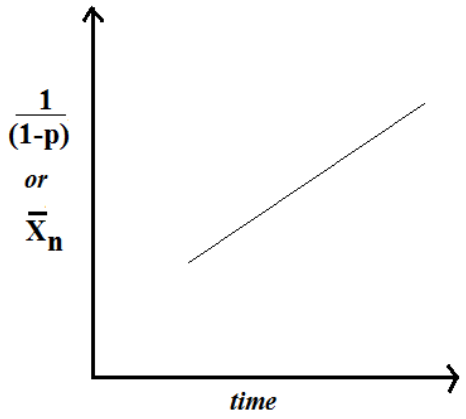


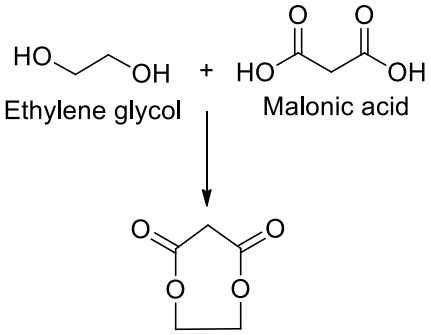
Figure 11.2: $\bar{X}_n$ versus time plot for acid catalysed polyesterification

The linearity of the plot of $\frac{1}{(1-p)}$ against 't' has been established for a variety of polyesterification reactions. e.g. Reaction between diethylene glycol with

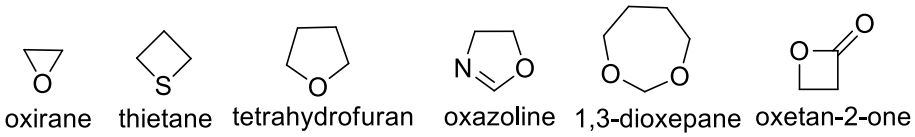
adipic acid at 109ºC catalysed by 0.4 mole percent of p-toluene sulphonic acid.

11.3.7 Ring Opening Polymerization

Condensation of bimolecular low molecular weight compounds can give cyclic or ring compounds having strain free configuration.



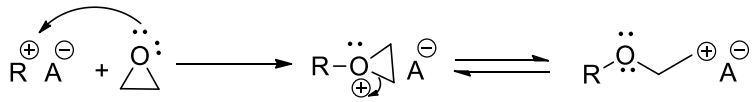
The converse also holds good. Thus, cyclic compounds such as lactones and oxiranes can be opened up by aqueous alkali or acids to form an intermediate with active ends capable of undergoing further polymerization.



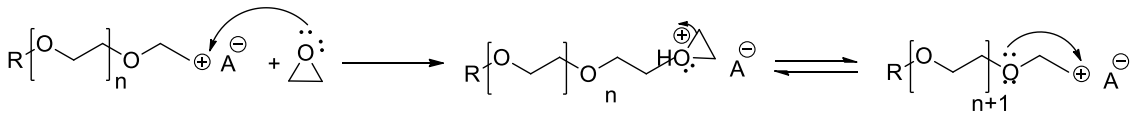
A general ring opening polymerization proceeds via three steps *via* Initiation step, Propagation step and Termination step. Mechanism of some ring opening polymerizations are discussed below.

Example-1: Polymerization of oxirane (ethylene oxide) initiated by cationic initiator.

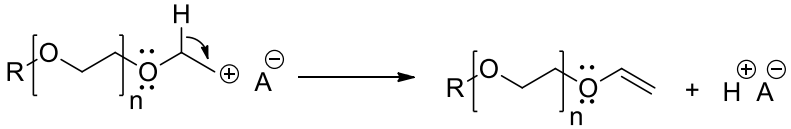
Initiation step



Propagation

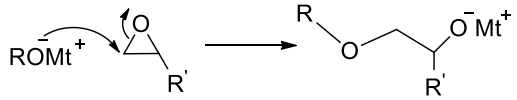


Termination via rearrangement



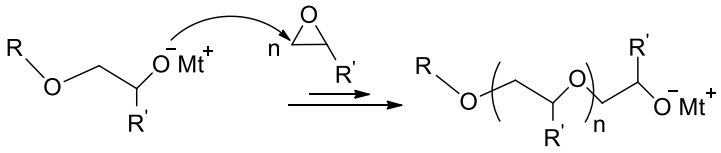
Example-2: Polymerization of substituted ethylene oxide initiated by anionic initiator. Here, the termination may occur through chain transfer.

Initiation

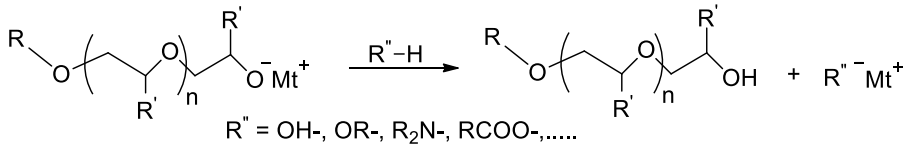


Mt = Na, K, Cs
R = H, alkyl, polymer,....

Propogation

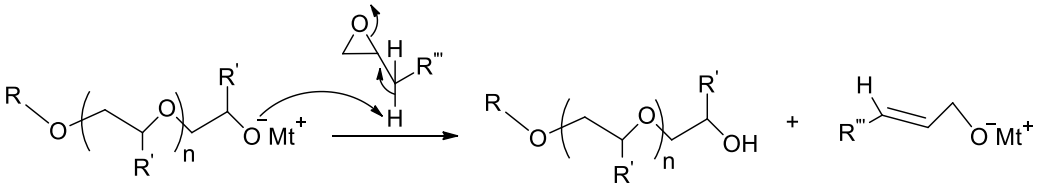


Termination

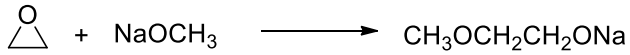


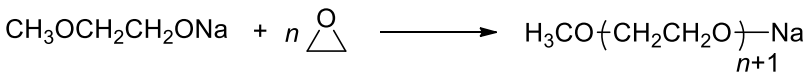
R" = OH-, OR-, R_2N-, RCOO-,.....

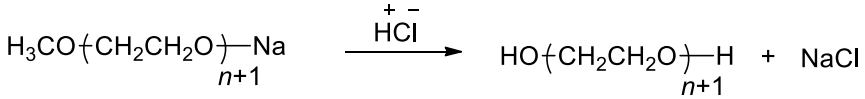
Transfer



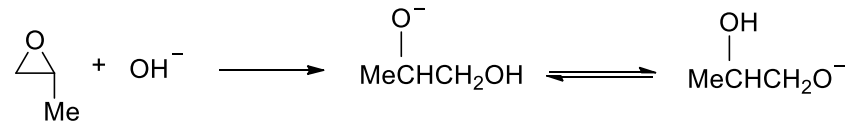
Example-3: Polymerization of ethylene oxide in presence of sodium methoxide. Here, sodium methoxide acts as anionic initiator. This mechanism is similar to anionic chain polymerization except that, in the later, the attack by the anion is on the π- electron pair of the C=C, while here it is on the activated complex ring.

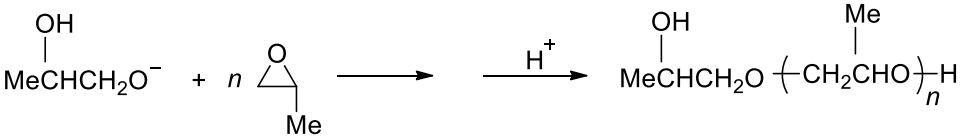






Example-4: An alkali may also initiate a ring opening polymerization.

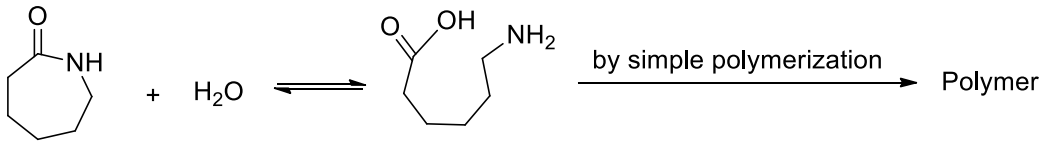




Example-5: The polymerization of caprolactam to form Nylon-6 may occur either by simple linear polycondensation or by ring opening mechanism.

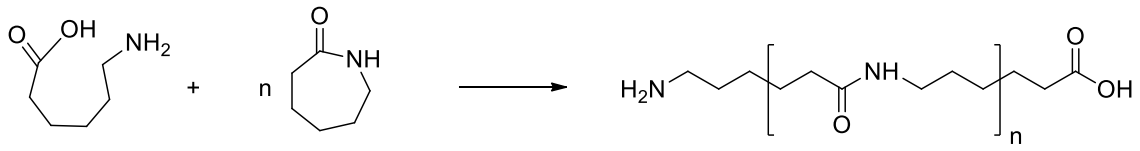
Ɛ-caprolactam ring open up on hydrolysis forming Ɛ-aminocaproic acid. If all Ɛ-caprolactam undergoes hydrolysis to form Ɛ-aminocaproic acid before entering to the chain propagation step, this is called linear polycondensation.

Polymerisation of ε-caprolactam to polyamide 6



ε-Caprolactam ε-Aminocaproic acid

On the other hand, the Ɛ-aminocaproic acid, formed in the initiation step, attack a Ɛ-caprolactam molecule thereby opening its ring in the propagation step, then it is the ring opening mechanism.



ε-Aminocaproic acid ε-Caprolactam Nylon-6

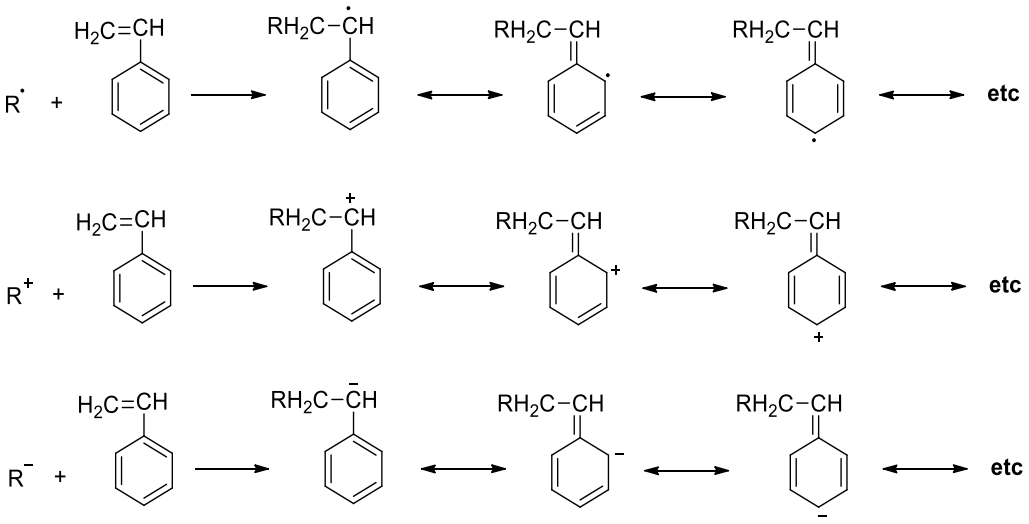
11.4 ADDITION POLYMERISATION

Addition polymerization is a process by which unsaturated monomers are converted to polymers of high molecular weight, exhibiting the characteristics of a typical chain reaction. The characteristics of addition polymerisation are-

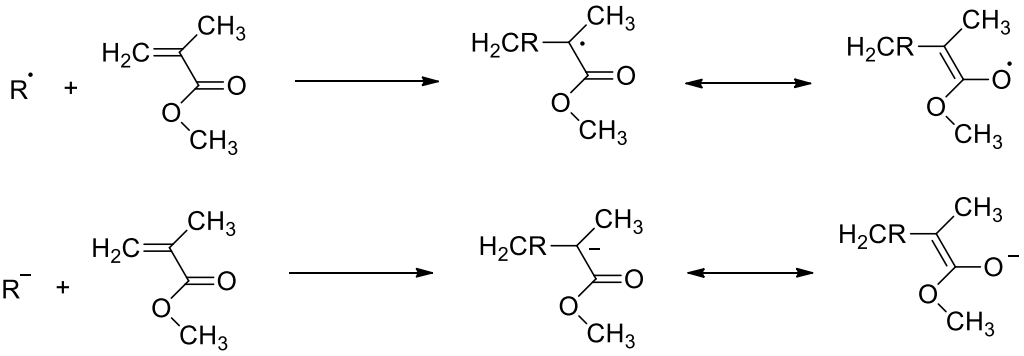
- Self-addition of the monomer molecules to each other very rapidly through a chain reaction.
- No byproducts are formed.
- The product has the same elemental composition as that of the monomers.
- The reactions are typified by three normally distinguishable steps viz. (i) Chain initiation, (ii) Chain Propagation and (iii) Chain Termination.
- The process can be brought about by (i) Free radical, (ii) Ionic or (iii) Coordination Mechanism.

Whether an unsaturated monomer undergoes polymerisation through free radical, anionic, or cationic pathways is determined by the structural features and substituents present in the vinyl monomer. For example-

(i) Styrene undergoes polymerization by free radical, cationic or anionic way because of the resonance stabilization of the resultant carbon free radical, carbocation or carbanion.

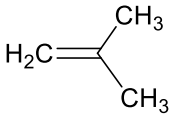


(ii) Methyl Methacrylate undergoes polymerization by free radical and anionic pathway.

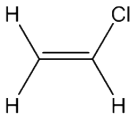


(iii) Vinyl compounds like CH_2=CHX, where X is an electron withdrawing group, it gives readily polymer by anionic pathway.

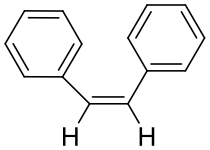
(iv) 2-methyl propene undergo polymerization only by cationic pathway.



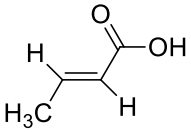
(v) Vinyl Chloride undergo polymerization simply by free radical.



(vi) Stilbene (cis- or trans-) and Crotonic acid (cis- or trans-) does not undergo homopolymerization due to steric effect.



Stilbene



Crotonic acid

11.4.1 FREE RADICAL POLYMERISATION

Mechanism:

The polymerization of vinyl or related monomer M, induced in presence of a free radical initiator may be schematically expressed as-

Initiation

$$\text{Initiator} \xrightarrow{k_d} R^{\bullet}$$

$$R^{\bullet} + M \xrightarrow{k_i} M_1^{\bullet}$$

Propogation

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$M_2^{\bullet} + M \xrightarrow{k_p} M_3^{\bullet}$$

$$M_x^{\bullet} + M \xrightarrow{k_p} M_{(x+1)}^{\bullet}$$

Termination

$$M_x^{\bullet} + M_y^{\bullet} \xrightarrow{k_{tc}} M_{(x+y)} \qquad \text{Coupling}$$

$$M_x^{\bullet} + M_y^{\bullet} \xrightarrow{k_{td}} M_x + M_y \qquad \text{Disproportioation}$$

Kinetics:

Rate of formation of the primary radical, R•

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

Where, $k_d$is the initiator decomposition rate constant and $[I]$ is the molar concentration of the initiator.

As free radicals are highly reactive, primary radicals instantly react with monomer to give secondary free radical $M\bullet$,

$$R_i = \frac{d[M\bullet]}{dt} = k_i[R\bullet][M]$$

Where, k_i is the initiation rate constant and $[M\bullet]$ is the molar concentration of radical.

Since the decomposition of initiator is slower and rate determining step, for all practical purpose,

$$R_i = 2fk_d[I]$$

Where, f is the Initiator efficiency defined as

$$f = \frac{\text{radicals that initiate a polymer chain}}{\text{radicals formed from Initiator}}$$

Rate of propagation, secondary free radical generated at initiation step react with monomer to give extended structure,

$$R_p = k_p[M\bullet][M]$$

Rate of termination is given by-,

$$R_t = -\frac{d[M\bullet]}{dt} = 2k_t[M\bullet]^2$$

Applying steady state approximation, $R_i = R_t$; we have -

$$[M\bullet] = \sqrt{\frac{fk_d[I]}{k_t}}$$

Since most of the monomers consumed at propagation step, Rate of propagation is equal to rate of polymerisation and given by,

$$R_p = k_p[M\bullet][M] = \frac{k_p}{(k_t)^{\frac{1}{2}}}(fk_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}[M]$$

This is the overall rate of polymerization.

Kinetic Chain length ($\bar{\nu}$):

The average chain length represents the average numbers of monomer molecules consumed by a given active centre from its initiation to its termination. Under steady state, $R_i = R_t$; therefore, -

$$\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M][M\bullet]}{2k_t[M\bullet]^2} = \frac{k_p[M]}{2k_t[M\bullet]} = \frac{k_p[M]}{2k_t\sqrt{\frac{fk_d[I]}{k_t}}} = \frac{k_p[M]}{2(fk_tk_d[I])^{\frac{1}{2}}}$$

Hence,

$$\bar{\nu} \propto [M]$$
$$\bar{\nu} \propto \frac{1}{[M\bullet]}$$
$$\bar{\nu} \propto \frac{1}{[I]^{\frac{1}{2}}}$$

Therefore, the degree of polymerization is given by-

$\bar{X}_n = 2\bar{\nu}$; (when termination occurs by combination)

$\bar{X}_n = \bar{\nu}$; (when termination occurs by disproportionation)

11.4.1.1 Production of free radicals and Cage effect

Free radical can be produced as follows, -

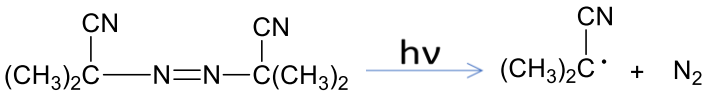
(a) **Thermal decomposition of certain peroxides:**

e.g

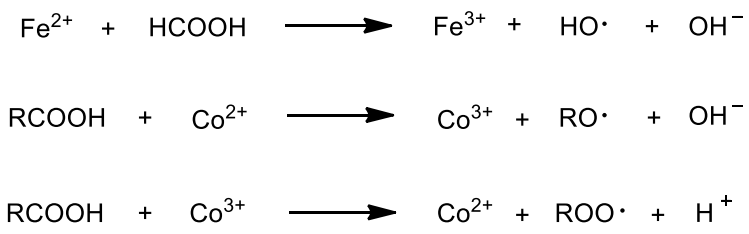


(b) By pyrolysis

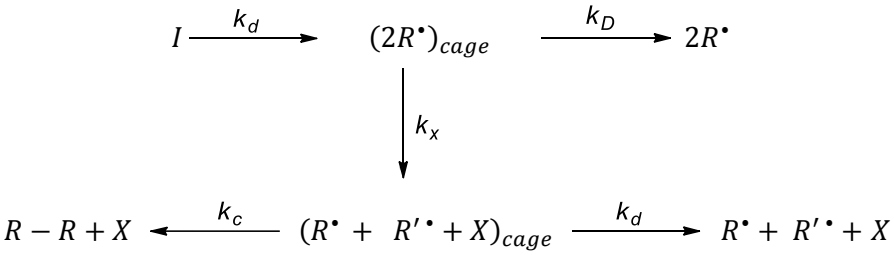
Azobis(isobutyronitile) (AIBN) breaks down into cyanopropyl radicals and nitrogen at ambient temperature under the action of UV radiation-



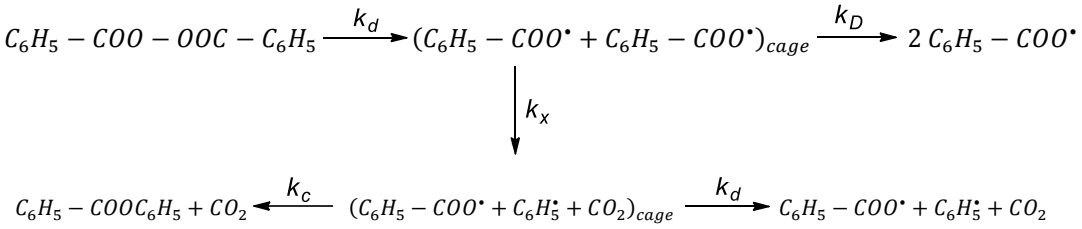
(c) By chemical reaction (Redox polymerization)



The efficiency of an initiator is not an exclusive property of the initiator molecule but depends on the prevailing conditions and solvent used. The initiator efficiency takes into the fact that not all of the radicals produced initiate a chain. Values of **initiator efficiency, f** usually range from 0.6 to 1. Reduced efficiency is attributed to CAGE EFFECT in which radicals formed in the initiation reaction have a finite probability of recombining before they can diffuse through the cage of the surrounding liquid molecules and initiate polymerization. Hence the confining effect of solvent molecules is known as **Cage Effect**.

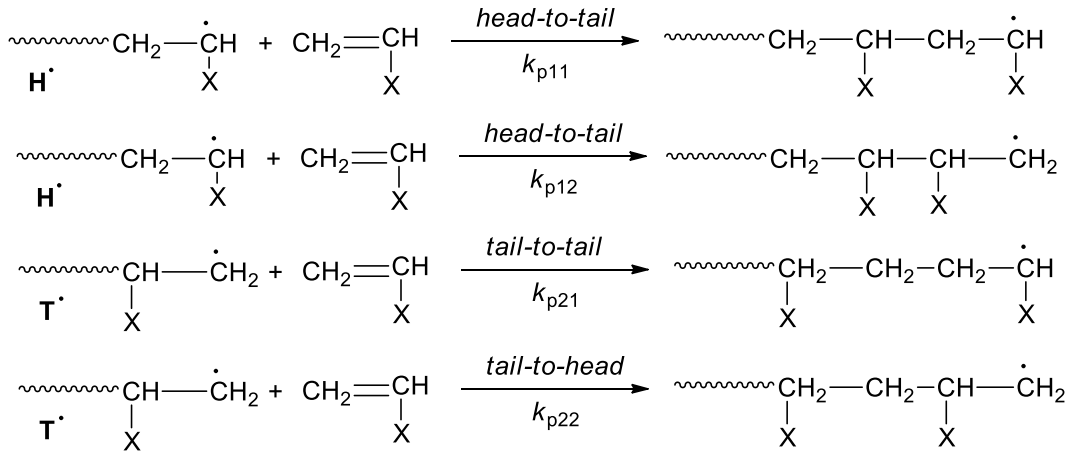


e.g



11.4.1.2 Chain Propagation

There are two possibilities of the way in which addition in the propagation sequence take place, - (a) head-to-head addition (or tail-to-tail) and (b) head-to-tail (tail-to-head) addition.

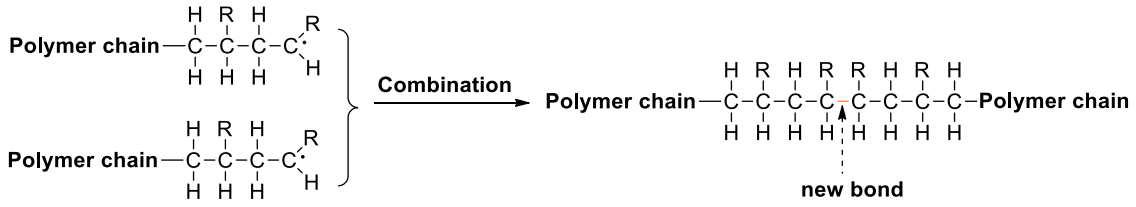


For mainly steric reason, the addition reactions are head-to-tail combination; head-to-head combinations are less favoured. If the X group is very small, head-to-head combination may observe. e.g vinyl fluoride, CH_2=CHF, has 16% H-H combinations.

11.4.1.3 Chain Termination

Chain termination may occur by two ways depending on factors such as temperature, time and monomer & initiator concentration; - (a) Termination by Combination and (b) Termination by Disproportionation.

In the first case two growing centres unite by coupling of the free radicals to form an electron pair, thus nullify their reactiveness. Actually, this process requires no external energy (free energy). In the second case, one H• from one growing chain is abstracted by the other growing chain and two polymer molecules are formed. This process requires energy. Hence termination by disproportionation generally happens at relatively high temperature. e.g in PMMA at 60 to 70ºC the termination is mainly by disproportionation.

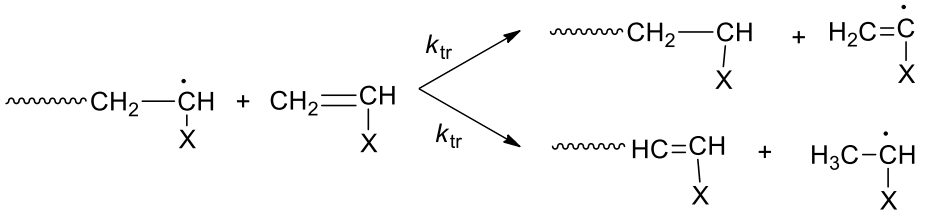




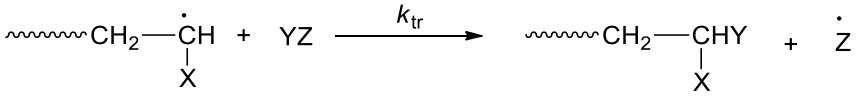
11.4.1.4 Chain Transfer Reactions

Termination of a growing polymer chain can take place also through chain transfer which could be represented as-

(a) Chain transfer to monomer



(b) Chain transfer to solvent or chain transfer agent



A chain transfer agent used for the purpose of controlling the molecular weight of polymer is called **chain modifier**. The modifiers prevent the uncontrolled growth of a polymer chain. Example of chain modifiers are, - diisopropyl xanthate disulphate, mercaptans etc.

A substance which acts as a chain-transfer agent produces less reactive free radical is known as **retarder** to slow down the rate of polymerisation. e.g nitrobenzene, oxygen etc.

An additive which reacts with an active chain-forming radical to produce non-radical products or radicals of low reactivity, incapable of adding fresh monomer units is called **inhibitor** to stop the polymerisation. e.g benzoquinone, DPPH, Catechol etc. If higher quantity of a retarder is used, they may inhibit a polymerization.

When the monomer itself acts as retarder or inhibitor and leads to degradative chain transfer, the phenomenon is known as **autoinhibition**.

W CHECK YOUR PROGRESS

Q3. Write the mechanism of polymerisation of styrene initiated by alkyl free radical R^* to form polystyrene.

Q4. Write the general mechanism of polymerisation of unsaturated monomer M using AIBN as initiator.

11.4.2 IONIC POLYMERISATION

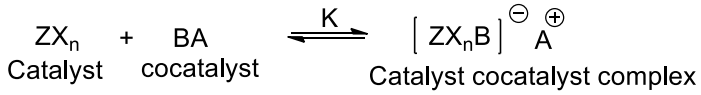
11.4.2.1 Cationic Polymerization

Generally, monomers with electron donating or releasing substituents such as alkoxy, 1,1-dialkyl or diaryl, phenyl and vinyl etc. are susceptible to cationic polymerization.

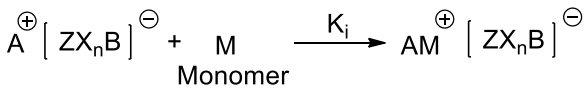
Mechanism:

A general kinetic scheme for cationic polymerization may be written as-

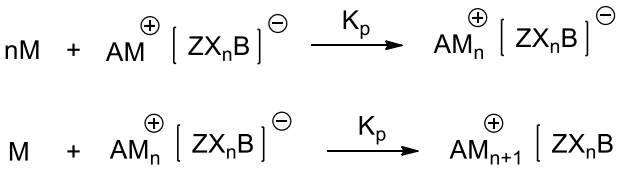
Pre-initiation equilibrium



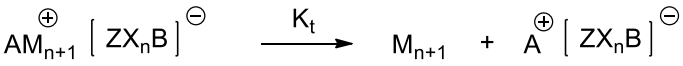
Initiation



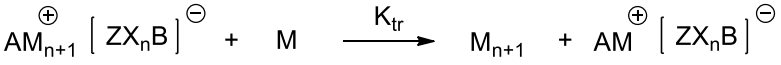
Propogation



Termination



Transfer



Kinetics:

Rate of initiation, $R_i = k_i[M][C]$

where, C is the catalyst-cocatalyst complex.

Rate of termination, $R_t = k_t[M^+]$

Rate of chain transfer, $R_{tr} = k_{tr}[M^+][M]$

Under steady state, $R_i = R_t$

$k_i[M][C] = k_t[M^+]$

Therefore, $[M^+] = \frac{k_i}{k_t}[M][C]$

Rate of propagation (equivalent to rate of polymerisation),

$$R_p = k_p[M^+][M] = k_p.\frac{k_i}{k_t}[M]^2[C]$$

Assuming little chin transfer, average degree of polymerization,

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p}{k_t}[M]$$

For termination exclusively by monomer transfer, -

$$\bar{X}_n = \frac{R_p}{R_{t_r}} = \frac{k_p[M^+][M]}{k_{t_r}[M^+][M]} = \frac{k_p}{k_{t_r}}$$

If both termination and transfer take place,

$$\bar{X}_n = \frac{R_p}{R_t + R_{tr}} = \frac{k_p[M]}{k_t + k_{t_r}[M]}$$

The above kinetic scheme is agreed with the polymerization of styrene initiated by *$SnCl_4$* in ethylene dichloride at 298K. However, the above scheme is not universally applicable.

More about initiation step:

Cationic polymerization may be initiated by-

(i) Classical protonic acids; e.g. H_2SO_4, $HClO_4$ etc.

(ii) Lewis acids/ Friedel craft catalyst; e.g. BF_3, $AlCl_3$, $SnCl_4$, $AlBr_3$, $TiCl_4$, etc.

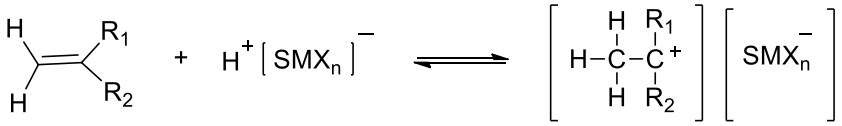
(iii) Carbonium ion salts; e.g. Triphenyl methyl salts ($Ph_3C^+ X^-$), Tropylium salts ($C_7H_7^+ X^-$) , where X^- may be stable anion such as ClO_4^-, $SbCl_6^-$, PF_6^-.

(iv) By charge transfer mechanism

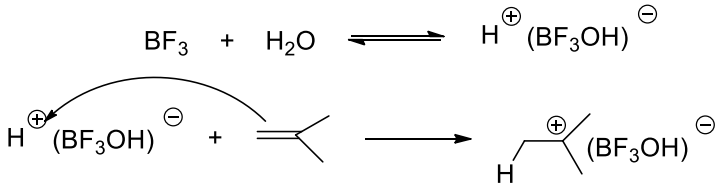
Almost all Lewis acids or Friedel-Craft catalysts become effective in the presence of a co-catalyst, which complexes with the catalyst and acts as a proton donor. Co-catalyst may be water, alcohol, organic acids, alkyl halide or even hydrogen.

$$MX_n + SH \leftrightharpoons [SMX_n]^- H^+$$

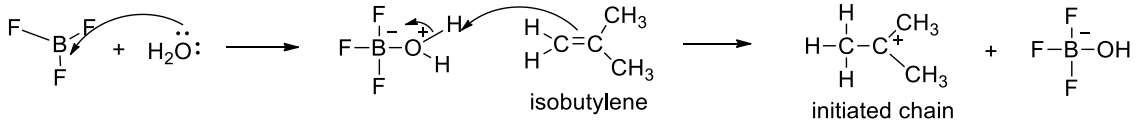
The probable initiation mechanism is-



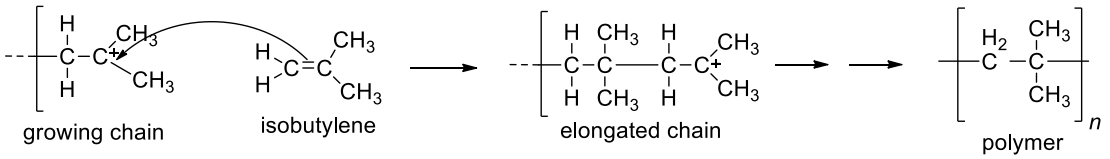
The presence of co-catalyst can be exemplified by the polymerization of isobutylene. If polymerization of isobutylene with BF_3 in absence of water (i.e. anhydrous condition) is carried out, no polymerization occurs; if trace amount of moisture is used, the reaction occurs. The nature of the co-catalyst is such that it gives up proton to the catalyst BF_3.



Or,



Propogation step: Another molecule of monomer adds to the chain



Similarly, if the polymerization reaction is carried out in presence of $SnCl_4$ as catalyst, then CH_3COOH, nitrobenzene, phenol and water may be used as co-catalyst.

Iodine can also initiate a polymerization reaction, -

$2I_2 \rightarrow I^+I_3^-$; where, I^+ is the catalyst and I_3^- is the co-catalyst.

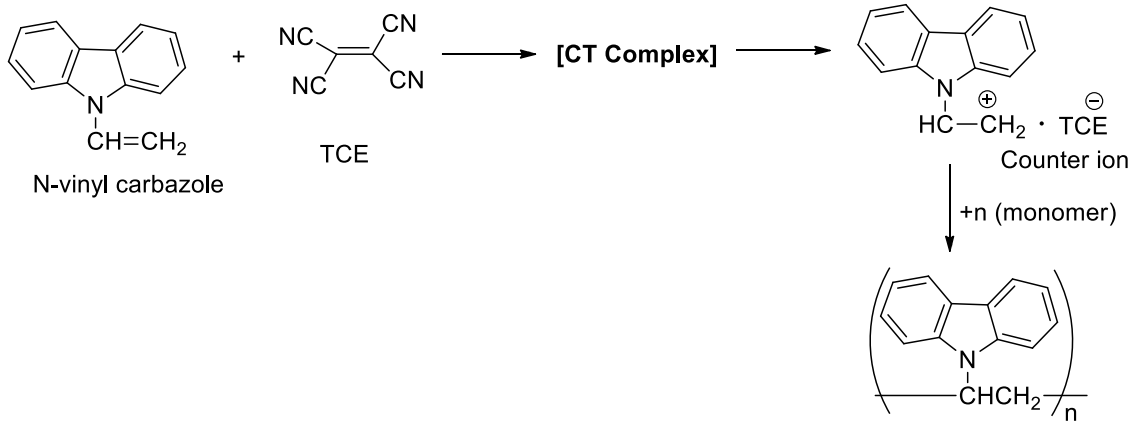
$CH_2 = CHR + I^+I_3^- \rightarrow I^-CH_2C^+(HR).I_3^-$

For the formation of catalyst-co-catalyst complex high energy radiation are used; such condition also produces free radicals. Therefore, it may not purely cationic polymerization.

The general scheme cationic polymerisation using charge transfer initiator is-

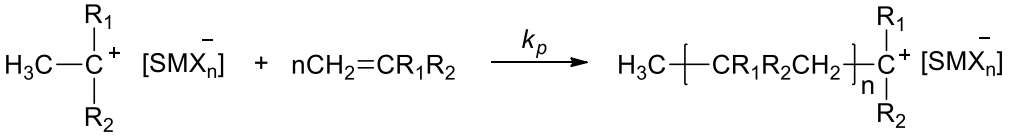
Monomer + Acceptor → [Charge transfer complex] $\xrightarrow{heat\ or\ hv}$ dissociated product $\xrightarrow{+\ monomer}$ $Polymer$

Common acceptors are p-chloramine, tetracyanoethylene (TCE). e.g.



More about Propagation Step:

Polymerization by cationic chain carriers can be shown as-



Note that the counter ion remain close to the growing carbonium ion.

If BF_3 is used as catalyst the reaction is very fast but if $SnCl_4$ is used, it takes several days. The effect of medium (solvent) and catalyst type on the rate of propagation can be understood from the following **Table 11.1**.

Table 11.1: Kinetic data for polymerisation of styrene in various condition (CCl_4: tetrachloromethane; $(CH_2Cl)_2$: 1, 2-dichloroethane)

Solvent	Dielectric constant, ε	Catalyst	Rp, ($dm^3\ mol^{-1}\ sec^{-1}$)
CCl_4	2.3	$HClO_4$	0.0012
$CCl_4 + (CH_2Cl)_2$ (40:60)	5.16	$HClO_4$	0.4
$CCl_4 + (CH_2Cl)_2$ (20:80)	7	$HClO_4$	3.2
$(CH_2Cl)_2$	9.72	$HClO_4$	17.0
$(CH_2Cl)_2$	9.72	$TiCl_4/H_2O$	6.0
$(CH_2Cl)_2$	9.72	I_2	0.003

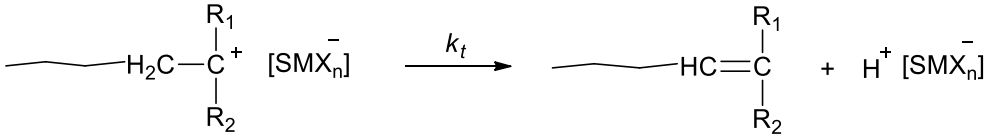
The above table indicates that if dielectric constant (hence polarity of the medium) of the solvent increases, the rate of propagation increases provided that the catalyst used is same. This is due to the fact that a highly polar solvent can separate the ion-pair (i.e. the cation and the counter ion) and hence a monomer can approach to the cationic chain carrier.

The table also implies that rate of propagation also depends on the catalyst used as an initiator. The I_2 initiated polymerization is 2000 times slower than the $TiCl_4/H_2O$ initiated system although the solvent polarity is kept same (ε = 9.72). This is due to the fact that the I_3^- counter ion is very larger than $[TiCl_4OH^-]$ and hence large steric effect.

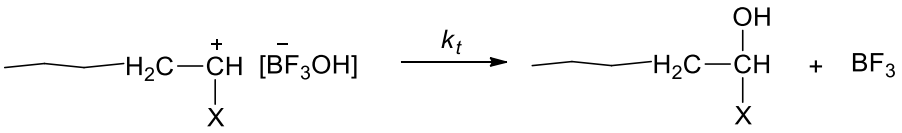
More about Termination Step:

Termination may be unimolecular termination or bimolecular transfer.

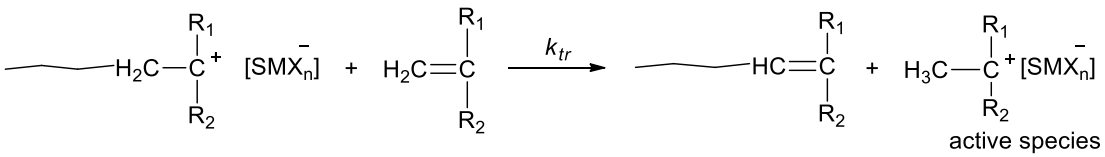
(a) Unimolecular rearrangement of the ion pair.



Or,



(b) Bimolecular transfer reaction with monomer



11.4.2.1 Anionic Polymerization

Basic compounds such as amides, alkoxides, alkyls and aryls of alkali metals and different Grignard reagents have been used as catalysts for anionic polymerization of monomers having electron withdrawing substituents.

Mechanism:

A general scheme for the anionic polymerization may be written as –

Ion-pair formation; $IA \xrightarrow{k_d} I^+A^-$

Initiation; $I^+A^- + M \xrightarrow{k_i} AM^-I^+$

Propagation; $AM^-I^+ + M \xrightarrow{k_p} AMM^-I^+$

$AMM^-I^+ + (n-1)M \xrightarrow{k_p} AM_nM^-I^+$

Termination; $AM_nM^-I^+ + HA \xrightarrow{k_t} AM_nMH + A^-I^+$

Where, IA is the initiator, HA is a protonating agent and k_d, k_i, k_p and k_t are the dissociation, initiation, propagation and termination rate constant respectively.

Kinetics:

Assuming that the initiator IA is completely dissociates very before the addition of monomer M, the rate of polymerization can be determined.

$$R_i = k_i[A^-][M]$$
$$R_p = k_p[AM^-][M]$$
$$R_t = k_t[AM^-][HA]$$

Applying steady state approximation,

$$R_i = R_t$$
$$k_i[A^-][M] = k_t[AM^-][HA]$$
$$[AM^-] = \frac{k_i[A^-][M]}{k_t[HA]}$$

Therefore, $R_p = \frac{k_p k_i}{k_t}\frac{[A^-][M]^2}{[HA]}$

Degree of polymerization:

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p}{k_t}\frac{[M]}{[HA]}$$

In anionic polymerization, actually termination step not involves, then-

Case-I: if the initiating species is a monoanion, then,

$$\bar{X}_n = \frac{[M]}{[IA]}.$$

$$\bar{X}_n = \frac{\frac{m_{monomer}}{M_{monomer}}}{\frac{m_{initiator}}{M_{initiator}}} = \frac{m_{monomer}}{M_{monomer}} \times \frac{M_{initiator}}{m_{initiator}}$$

$$\bar{M}_n = \frac{m_{monomer}.M_{initiator}}{m_{initiator}}$$

Case-II: For dianion propagation,

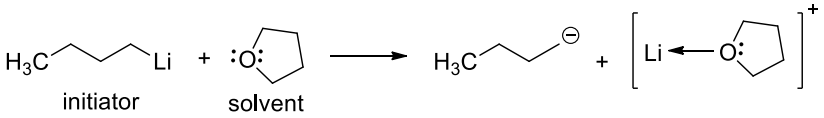
$$\bar{X}_n = 2\frac{[M]}{[IA]}$$

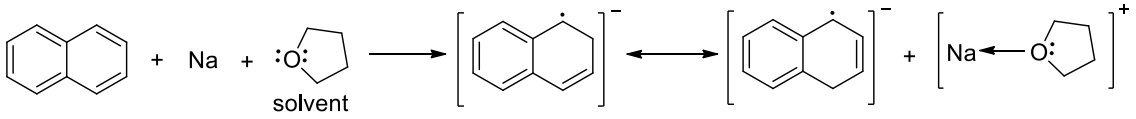
$$\bar{X}_n = 2\frac{m_{monomer}}{M_{monomer}} \times \frac{M_{initiator}}{m_{initiator}}$$

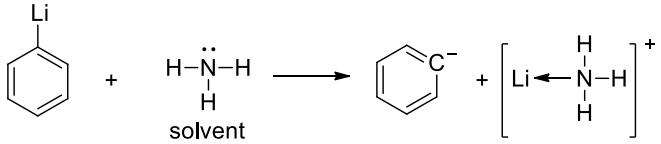
$$\bar{M}_n = 2\frac{m_{monomer}.M_{initiator}}{m_{initiator}}$$

More about Initiation and Propagation:

Initiator may be phenyl lithium, butyl lithium, sodium naphthalene in solvent with unshared electron pairs (i.e. the solvent should be Lewis base e.g. THF, ammonia etc.)



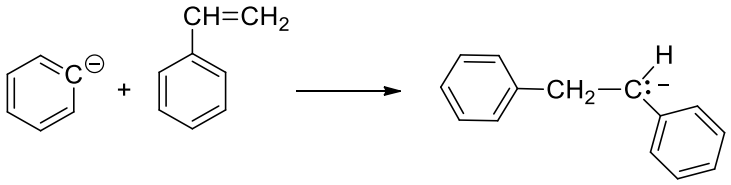




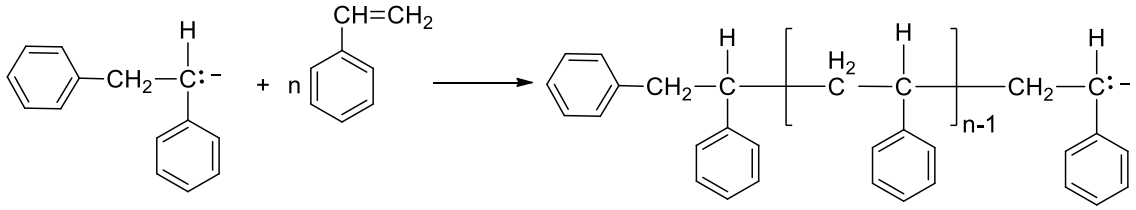
Let us consider the polymerization of styrene-

(a) With phenyl Lithium as initiator:

Initiation step:

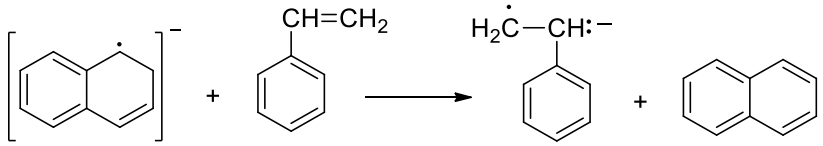


Propagation step:



(b) With sodium naphthalene as initiator:

Initiation:

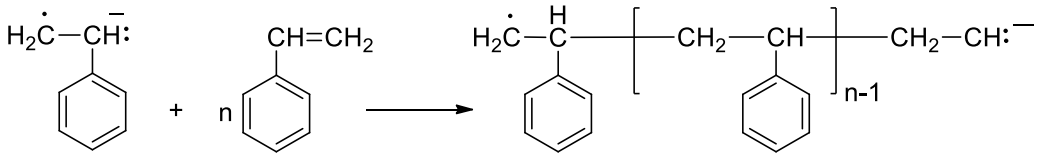


Propagation:

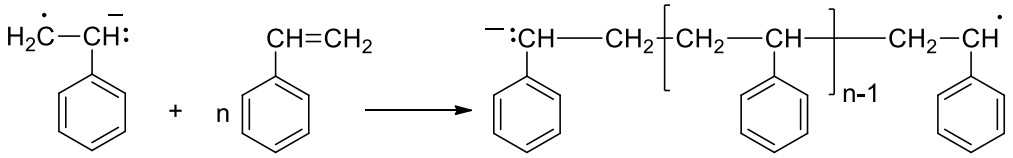
The propagation can take place by two ways-

Propagation (A):

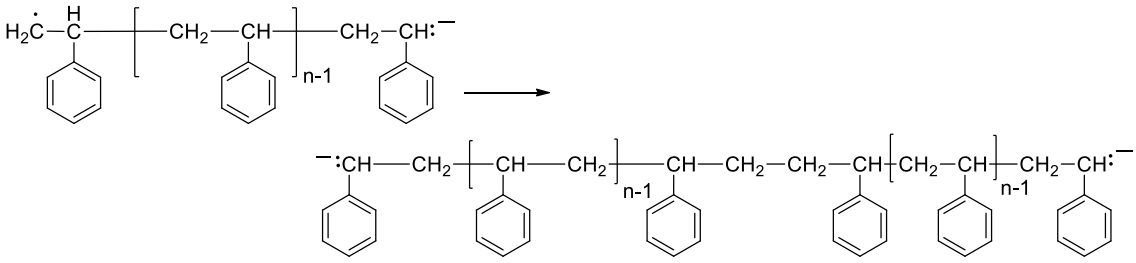
† Propagation at anionic end:



†† Propagation at the radical end:

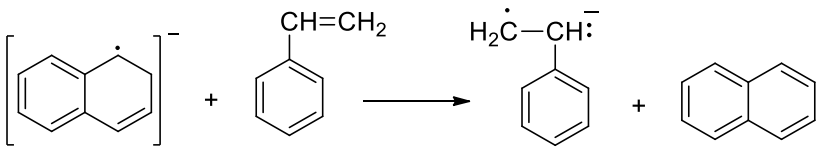


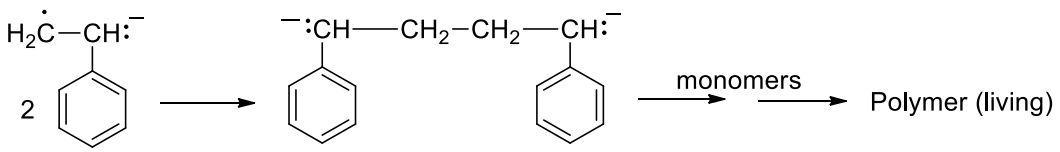
††† propagation by radical combination:



Propagation (B):

Dianion is first formed and the chain growing takes place at both ends.

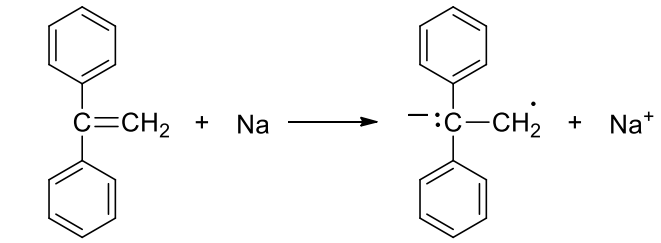




More about Termination:

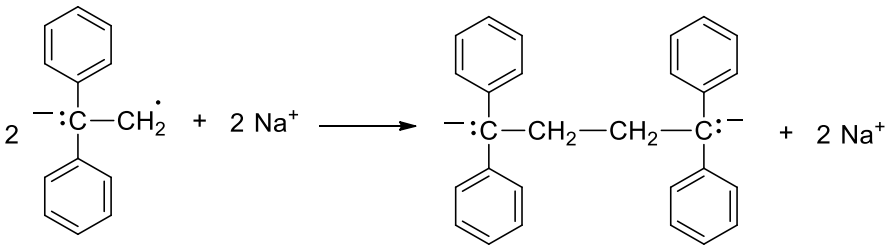
Termination takes place only in the presence of impurity such as water, CO_2 etc. which requires in trace quantities. E.g.

Initiation:

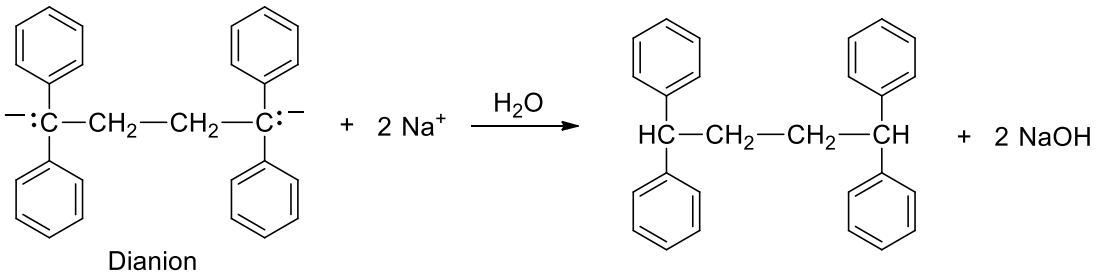


Diphenyl ethylene

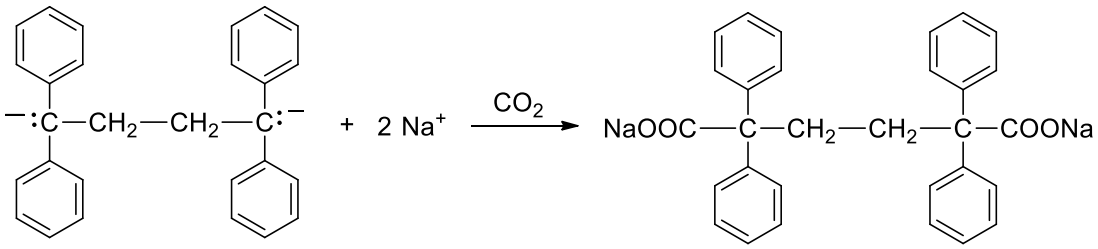
Dianion formation:



Termination:



Dianion



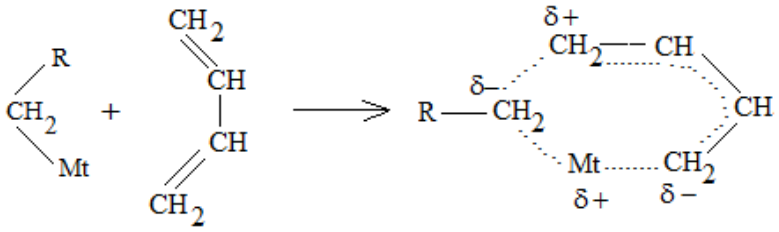
Dianion

CHECK YOUR PROGRESS

Q5. For the formation of polystyrene of molecular weight 3000000 from 1Kg styrene, how much sodium will necessary?

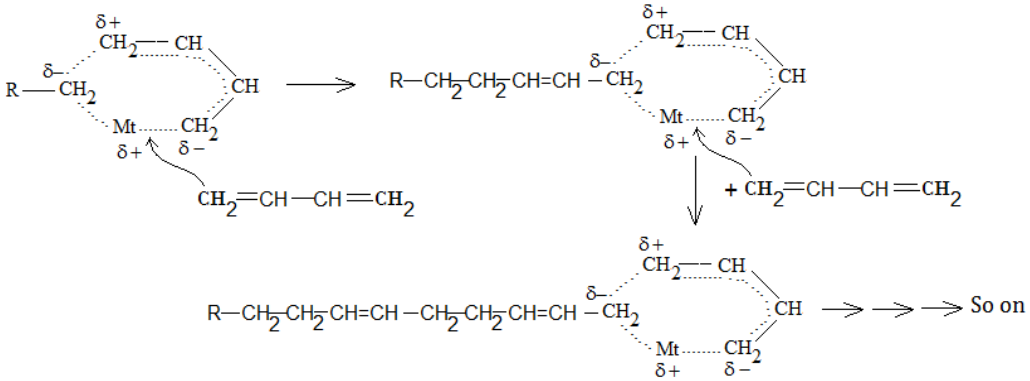
11.5 COORDINATION POLYMERISATION

Polymerization often carried out with dienes and olefins catalyzed by organometallic compounds, fall under the category of coordination polymerization. The first step is the formation of a monomer-catalyst complex between the organometallic compound and the monomer.

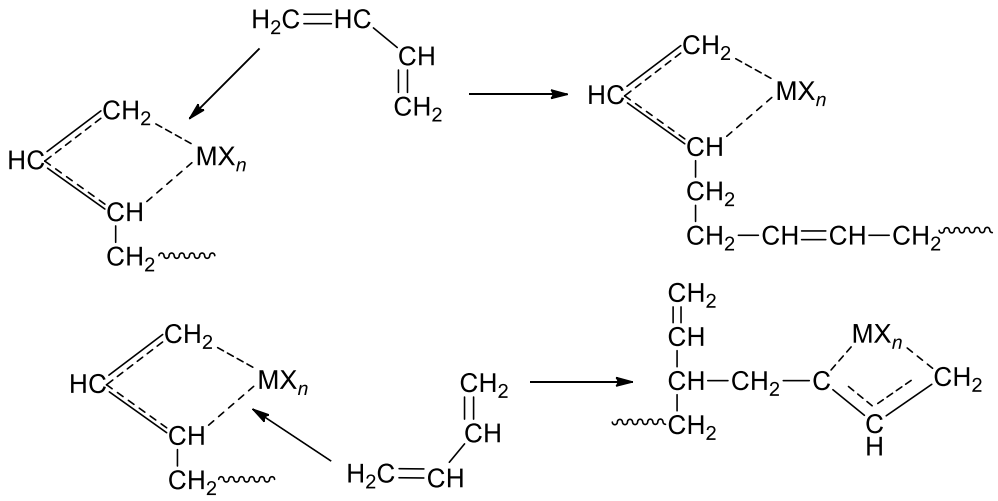


Where, *Mt* represents transition metals such as Ti, Mo, Cr, V, Ni, etc. Here a coordination bond is formed between a carbon atom of the monomer and the metal of the catalyst; hence the name coordination polymerization.

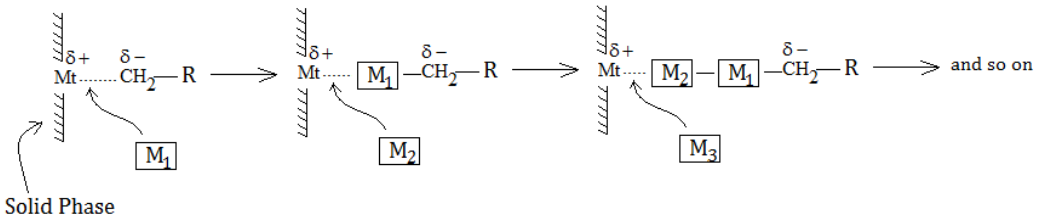
The coordinated metal-carbon bond formed in the monomer-catalyst complex acts as the active centre from where propagation starts.



In the polymerization of butadiene, 1, 2- and 3, 4-addition may occur beside 1, 4-addition.



In coordination polymerization, the catalyst-monomer complex is a heterogeneous system, with the metal ion in the solid phase and the carbanion of the alkyl group in the solvent phase. The monomer is inserted in between the metal ion and the carbanion with the result that the polymer chain formed is pushed out from the solid catalyst surface. It is for this reason; coordination polymerization is also known as insertion polymerization.



Ziegler-Natta catalyst:

Coordination polymerisation, often catalysed by **Ziegler-Natta catalysts**, involves the formation of a monomer-metal complex followed by insertion of the monomer into a metal-carbon bond, producing **stereoregular polymers**. Polymerization which results in the formation of an ordered structure is called stereospecific polymerization and the ordered structures are called stereoregular polymers.

It is a special type of coordination catalyst, comprising of two components as against one component organometallic compounds. The two components are generally referred to as Catalyst and Co-catalyst. The catalyst components consist of halides of group IV to VIII elements having transition valence and the co-catalysts are organometallic compounds such as alkyls, aryls of group I to IV metals. $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$ in combination with $TiCl_3$ and $TiCl_4$ are most commonly used. Ziegler Natta catalysts are used for the synthesis of stereoregular polymers.

11.6 COPOLYMERISATION

Copolymerization is a process of polymerizing two or more monomer units or monomer pair simultaneously. The polymer that composed of more than one type (generally two) of repeat units (monomer) are called copolymers. Four types of copolymers are-

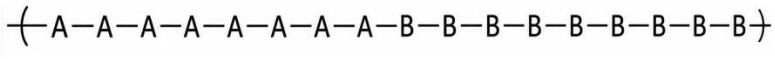
(a) **Random copolymer**: In a random copolymer, the two different monomer units are distributed randomly along the polymer chain without any regular pattern. If A and B represent two different types of monomer units, then, -

$$–A–A–B–A–B–B–A–B–A–$$

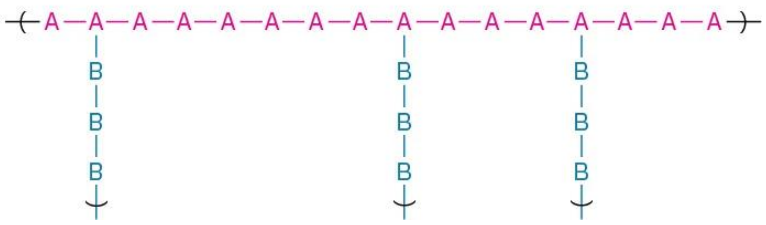
(b) **Alternating or Regular copolymer**: In an alternating copolymer, the two monomer units occur in a strictly alternating sequence along the chain as shown below.

$$–A–B–A–B–A–B–A–B–$$

(c) **Block copolymer**: A block copolymer contains long sequences (blocks) of one monomer followed by blocks of another monomer as shown below.



(d) **Graft copolymer**: In a graft copolymer, the main polymer chain is made of one type of monomer, while side chains of another polymer are attached (grafted) onto the backbone.



Technical significance of copolymerization:

The modification of a polymer by introducing a second monomer during polymerization process has long been used to alter the physical properties and sometimes to achieve processing characteristics. Incorporation of a second monomer structure as repeating unit in a copolymer, reduces overall molecular symmetry leading to lowering (or loss) of degree of crystallinity and of softening temperature; i.e. glass transition temperature can be decreased. Thus, a "softer" polymer is made. Therefore, copolymerization is considered as a case of internal plasticization.
By combining different monomers and produce copolymers it is possible to "tailor-make" the final polymer. So, there are practically unlimited scopes of variation of polymer structure and polymer properties through copolymerization. e.g.

Kinetics of Copolymerization:

The four chain propagation reactions in a binary copolymerization may be-

$$\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1^*$$

$$\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim M_2^*$$

$$\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_1^*$$

$$\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim M_2^*$$

The rate of disappearance of M_1 monomer-

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \qquad (11.6)$$

The rate of disappearance of M_2 monomer-

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \quad (11.7)$$

Dividing (11.6) by (11.7), we have-

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1]+k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2]+k_{22}[M_2^*][M_2]} \quad (11.8)$$

Applying the steady state approximation,

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \quad (11.9)$$

Putting the $[M_1^*]$ from equation (11.9) in equation (11.8) we have,

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}k_{21}[M_2^*][M_1]^2}{k_{12}[M_2]}+k_{21}[M_2^*][M_1]}{k_{21}[M_2^*][M_1]+k_{22}[M_2^*][M_2]} \quad (11.10)$$

Let,

$$r_1 = \frac{k_{11}}{k_{12}} \;\&\; r_2 = \frac{k_{22}}{k_{21}}$$

Where, r_1 and r_2 are called reactivity ratios.

Rearranging the above equation and putting the value of r_1 and r_2 we have,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])} \quad (11.11)$$

Where, $d[M_1]$ is the amount of M_1 present in the polymer, $[M_1]$ is the amount of M_1 taken in the feed ratio.

If $f_1 \& f_2$ are the mole fraction of monomer $M_1 \& M_2$ in the feed and $F_1 \& F_2$ are the mole fraction of monomer $M_1 \& M_2$ in the copolymer, then-

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1]+[M_2]}$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1]+d[M_2]}$$

Putting these values in equation (11.11), we have-

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (11.12)$$

and,

$$\frac{F_1}{F_2} = \frac{f_1(r_1 f_1 + f_2)}{f_2(r_2 f_2 + f_1)} \quad (11.13)$$

Equations (11.11), (11.12) and (11.13) are known as **copolymerization equation**.

Reactivity ratios and its significance:

Reactivity ratio is defined as the ratio of the rate constant for a propagating species adding to its own monomer to the rate constant for its addition to the other monomer.

$$r_1 = \frac{k_{11}}{k_{12}} \ \& \ r_2 = \frac{k_{22}}{k_{21}}$$

The value of $r_1 > 1$ means that chain radical M_1^* has a preference to add the like monomer M_1 over unlike monomer, M_2 and $r_1 < 1$ is just the opposite case. The same concept applies for r_2. The copolymer equation can be used to predict chain structure in the different ways, already mentioned.

Case-1: The formation of regular alternating copolymers of the type ABABAB…… is favoured when each growing radical prefers to add to monomer of the opposite type. In this case

$$r_1 \approx r_2 \approx 0$$

and Equation (11.11) therefore becomes $\frac{d[M_1]}{d[M_2]} = 1$ or $d[M_1] = d[M_2]$. In other words, both monomers will disappear from the reaction vessel at the same rate.

Case-2: An ideal copolymer will tend to form when each type of chain end shows an equal preference for adding on to either monomer. In this case,

$$r_1 = \frac{1}{r_2}$$

and the copolymer equation becomes

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]}$$

Hence composition depends on the relative amounts of monomer present at any time and the relative reactivities of the two monomers.

Case-3: Block copolymers are formed when the growing chain end has a marked preference for adding on to the same kind of monomer. In this case $r_1 > 1$ and $r_2 > 1$.

Case-4: When $r_1 \gg 1$ and $r_2 \gg 1$, then probably two independent homopolymers should be obtained.

Azeotropic copolymerization: When $r_1 < 1$ and $r_2 < 1$, the propagation type 12 & 21 are preferred over 11 & 22. M_2 can add on to M_1^* , M_1 can add on to M_2^* at the same time. The preference for one of these two will depends on the actual value of r_1 and r_2 and also on monomer feed ratio. e.g. when r_1 and r_2 are equal, the copolymer formed will be richer in M_1 upto an f_1 values of 0.5 and then onwards the copolymer will be richer in M_2. Hence, under this condition, when $f_1 = 0.5$, then $F_1 = 0.5$. That means copolymer composition and monomer feed composition are the same. It is called azeotropic composition (**Figure 11.3**).

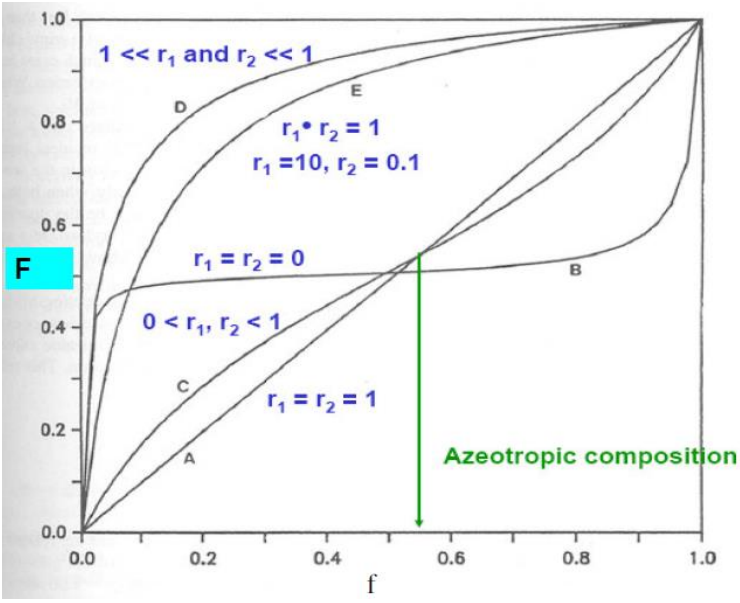


Figure 11.3: Copolymerisation behaviour as a function of reactivity ratios and monomer feed ratios.

2 11.7 LET US SUM UP

Polymerisation is the chemical process in which small molecules called monomers combine to form large macromolecules known as polymers. These reactions are essential for producing many important materials such as plastics, fibres, rubbers, and resins. Polymerisation reactions are broadly classified into **step-growth** (condensation) polymerisation and **chain-growth** (addition) polymerisation.

In condensation polymerisation, bifunctional or polyfunctional monomers react step by step to form polymers, often with the elimination of small molecules such as water or HCl. Important concepts in this process include average functionality, extent of reaction, and degree of polymerisation. **Carothers' equation** relates the extent of reaction to the degree of polymerisation and helps predict the formation of cross-linked networks at the **gel point**. Molecular weight in such reactions can be controlled by stoichiometric imbalance or by adding monofunctional compounds. Some cyclic compounds may also polymerise through **ring-opening polymerisation**.

In addition polymerisation, unsaturated monomers polymerise through chain reactions without forming by-products. The process involves initiation, propagation, and termination steps and may occur through free radical, cationic, or anionic mechanisms. Free radical polymerisation is widely used and may involve chain transfer, retarders, and inhibitors.

The unit also discusses **copolymerisation**, where two or more types of monomers polymerise together to form copolymers such as random, alternating, block, and graft types. Copolymerisation is important for modifying polymer properties and tailoring materials for specific applications.

K 11.8 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1:

$$r = \frac{100}{102} = 0.98$$

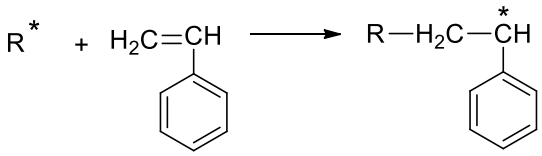
$$\bar{X}_n = \frac{1+r}{1+r-2rp} = \frac{1+0.98}{1+0.98-2\times 0.98\times 0.98} = 33.44 = 33$$

Answer to Q2:

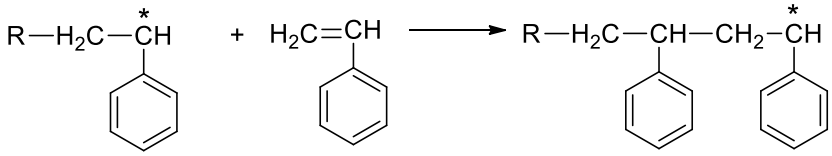
$$\bar{X}_n = \frac{1+r_1}{1+r_1-p} = \frac{1+\frac{2}{98}}{1+\frac{2}{98}-0.98} = 25$$

Answer to Q3:

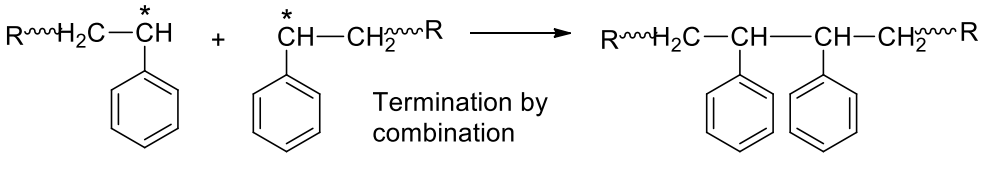
Initiation

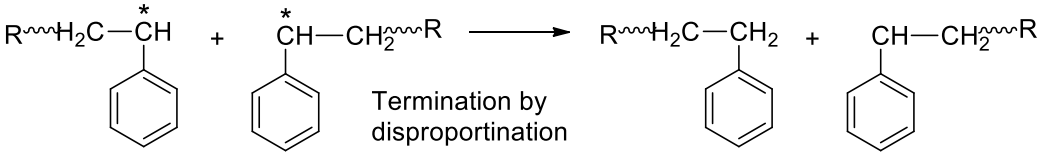


Propogation



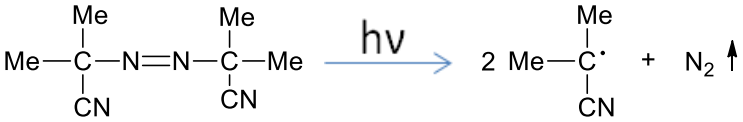
Termination

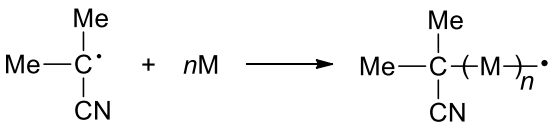


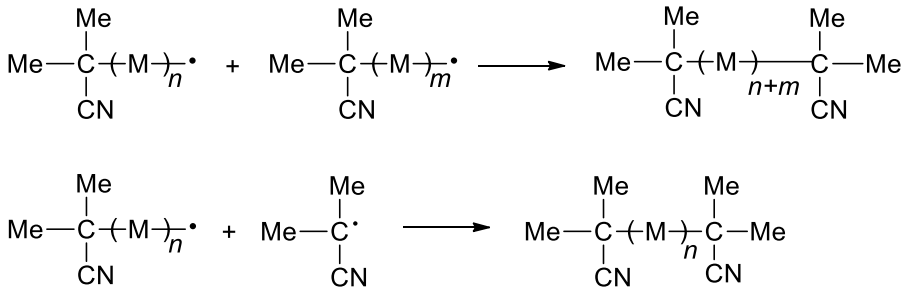


Answer to Q4:

Polymerization using AIBN as initiator:







Answer to Q5:

Here,

$$\bar{M}_n = 3000000,\ m_{monomer} = 1Kg = 1000g\ ,\ M_{initiator} = 23g$$

Since,

$$\bar{M}_n = 2\frac{m_{monomer}.M_{initiator}}{m_{initiator}}$$

$$3000000 = 2 \times \frac{1000 \times 23}{m_{initiator}}$$

$$\therefore m_{initiator} = 0.0153g$$

i.e. very trace quantity of the initiator is necessary. Similarly, trace quantities of impurity (H_2O/CO_2) are required to stop the reaction.

O 11.9 FURTHER READING

- Billmeyer, F. W., Jr. (1984). *Textbook of polymer science* (3rd ed.). New York: John Wiley & Sons.
- Misra, G. S. (1993). *Introduction to polymer chemistry*. New Delhi: Wiley Eastern Limited.
- Gowariker, V. R., Viswanathan, N. V., & Sreedhar, J. (1986). *Polymer science*. New Delhi: New Age International Publishers.

M 11.10 MODEL QUESTIONS

Q1. Define polymerisation. Distinguish between step-growth polymerisation and chain-growth polymerisation.

Q2. What is condensation polymerisation? Explain the difference between condensation reaction and polycondensation reaction with suitable examples.

Q3. What is meant by self-polycondensation? Under what conditions does this type of polymerisation occur?

Q4. Define the following terms used in polycondensation reactions:
(a) Average functionality
(b) Extent of reaction
(c) Degree of polymerisation

Q5. State and explain Carothers' equation. What information does it provide about step-growth polymerisation?

Q6. What is the gel point in polycondensation reactions? Why is it important in polymer synthesis? Why gelation occurs very before the theoretical gel point value?

Q7. Discuss the methods used to control the molecular weight in condensation polymerisation.

Q8. Describe the mechanism of free radical polymerisation with suitable example.

Q9. Differentiate between cationic and anionic polymerisation. Mention the types of monomers and initiators involved in each case.

Q10. What is copolymerisation? Describe the different types of copolymers formed in this process.

UNIT 12: SURFACE CHEMISTRY AND SURFACTANTS

UNIT STRUCTURE

12.1 Learning Objectives
12.2 Introduction
12.3 Nature of Surfaces
12.4 Thermodynamics of Adsorption Processes
  12.4.1 Gibbs Free Energy Change (ΔG)
  12.4.2 Enthalpy Change (ΔH)
  12.4.3 Entropy Change (ΔS)
12.5 Physical and Chemical Adsorption
12.6 Adsorption Isotherms
  12.6.1 Langmuir Adsorption Isotherm
  12.6.2 BET Adsorption Isotherm
12.7 Determination of Surface Area of Adsorbents
12.8 Capillary condensation, Adsorption in micropores and hysteresis loop
12.9 Surfactants: Definition and Classification
  12.9.1 Anionic Surfactants
  12.9.2 Cationic Surfactants
  12.9.3 Non-ionic Surfactants
  12.9.4 Amphoteric (Zwitterionic) Surfactants
12.10 Micelle Formation and Critical Micelle Concentration (CMC)
  12.10.1 Shape of Micelles
  12.10.2 Critical Micelle Concentration (CMC)
  12.10.3 Thermodynamics of Micellization
12.11 Reverse Micelles, Solubilisation and Microemulsions
  12.11.1 Reverse Micelles
  12.11.2 Solubilisation
  12.11.3 Microemulsions
12.12 Let Us Sum Up
12.13 Answers to Check Your Progress
12.14 Further Reading
12.15 Model Questions

12.1 LEARNING OBJECTIVES

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

- explain the nature of surfaces and their role in adsorption phenomena.
- understand the thermodynamic aspects of adsorption processes like enthalpy, entropy and Gibbs free energy ones.
- differentiate between physical adsorption and chemical adsorption.
- understand the Langmuir and the BET adsorption isotherms and explain their significance.
- determine the surface area of adsorbents using adsorption techniques.

- describe capillary condensation, adsorption in micropores, and the formation of hysteresis loops.
- define and classify surfactants.
- understand and explain the concept of micelle formation and critical micelle concentration (CMC).
- describe reverse micelles, solubilisation, and microemulsions with their importance.

12.2 INTRODUCTION

This is the first unit of Surface Chemistry and Catalysis section. We will start with the basics of surface chemistry. Surface chemistry is an interdisciplinary area of science that has gained substantial importance in industrial processes and technology over the years, and is expected to play an even greater role in the future. It deals with the study of phenomena occurring at the interfaces of different phases, such as solid-liquid, liquid-liquid and solid-gas interfaces. The atoms or molecules present at a surface possess residual unbalanced forces and excess energy compared to those in the bulk, giving rise to unique surface properties. These surface characteristics play a crucial role in many physical and chemical processes, particularly adsorption. The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as **adsorption.**

The solid that takes up a gas or vapour, or a solute from a solution is known as the **adsorbent** while the gas or vapour or the solute, which is held to the surface of the solid is known as the **adsorbate**. The extent and nature of adsorption depend on the surface properties of the adsorbent and the thermodynamic conditions of the system. Understanding the thermodynamics of adsorption helps in explaining the feasibility and the spontaneity of adsorption processes.

Adsorption is very much different from absorption. Adsorption may occur through weak intermolecular forces (physical adsorption or physisorption) or through the chemical bonds (chemical adsorption or chemisorption). These two types of adsorption differ significantly in their mechanism, energy changes, and reversibility. The quantitative relationship between the amount of substance adsorbed and the pressure or the concentration at constant temperature is described by adsorption isotherms. Among these, the Langmuir and the BET isotherms are widely used to explain monolayer and multilayer adsorption respectively, and to determine surface areas of the solid adsorbents.

In porous solids, the adsorption process is not limited to the formation of adsorbed layers on the external surface but is significantly affected by the presence of pores of different sizes and shapes within the solid. In mesoporous and microporous materials, adsorption may occur through **capillary condensation**, where the adsorbate condenses within the pores at pressures lower than the saturation vapour pressure of the adsorbate. In **micropores**, whose dimensions are comparable to the size of the adsorbate molecules, adsorption occurs by a pore-filling mechanism rather than by layer-by-layer adsorption. The strong overlap of adsorption potentials from opposite pore walls leads to higher adsorption capacity at low relative pressures. During adsorption and desorption, the pathways followed by the adsorbate molecules are

often different, resulting in *hysteresis loops* in adsorption-desorption isotherms. These phenomena are important in understanding the structure and pore size distribution of adsorbents.

Surfactants or surface-active agents are another important class of surfaces and interfaces that lowers surface or interfacial tension. Because of their ability to reduce interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents etc. They consist of both hydrophilic and hydrophobic parts and are classified based on the nature of the hydrophilic group. At a particular concentration known as the critical micelle concentration (**CMC**), surfactant molecules aggregate to form micelles. In non-aqueous systems, reverse micelles may form, leading to solubilisation and the formation of microemulsions. These concepts are of great significance in detergents, pharmaceuticals, catalysis, and industrial applications.

12.3 NATURE OF SURFACES

A surface is formed when a bulk phase (solid or liquid) gets terminated. The behaviour of molecules or atoms present at the surface differ significantly from those in the bulk because they are not completely surrounded by similar neighbouring particles. As a result, surfaces exhibit special physical and chemical properties. Surfaces possess higher free energy, experience unbalanced cohesive forces and are more reactive than bulk molecules.

Surface free energy is the excess energy of surface molecules compared to those in the bulk. Systems naturally tend to minimize surface free energy, leading to adsorption and surface rearrangements. Molecules in the bulk experience equal attractive forces from all directions, resulting in no net force. In contrast, surface molecules experience *unbalanced cohesive forces*, since there are fewer neighbouring particles on the outer side. Due to excess energy and unsatisfied bonds, surface atoms or molecules are in a thermodynamically unstable state compared to bulk molecules. As a result, they are *more reactive* than that of bulk molecules.

12.4 THERMODYNAMICS OF ADSORPTION PROCESSES

Adsorption is a surface phenomenon in which atoms, ions, or molecules of a substance (adsorbate) accumulate on the surface of another substance (adsorbent). The feasibility, extent and nature of adsorption process are governed by thermodynamic parameters. These parameters are Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS).

12.4.1 Gibbs Free Energy Change (∆G)

The spontaneity of an adsorption process is determined by the change in Gibbs free energy ΔG, which, at a given temperature T, is related to the change in enthalpy ΔH and in entropy ΔS as:

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

- For adsorption to be **spontaneous**, ΔG must be **negative**.

- In most adsorption processes, ΔG is negative at low temperatures, indicating that adsorption occurs naturally.
- As temperature increases, ΔG becomes less negative, leading to decreased adsorption. This is because for an adsorption process, ΔS is generally negative.

Thus:

(i). $\Delta G < 0 \rightarrow$ spontaneous adsorption
(ii). $\Delta G = 0 \rightarrow$ equilibrium state
(iii). $\Delta G > 0 \rightarrow$ non-spontaneous adsorption

12.4.2 Enthalpy Change (ΔH)

Adsorption is generally an exothermic process, as energy is released when adsorbate molecules adhere to the surface. Negative ΔH favours adsorption at lower temperatures. According to Le Chatelier's principle, extent of adsorption so decreases with rise in temperature.

12.4.3 Entropy Change (ΔS)

Entropy change reflects the change in the degree of **disorder** during adsorption. During adsorption, gas or solute molecules become more ordered on the surface. Hence, ΔS is usually **negative.** Thus we can say that the free-moving molecules in bulk phase become restricted on the surface, as a result a decrease in randomness occurs which leads to decrease in entropy.

12.5 PHYSICAL AND CHEMICAL ADSORPTION

On the basis of forces of attraction between the adsorbate and adsorbent, adsorption has been classified into two categories, namely physical adsorption (physisorption) and chemical adsorption (chemisorption). Understanding these two types is important for applications in catalysis, separation processes, gas storage, and surface reactions.
The general characteristics of these adsorptions are described below:

Physical Adsorption	Chemical Adsorption
1. Physical adsorption is the type of adsorption in which the adsorbate molecules are held on the surface of the adsorbent by weak van der Waals forces.	1. Chemical adsorption is the type of adsorption in which the adsorbate molecules are held on the surface of the adsorbent by strong chemical bonds (covalent or ionic).
2. Mainly occurs at low temperature.	2. Usually occurs at high temperature.
3. Almost all gases show this type of adsorption at low temperature.	3. It is highly specific in nature.
4. The enthalpy of adsorption is low (20 kJ mol^{-1} or less).	4. The enthalpy of adsorption is high (80 to 420 kJ mol^{-1}).
5. Reversible in nature.	5. Usually irreversible in nature.
6. Non-specific in nature (most gases can be physically adsorbed on any	6. Highly specific (depends on the nature of both adsorbent and adsorbate).

solid surface)	
7. It attains equilibrium very rapidly by changing temperature and pressure of the system.	7. It attains equilibrium relatively slower.
8. The activation energy is very small (even less than 5 $kJmol^{-1}$). That's why it can attain at low temperature.	8. The activation energy is high. That's why it can attain only at high temperature.
9. It is multilayer adsorption.	9. Adsorption is monolayer.

W CHECK YOUR PROGRESS

Q.1. Define surface free energy.
Q.2. Why are surface molecules more reactive than bulk molecules?
Q.3. Why is chemical adsorption or chemisorption highly specific?

12.6 ADSORPTION ISOTHERMS: LANGMUIR AND BET

An adsorption isotherm represents the relationship, at constant temperature, between the amount of gas adsorbed and pressure or concentration. Adsorption isotherms are useful for understanding the mechanism of adsorption, comparing the adsorption capacities of different adsorbents and determining surface area of solids. Among various adsorption isotherms proposed, the Langmuir and the BET (Brunauer-Emmett-Teller) are the most widely used ones.

12.6.1 Langmuir Adsorption Isotherm

In 1916, Langmuir proposed a theory for the adsorption of gases on solid surfaces. He assumed that:

1. The surface of the adsorbent is homogeneous.
2. Adsorption occurs only at fixed sites on the surface
3. The adsorbed gas molecule behaves ideally in the vapour phase.
4. Each elementary site can hold only one adsorbate molecule.
5. Adsorption results in the formation of a **monolayer**.
6. There are no interactions between the adsorbed molecules.
7. A dynamic equilibrium exists between the adsorbed molecules and the free molecules.

Derivation of Langmuir Adsorption Isotherm:
Let us consider **A** is the gas molecule and **M** is the surface site, then

$$A(g) + M(\text{surafce}) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AM$$

Where,
K_a = rate constant for adsorption
K_d = rate constant for desorption
p_A = Partial pressure of A

N = total number of surface sites
θ = fraction of surface sites occupied by the gas molecules
Hence, Number of vacant sites on the surface = $[N(1-\theta)]$

and Number of occupied sites = $N\theta$
Thus, the rate of adsorption = $k_a p_A N(1-\theta)$ (12.1)
The rate of desorption ∝ number of adsorbed molecules, *Nθ*.
Thus, the rate of desorption = $k_d N\theta$ (12.2)
Since at equilibrium,
Rate of adsorption = rate of desorption
it follows that,

$$k_a p_A N(1-\theta) = k_d N\theta$$

$$Kp_A(1-\theta) = \theta \quad (12.3)$$

Where $K = \frac{k_a}{k_d}$
Therefore, equation (12.3**)** can be written as:

$$\frac{1-\theta}{\theta} = \frac{1}{Kp_A}$$

Or

$$\frac{1}{\theta} - 1 = \frac{1}{Kp_A}$$

$$\frac{1}{\theta} = \frac{1}{Kp_A} + 1$$

$$\frac{1}{\theta} = \frac{1+Kp_A}{Kp_A}$$

Hence, $\theta = \frac{Kp_A}{1+Kp_A}$ (12.4)

Equation (12.4) is known as **Langmuir adsorption isotherm.**

Conditions:
(i). At low pressure, K p_A << 1 so that equation (4) becomes

$$\theta = \mathrm{KP_A} \quad (12.5)$$

i.e. the fraction of the surface covered is directly proportional to the partial pressure of the gas molecule and its behaviour corresponds to the *first-order* reaction.

(ii). At high pressure, K p_A >> 1 so that equation (4) become

$$\theta = 1 \quad (12.6)$$

Therefore, at high pressure, the *θ* tends to become unity i.e. the entire surface gets covered by a **monolayer** of the gas making reaction rate independent of the pressure. Thus the reaction becomes *zero-order* as shown in **Figure 12.1**.
According to this theory, it is evident from equation (12.4 & 12.5) that the magnitude of adsorption at a given temperature should first increase in pressure and then finally tend to attain a certain limiting value.
The above results can looked at in another way, since at low pressure adsorption is proportional to pressure

i.e. $\theta = K(p_A)^1$
and at high pressure, $\theta = 1 = (p_A)^0$
Therefore, it shows that at intermediate pressures, the following expression should hold good:

$$\theta = K(p_A)^n$$

where n lies between o and 1.

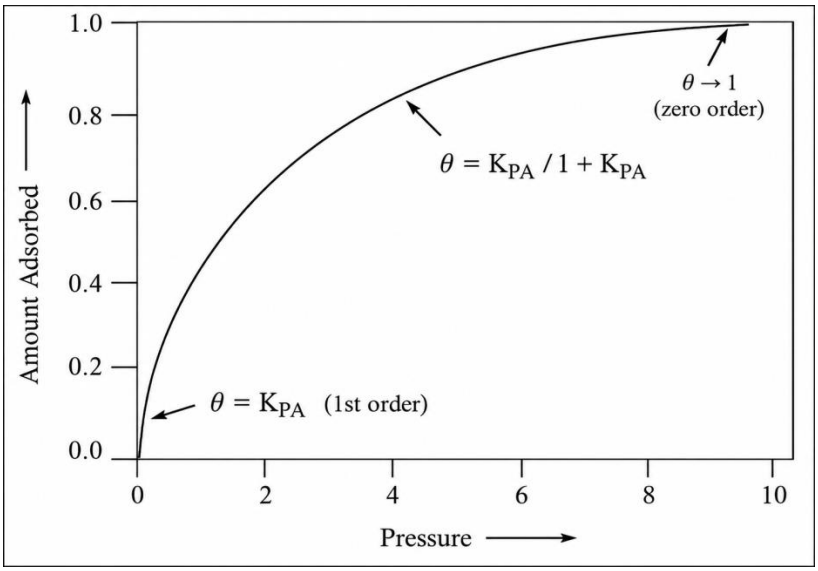


Figure: 12.1: The Langmuir adsorption isotherm graph

Limitations of Langmuir isotherm:

1. Real surfaces are heterogeneous, not perfectly homogenous.
2. Multilayer adsorption is not explained (i.e. it is limited to monolayer only)
3. Adsorbate-adsorbate interactions are neglected.
4. Fails at high pressure where multilayers are formed.

12.6.2 BET Adsorption Isotherm

BET adsorption isotherm was proposed by Brunauer, Emmett and Teller (1938**)** as an extension of the Langmuir adsorption isotherm. While Langmuir theory is restricted to monolayer adsorption, the BET theory explains **multilayer** adsorption of gases on solid surfaces. It is widely used for the determination of surface area of porous and non-porous solids.
In the BET theory, it is assumed that:

1. The solid surface is homogeneous or uniform.
2. Adsorption takes place in multiple layers.
3. Each adsorption site can adsorb one molecule in each layer, resulting in multilayer formation.
4. There is no lateral interaction between adsorbed molecules in the same layer.
5. The heat of adsorption for the first layer is different from that of subsequent layers.

6. The heat of adsorption of all layers beyond the first is equal to the heat of liquefaction of the adsorbate.
7. Adsorption-desorption equilibrium exists for each layer.

Based on above assumptions, BET derived an equation called **BET equation**:

$$\frac{P}{V(P_o-P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right) \qquad (12.7)$$

Where:

V = volume of gas adsorbed at pressure P
P = equilibrium pressure of the adsorbate gas
P_0 = saturation vapour pressure of the adsorbate
V_m = volume of gas required to form a monolayer
C = The BET constant, it depends upon the nature of gas.

Since C is a constant for a given gas and V_m is constant for a given gas-solid system, the plot of $P/V(P_o - P)$ against P/P_o should give a *straight line*, which has been verified using various gases that adsorbed solid adsorbents. An example of such results was obtained in case of adsorption of nitrogen on silica gel at –183 ^oC, shown in **Figure 12.2**.

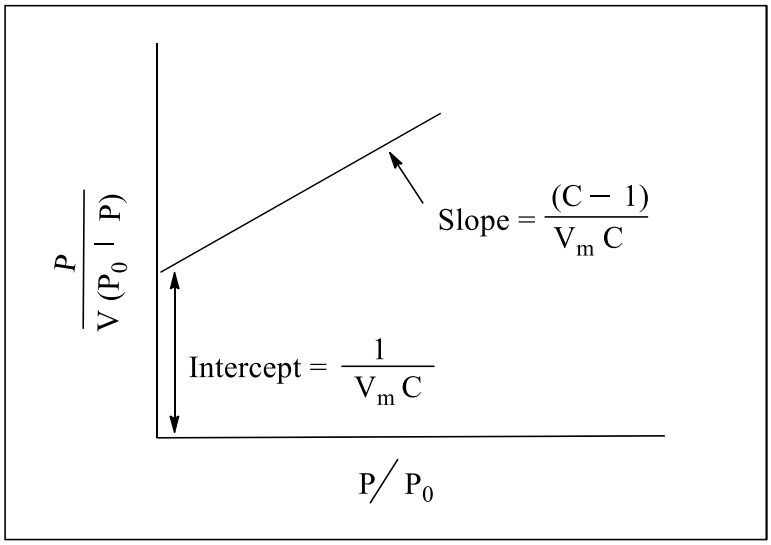


Figure 12.2: BET plot for the adsorption of N_2 on silica gel at -183 ^oC

From the figure it is clear that a straight line is obtained, and a fairly accurate straight line is obtained as long as pressure (P) does not exceed one-third of the saturation pressure (P_0). That means the pressure required to condense the gas into liquid at the prevailing temperature. However, at higher pressure deviation begins. The *slope* of the linear plot gives the value of (C − 1/ V_m C) while (1/ V_m C) is the intercept. Thus from the slope and intercept, both V_m and C can be evaluated.

12.7 DETERMINATION OF SURFACE AREA OF ADSORBENTS

The surface area of an adsorbent is an important parameter that determines its adsorption capacity and catalytic activity. Since adsorption is a surface phenomenon, the extent of adsorption depends directly on the available surface area of the solid. Hence, accurate determination of surface area is essential in surface chemistry. The surface area of solids is commonly determined by gas adsorption methods, especially using inert gases such as nitrogen at low temperatures.

By knowing the value of 'V_m' using BET equation as discussed in section **12.6.2.**, the surface area of the adsorbents can easily be calculated with the assumption that the molecules of the gas adsorbed in the first layer are closely packed on the surface.

12.8 CAPILLARY CONDENSATION, ADSORPTION IN MICROPORES AND HYSTERESIS LOOP

Adsorption on porous solids is not confined to monolayer or multilayer formation on external surfaces alone. In materials such as silica gel, alumina and activated carbon, adsorption is strongly influenced by the presence of pores of different sizes. As a result several important phenomena arise in porous adsorbents including capillary condensation, adsorption in micropores and occurrence of hysteresis loop in adsorption-desorption isotherms.

Capillary condensation is the phenomenon in which a gas condenses into the liquid state within the fine pores (capillaries) of a porous solid, even at pressures lower than the saturation vapour pressure of the adsorbate. This happens because the pores act like tiny capillary tubes, where condensation becomes easier due to surface forces. Capillary condensation is commonly observed in mesoporous solids such as silica gel and alumina and plays an important role in adsorption-desorption hysteresis.

Adsorption in micropores occurs in very small pores having diameters less than 2 nm. In such pores, adsorption does not occur layer by layer as seen on open surfaces. Instead, the adsorbate molecules fill the entire pore volume due to strong interactions between the pore walls and the adsorbed molecules. As a result, adsorption in micropores takes place rapidly even at very low pressures and makes a significant contribution to the total amount of gas adsorbed.

A **hysteresis loop** is observed when the adsorption and desorption isotherms of a gas on a porous solid do not overlap. During adsorption, capillary condensation takes place inside the pores at a particular pressure, whereas during desorption, evaporation of the liquid from the pores occurs at lower pressure. Due to this difference between condensation and evaporation pressures, a loop-shaped curve known as the hysteresis loop is formed as shown in **Figure 12.3**. The appearance of a hysteresis loop indicates the presence of mesopores (i.e., pores having diameters between 2 nm and 50 nm) and gives useful information about the pore structure of the adsorbent.

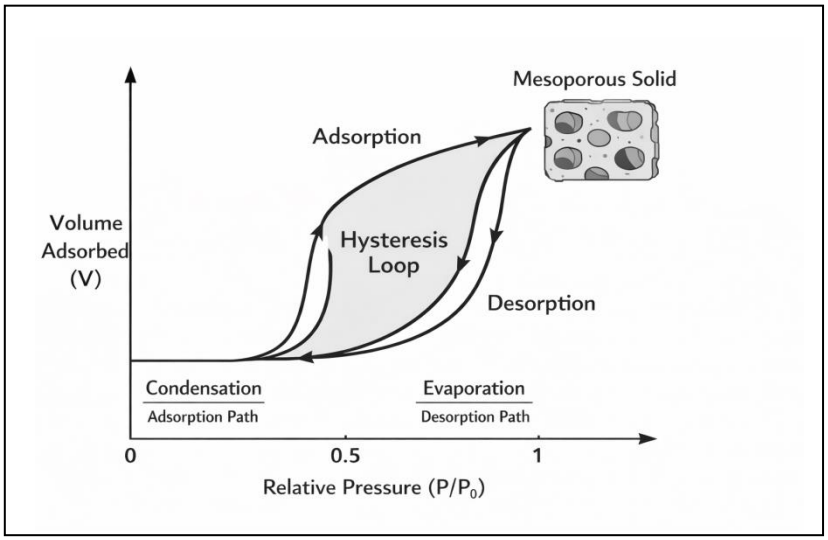


Figure 12.3: Hysteresis loop observed in adsorption-desorption isotherms of a gas in a mesoporous solid.

W CHECK YOUR PROGRESS

Q4. The adsorption of a gas on a solid surface follows Langmuir adsorption isotherm:

$$\theta = \frac{KP}{1 + KP}$$

Where,
θ = fraction of surface sites occupied by the gas molecules.
K = Langmuir constant
P = Pressure of gas
For a certain gas-solid system, the value of K=0.5 atm^{-1}.
Calculate the fraction of surface covered (θ) when the pressure is 2 atm.

Q5. What information is obtained from the hysteresis loop in adsorption isotherms?

12.9 SURFACTANTS: DEFINITION AND CLASSIFICATION

Surfactants (surface-active agents) are substances which reduces the surface tension of a liquid allowing it to spread between two immiscible phases such as liquid-liquid or liquid-solid systems. Because of this property, surfactants are widely used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents and penetrating agents etc.
Although surfactants differ in chemical nature, they all share one common feature: the presence of both a hydrophobic (water repelling) part and a hydrophilic (water loving) part within the same molecule. This property is known as **amphipathy**. The hydrophobic portion is usually a long hydrocarbon chain (alkyl or aryl group), while the hydrophilic portion is a polar or ionic group. Due to the presence of these two

contrasting parts, surfactant molecules are also described as amphiphilic (or amphipathic) molecules.
In a surfactant molecule the hydrophilic group is often called the **head** and the hydrophobic group is called the **tail**. The presence of a hydrophilic head makes surfactants slightly soluble in water, while the hydrophobic tail tends to avoid contact with water. This dual nature is responsible for the unique physicochemical behaviour of surfactant solutions.

Classifications:
Surfactants are classified on the basis of the charge carried by the hydrophilic or polar head group into:

1. Anionic surfactants (Soaps, detergents)
2. Cationic surfactants (CTAB)
3. Non-ionic surfactants (Alcohol ethoxylates)
4. Amphoteric (zwitterionic) surfactants (Amino acid surfactants)

A pictorial representation of different types of surfactants is shown in **Figure 12.4.**

12.9.1 Anionic Surfactants

Anionic surfactants are surface-active agents in which the hydrophilic head carries a negative charge when dissolved in water. They have high cleaning efficiency and are the easily available inexpensive surfactants.
General Structure:
Hydrophobic hydrocarbon chain + negatively charged polar head group (e.g., $-COO^-$, $-SO_4^-$, $-SO_3^-$ etc.)
Characteristics:

- Possess excellent detergency and cleansing action
- Produce good foaming
- Effective in removing oily and greasy dirt
- Sensitive to hard water
- Most widely used class of surfactants

Common types:
(i) Soaps- Sodium or potassium salts of fatty acids; e.g., Sodium stearate
(ii) Sulfates- e.g., Sodium dodecyl sulfate (SDS);
(iii) Sulfonates**-** e.g., Sodium alkyl benzene sulfonates ($RSO_3^-\ M^+$)

Applications:
Anionic surfactants are widely used in Soaps and detergents, shampoos and toothpaste, household and industrial cleaners and emulsifying agents.

12.9.2 Cationic Surfactants

Cationic surfactants are surface-active agents in which the hydrophilic head carries a positive charge when dissolved in water. They are effective against bacteria and fungi, having good conditioning and softening properties.

General Structure:
Hydrophobic hydrocarbon chain + positively charged polar head group (e.g., $-NH_3^+$, quaternary ammonium ion)
Characteristics:

- Carry a positive charge on the surface-active head
- Exhibit poor detergency compared to anionic surfactants
- Strongly adsorb on negatively charged surfaces
- Possess antimicrobial and germicidal properties

Common Types:
(i). Amine salts and (ii). Quaternary ammonium compounds
Examples: Cetyltrimethylammonium bromide (CTAB), Cetylpyridinium chloride (CPC), Benzalkonium chloride.
Applications:
Cationic surfactants are widely used in disinfectants and antiseptics, fabric softeners, hair conditioners, antistatic agents and corrosion inhibitors.

12.9.3 Non-ionic Surfactants

Non-ionic surfactants are surface-active agents that do not carry any electrical charge on their hydrophilic head group in aqueous solution. Their surface activity arises due to the presence of polar groups capable of hydrogen bonding with water molecules rather than ionization. Non-ionic surfactants reduce surface and interfacial tension by adsorbing at interfaces. The hydrophilic portion interacts with water through hydrogen bonding, while the hydrophobic chain associates with oils or non-polar substances, thereby facilitating emulsification and detergency

General Structure:
A non-ionic surfactant molecule consists of **hydrophobic part** (long-chain alkyl or alkyl aryl group) and **hydrophilic part** (non-ionizable polar group such as polyoxyethylene units, hydroxyl or ester groups).

Characteristics:

- Do not ionize in aqueous solutions
- Exhibit excellent chemical stability
- Effective over a wide pH range (acidic, neutral, and alkaline)
- Less sensitive to hard water compared to ionic surfactants
- Generally mild in action but high detergency and emulsifying power.

Examples: Polyoxyethylene lauryl ether, tween series (Polysorbates), span series (Sorbitan esters), and alkyl polyglucosides.

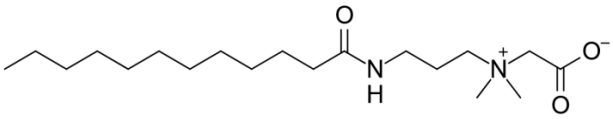
Applications:
They used as detergents and emulsifiers in pharmaceutical and cosmetic formulations, used in food industry as emulsifying agents, used in textile processing and leather industries, applied in pesticide formulations and widely used in biological and biochemical systems due to low toxicity.

12.9.4 Amphoteric (Zwitter-ionic) Surfactants

Amphoteric (zwitterionic) surfactants are surface active agents that contain both positive and negative charges in the same molecule. Depending on the pH of the medium, they can behave as cationic, anionic, or neutral (zwitterionic) surfactants. These surfactants are commonly derived from amino acids and hence are also called **amino acid surfactants**. Due to their mild nature, biodegradability, and excellent compatibility, they are widely used in cosmetic, pharmaceutical, and biomedical applications.

General Structure:

An amphoteric surfactant molecule consists of a hydrophobic hydrocarbon chain (long alkyl group), and a hydrophilic head group containing both positively charged group ($-NH_3^+$ or quaternary ammonium), and a negatively charged group ($–COO^–$, $–SO_3^–$, or $–PO_4^{2–}$). Following (lauramidopropyl betaine) is an example:



Characteristics:

- Stable over a wide pH range
- Mild and non-irritating to skin and eyes
- Good foaming and cleansing properties
- Excellent compatibility with anionic, cationic, and non-ionic surfactants
- Biodegradable and environmentally friendly

Examples: Glycine-based surfactants, Alanine-based surfactants, Betaine and sulfobetaine surfactants, Cocamidopropyl betaine, N-alkyl amino acid surfactants

Applications: They are used in baby care and sensitive skin products, pharmaceutical and cosmetic formulations, food and biomedical purposes, corrosion inhibitors and antistatic agents

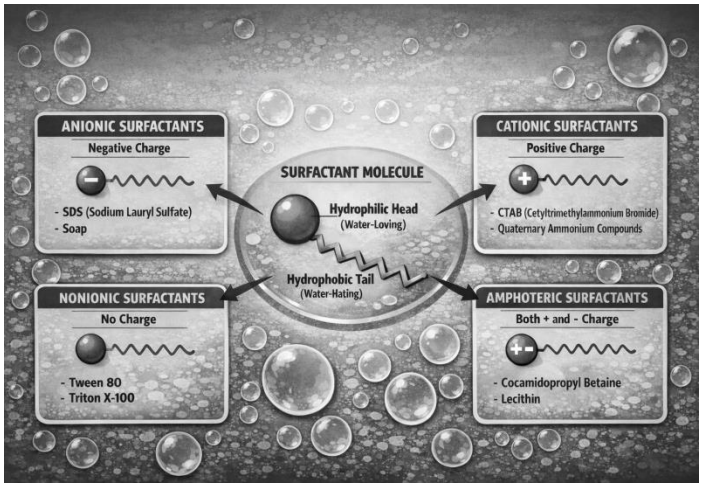


Figure 12.4: Surfactant and its classification

W CHECK YOUR PROGRESS

Q6. What are amphoteric (zwitterionic) surfactants? Give examples.

12.10 MICELLE FORMATION AND CRITICAL MICELLE CONCENTRATION (CMC)

An important property of amphiphilic molecules is their ability to undergo aggregation in solution. The extent and nature of this aggregation depend on the chemical structure of the amphiphilic species as well as the physicochemical conditions of the medium in which they are dissolved.

Surfactant molecules are amphiphilic in nature, consisting of a hydrophilic (water-loving) head and a hydrophobic (water-repelling) tail. When surfactants are added to water at low concentrations, they remain dispersed as individual molecules (monomers) and preferentially adsorb at interfaces such as air-water or solid-liquid interfaces, thereby reducing the surface or interfacial tension.

As the concentration of the surfactant increases, the interface becomes saturated. Beyond this stage, the excess surfactant molecules aggregate in the bulk of the solution to form **micelles**. This process is known as **micellization**.

A micelle is a colloidal aggregate in which the *hydrophobic* (water repelling) tails are oriented towards the interior (away from water), and the *hydrophilic* (water loving) heads are oriented towards the surrounding (outward) aqueous medium. Micelle formation is primarily driven by the hydrophobic effect, which lowers the free energy of the system by reducing contact between hydrophobic chains and water molecules.

12.10.1 Shape of Micelles

The shape of micelle formed in aqueous medium plays an important role in determining the various properties of surfactants in solutions, such as its viscosity and ability to solubilize water-insoluble substances. Depending on surfactant structure and solution conditions, micelles may adopt different shapes (**Figure 12.5**):

(i). Spherical micelles**:** most common at low surfactant concentrations (aggregation no. <100)

(ii). Cylindrical (rod-like) micelles: As concentration increases, spherical micelles can elongate into cylindrical, rod-like structures.

(iii). Lamellar (bilayer) micelles: In highly concentrated systems cylindrical micelles transition into planar or bilayer lamellar structures.

(iv). Reverse micelles: Formed in non-polar solvents (oils)

(v). Vesicles: more or less spherical consisting of lamellar micelles arranged in one or more concentric spheres.

In aqueous media, the surfactant molecules are oriented in all these structures, with their polar heads towards aqueous phase and their hydrophobic groups away from it. In vesicles, there will also be an aqueous phase in the interior of the structure.

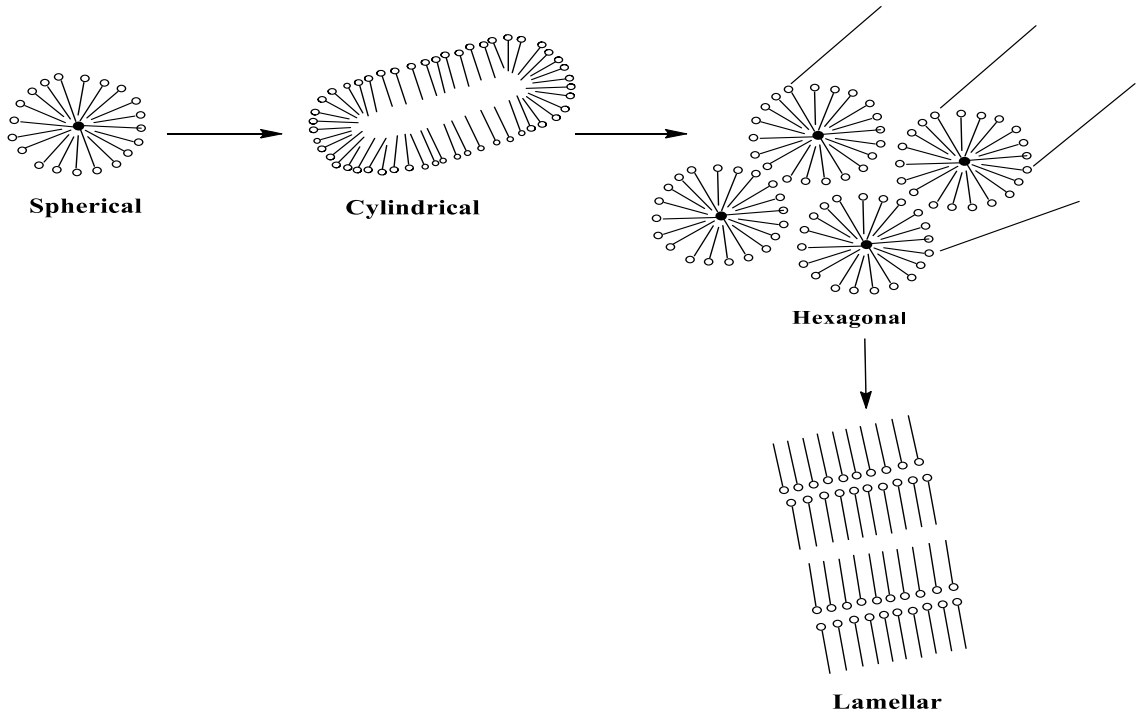


Figure 12.5: Changes in micelle shape and structure with change in surfactant concentration

12.10.2 Critical Micelle Concentration (CMC)

The critical micelle concentration (**CMC**) is defined as the minimum concentration of a surfactant in a solution above which the surfactant molecules begin to associate to form micelles. Below the CMC, the surfactant exists mainly as individual monomer molecules dispersed in the solvent.

At CMC, further addition of surfactant does not significantly increase the number of monomers in solution; instead, the added molecules are incorporated into micellar aggregates, shown in **Figure 12.6**. The formation of micelles at and above the CMC is accompanied by abrupt changes in several physicochemical properties of the solution, such as surface tension, electrical conductivity, osmotic pressure, viscosity, and solubilisation capacity.

The value of CMC depends on several factors:

(a). the nature of the surfactant.
(b). length of the hydrophobic chain.
(c). temperature, and
(d). the presence of electrolytes or additives.

In general, an increase in the hydrophobic chain length lowers the CMC, while the presence of electrolytes reduces the CMC of ionic surfactants by decreasing electrostatic repulsion between the head groups.

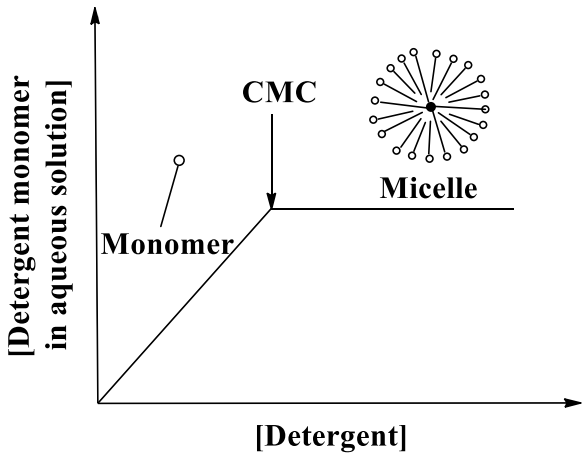


Figure 12.6: Schematic representation of CMC

12.10.3 Thermodynamics of Micellization

Micellization is the spontaneous aggregation of surfactant molecules in solution above a characteristic concentration called the critical micelle concentration (**CMC**)**.** The process is governed by changes in Gibbs free energy, enthalpy, and entropy. Micelle formation is thermodynamically feasible only when the overall Gibbs free energy change (ΔG_m) is negative.

Gibbs free energy of micellization (ΔG_m):
For micellization to occur spontaneously:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

Where,
ΔG_m= Gibbs free energy change of micellization
ΔH_m= Enthalpy change of micellization
ΔS_m= Entropy change of micellization
Expression for ΔG_m:
For ionic and non-ionic surfactants, the standard free energy of micellization is related to the mole fraction expression X of the CMC as:

$$\Delta G_m = RT \ln X\,(CMC)$$

or,
$$\Delta G_m = 2.303RT \log X\,(CMC) \qquad (12.8)$$

Where,
R = Gas constant
T = Absolute temperature (K)
X(CMC) = critical micelle concentration (in mole fraction unit)
Since X(CMC) is small, ΔG_m is negative ($\Delta G_m < 0$), indicating spontaneous micellization.

Enthalpy Change of Micellization (ΔH_m):
The enthalpy change is obtained from the temperature dependence of CMC using the van't Hoff equation:

$$\Delta H_m = -RT^2 \left[\frac{d \ln X(CMC)}{dT}\right] \qquad (12.9)$$

Sign of ΔH_m can be positive or negative and in many surfactants, micellization is entropy driven, not enthalpy driven.

Entropy Change of Micellization (ΔS_m):
Entropy change is calculated using:

$$\Delta S_m = \Delta H_m - \frac{\Delta G_m}{T} \quad (12.10)$$

Even though surfactant molecules become more ordered in micelles, the overall entropy **increases** due to solvent effects. Thus, micellization occurs mainly due to a large positive entropy change, overcoming any unfavourable enthalpy contribution. Hence, Thermodynamics of micellization can be interpreted as:

Thermodynamic Parameter	Nature	Sign
ΔG_m	Spontaneity	-ve
ΔH_m	Heat effect	+ve / -ve
ΔS_m	Disorder effect	+ve

12.11 REVERSE MICELLES, SOLUBILIZATION AND MICROEMULSIONS

Surfactant molecules, due to their ***amphiphilic*** nature, can self-assemble into different structures depending on the nature of the solvent, surfactant concentration, temperature and presence of additives. Besides normal micelles formed in aqueous media, surfactants can also form reverse micelles, cause solubilisation of insoluble substances, and produce microemulsions, which are thermodynamically stable systems.

12.11.1 Reverse Micelles

Reverse micelles are aggregates of surfactant molecules formed in non-polar solvents, in which the hydrophilic head groups are oriented towards the interior and the hydrophobic tails extend outward into the organic solvent.
Formation: They form when surfactant molecules aggregate in a non-polar organic solvent such as hexane, with their polar head groups facing inward to “trap” water molecules, forming “water pools”.
Structure: Unlike normal micelles in water (which have a hydrophobic core), reverse micelles have a hydrophilic (polar) core surrounded by the hydrophobic tails of the surfactant molecules, which extend into the surrounding non-polar solvent.
Properties:

- Thermodynamically stable systems
- Capable of solubilizing water, ions, and polar molecules in non-polar solvents
- Highly dynamic in nature
- Micelle size increases with water content

Solubilisation: Polar substances are solubilized in the aqueous core and act as micro-reactors for reactions involving polar reactants in organic media.
Applications: They are used to solubilize proteins, enzymes, and polar drugs in organic solvents without destroying their biological activity.

12.11.2 Solubilisation

A very important property of surfactants that is directly related to micelle formation is solubilisation. Solubilisation is the process of increasing the solubility of a normally insoluble substance (solubilisate) by incorporating it into micelles or reverse micelles.
Mechanism of Solubilisation:
When a surfactant is added to a solvent above its critical micelle concentration (CMC), it forms micelles that can trap hydrophobic or hydrophilic drugs within their structures (the hydrocarbon core in water or the polar core in oil).
Microemulsion Role: In W/O microemulsions (reverse micelles), water-insoluble hydrophobic drugs can be solubilized within the water pool or the surfactant interface.
Factors Affecting Solubilisation:

- Nature of surfactant
- Size and polarity of solubilisate
- Temperature
- Presence of electrolytes

Importance: This process is crucial for enhancing the bioavailability of hydrophobic drugs in pharmaceutical formulations**.**

12.11.3 Microemulsions

Microemulsions are transparent, clear and thermodynamically stable mixtures consisting of oil, water, surfactant and usually a co-surfactant, with droplet sizes typically in the range of 10-100 nm.
Types of Microemulsions:

1. Oil-in-Water (O/W): Oil droplets dispersed in continuous aqueous phase.
2. Water-in-Oil (W/O)**:** Water droplets dispersed in continuous oil phase (effectively reverse micelle)
3. Bicontinuous: Water and oil phases are intertwined, often forming a sponge-like structure.

Properties:

- Thermodynamically stable
- Low viscosity
- High solubilization capacity
- Large interfacial area

Applications: Due to their stability and ability to carry both lipophilic and hydrophilic drugs, they are used for drug delivery systems, enhanced oil recovery, food and cosmetic formulations, extraction and separation processes, synthesis of nanomaterials.

W CHECK YOUR PROGRESS

Q7. Define micelle. Explain the process of micelle formation in aqueous media.
Q8. What is a microemulsion? Write down a few applications of microemulsions.

2 12.12 LET US SUM UP

- **Surface chemistry** is the branch of chemistry concerned with the study of physical and chemical phenomena occurring at interfaces such as solid-gas, solid-liquid and liquid-liquid interfaces. The atoms or molecules present at the surface experience unbalanced forces and possess excess free energy compared to those in the bulk. Due to this excess energy, surfaces exhibit enhanced reactivity, giving rise to important surface phenomena such as adsorption.
- Adsorption is defined as the accumulation of molecules of a substance (adsorbate) on the surface of a solid (adsorbent). It depends on surface properties of the adsorbent and thermodynamic conditions. Adsorption differs from absorption, as adsorption is a surface phenomenon whereas absorption occurs throughout the bulk.
- The thermodynamics of adsorption is explained in terms of Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). An adsorption process is spontaneous when the Gibbs free energy change is negative. Most adsorption processes are exothermic in nature and are accompanied by a decrease in entropy due to restriction of molecular motion when adsorbate molecules become attached to the surface.
- Based on the nature of forces involved, adsorption is classified into physical adsorption (**physisorption**) and chemical adsorption (**chemisorption**). Physisorption involves weak van der Waals forces, is reversible, non-specific, occurs at low temperatures and leads to multilayer formation. Chemisorption involves strong chemical bonds, is highly specific, usually irreversible, requires higher activation energy and results in monolayer adsorption.
- The quantitative relationship between the amount of gas adsorbed and pressure at constant temperature is described by adsorption isotherms. The **Langmuir adsorption** isotherm explains monolayer adsorption on a homogeneous surface with no interaction between adsorbed molecules and is applicable at low and intermediate pressures. The **BET** adsorption isotherm extends the Langmuir theory to multilayer adsorption and is widely used for the determination of surface area of solids using gas adsorption methods, particularly nitrogen adsorption at low temperatures.
- In porous solids, adsorption is influenced by pore structure. Capillary condensation occurs when gases condense in mesopores at pressures lower than saturation vapour pressure. In **micropores**, adsorption occurs by pore-filling rather than layer-by-layer adsorption. The difference between adsorption and desorption pathways leads to hysteresis loops in adsorption-desorption isotherms, providing information about pore size and structure.

- Surfactants or surface-active agents are **amphiphilic** molecules containing both hydrophilic and hydrophobic groups. They reduce surface or interfacial tension and are widely used as detergents, emulsifiers, wetting agents and dispersing agents. Based on the nature of the hydrophilic head group, surfactants are classified as anionic, cationic, non-ionic and amphoteric (zwitterionic) surfactants.
- At low concentrations, surfactants exist as monomers, but above a certain concentration called the critical micelle concentration (CMC), they aggregate to form micelles. Micellization is driven mainly by the **hydrophobic effect** and is thermodynamically spontaneous (negative ΔG). Micelles can adopt different shapes such as spherical, cylindrical, lamellar, reverse micelles and vesicles depending on concentration and medium.
- Reverse micelles form in non-polar solvents with hydrophilic heads oriented inward, trapping water molecules. They facilitate solubilisation of polar substances in non-polar media. **Solubilisation** refers to the incorporation of insoluble substances into micelles or reverse micelles, enhancing solubility and bioavailability.
- **Microemulsions** are thermodynamically stable, transparent systems consisting of oil, water, surfactant and co-surfactant. They may exist as oil-in-water, water-in-oil or bicontinuous systems and possess high solubilisation capacity. Microemulsions find extensive applications in pharmaceuticals, catalysis, food technology and nanomaterial synthesis.

K 12.13 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: Surface free energy is the excess energy possessed by the molecules or atoms present at the surface of a solid or liquid compared to those in the bulk.

Answer to Q2: The surface molecules are more reactive than bulk molecules because they are subjected to unbalanced cohesive forces. In the bulk phase, each molecule is completely surrounded by neighbouring molecules and experiences equal attractive forces from all directions, resulting in a stable, low-energy state. However, molecules at the surface are not fully surrounded by similar neighbouring particles, and therefore some of their bonding forces remain unsatisfied. As a result, surface molecules possess excess free energy and exist in a thermodynamically unstable state. To attain stability and minimize this excess energy, surface molecules readily interact with other molecules, which increases surface reactivity and leads to phenomena such as adsorption.

Answer to Q3: Chemisorption is highly specific because it involves the formation of strong, directional chemical bonds (covalent or ionic) between the adsorbent and adsorbate, rather than weak physical forces. It only occurs when specific chemical interactions or reactions are possible between the molecules, making it a highly selective process.

Answer to Q4: Given, K=0.5 atm^{-1} and P = 2 atm

Using Langmuir equation, we have

$$\theta = \frac{\mathrm{KP}}{1 + \mathrm{KP}}$$

$$\theta = \frac{0.5 \times 2}{1 + (0.5 \times 2)}$$

$$\theta = \frac{1}{2}$$

$$\theta = 0.5$$

Thus, 50 % of the surface is covered at 2 atm pressure.

Answer to Q5: A hysteresis loop in an adsorption-desorption isotherm provides information about the pore structure and pore size distribution of a porous adsorbent. The presence of a hysteresis loop indicates the existence of **mesopores** in the solid and arises from the difference between capillary condensation during adsorption and evaporation during desorption. The shape and size of the hysteresis loop help in understanding the nature of pores, their connectivity, and the mechanism of adsorption, thereby giving valuable insight into the textural properties of the adsorbent.

Answer to Q6: Amphoteric (zwitterionic) surfactants are surfactants that contain both positive and negative charges within the same molecule. The net charge of the molecule depends on the pH of the medium; thereby they may behave as cationic, anionic, or neutral (zwitterionic). These surfactants are commonly derived from amino acids and hence are also called amino acid surfactants.
Examples: Amino acid based surfactants (cocamidopropyl betaine), betaine and sulfobetaine surfactants, imidazoline derivatives, N-alkyl amino acid surfactants etc.

Answer to Q7: A micelle is an aggregate of surfactant molecules formed in a liquid medium when the surfactant concentration exceeds a certain minimum value called the critical micelle concentration (CMC). In aqueous media, the hydrophobic tails are directed towards the interior of the micelle, while the hydrophilic head groups remain in contact with water.
Micelle formation in aqueous media occurs due to the hydrophobic effect, where surfactant molecules aggregate above the CMC to minimize unfavorable interactions between hydrophobic chains and water.

Answer to Q8: A microemulsion is a thermodynamically stable, transparent or translucent, isotropic system consisting of oil, water, and a surfactant, often along with a co-surfactant, in which the dispersed droplets are of nanometer size (10-100 nm).
Applications of microemulsions are:

i. Drug delivery systems for enhanced solubility.
ii. Enhanced oil recovery in petroleum industry.
iii. Food and cosmetic industry.
iv. Chemical reactions and catalysis.
v. Extraction and separation processes.
vi. Cleaning and detergency formulations.

O 12.14 FURTHER READING

- K.L. Kapoor. *A Textbook of Physical Chemistry, Vol. V.* Mc Graw Hill (India)
- B.R. Puri, L.R. Sharma, Madan S. Pathania. *Principles of Physical Chemistry*
- D.J. Shaw. *Colloid and Surface Chemistry*. Taylor and Francis.
- P.W. Atkins. *Physical Chemistry*. Oxford University Press.

M 12.15 MODEL QUESTIONS

Q1. Explain the thermodynamics of adsorption.
Q2. Derive the Langmuir adsorption isotherm.
Q3. Discuss BET theory and surface area determination.
Q4. At 0 °C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel assuming Langmuir monolayer adsorption is found to be 130 $cm^3\ g^{-1}$ of the gel.
Given that the area occupied by one nitrogen molecule is 0.162 nm^2, calculate the surface area per gram of silica gel. (Given: the area occupied by N_2 is 0.162 nm^2)
Q5. Write down the assumptions of BET theory.
Q6. Explain how surfactants reduce surface tension.
Q7. What are surfactants? Explain micelle formation and critical micelle concentration (CMC).
Q8. Write short notes on:
(a). Hysteresis loop
(b). Micelles
(c). Reverse micelles
(d). Microemulsions

UNIT 13: CHEMISORPTION

UNIT STRUCTURE

13.1 Learning Objectives
13.2 Introduction
13.3 Chemisorption on Metals
13.3.1 Nature of Chemisorption on Metals
13.3.2 Mechanism of Chemisorption on Metals
13.3.3 Factors Affecting Chemisorption
13.3.4 Importance of Chemisorption on Metals
13.4 Chemisorption on Semiconducting and Insulating Oxides
13.4.1 Chemisorption on Semiconducting Oxides
13.4.2 Chemisorption on Insulating Oxides
13.5 Electrical Aspects of Surface Chemistry
13.6 Electrical Double Layer and Zeta Potential
13.6.1 Formation of Electrical Double Layer (EDL)
13.6.2 Zeta Potential
13.7 Measurement of Zeta Potential and Colloidal Stability
13.7.1 Colloidal Stability
13.8 Let Us Sum Up
13.9 Answers to Check Your Progress
13.10 Further Reading
13.11 Model Questions

13.1 LEARNING OBJECTIVES

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

- understand the concept and fundamental principles of chemisorption.
- describe chemisorption on metal surfaces, semiconducting and insulating oxides.
- understand the electrical aspects of surface chemistry.
- explain the concept of electrical double layer and zeta potential.
- describe methods for measurement of zeta potential.
- correlate zeta potential with colloidal stability.

13.2 INTRODUCTION

In previous unit we have learnt about surface chemistry and surfactants, now you will learn how chemisorption take place at surfaces. Adsorption is a surface phenomenon in which atoms, ions, or molecules (adsorbate) from a gas or liquid phase accumulate on the surface of a solid or liquid (adsorbent). Since the process occurs only at the surface, adsorption is different from absorption, which involves the entire bulk of the material. Based on the nature of forces involved between the adsorbate and adsorbent, adsorption is classified into physisorption and chemisorption. A more detailed study on

distinguishing features of physisorption and chemisorption has been already discussed in **Unit 12** (Section **12.5**).

Chemisorption involves the formation of strong chemical bonds (covalent or ionic) between the adsorbate and the surface of the adsorbent and is highly specific, as it occurs only when the adsorbate and adsorbent have suitable chemical compatibility. It is generally irreversible, involves high heat of adsorption, and usually requires activation energy.

Chemisorption plays a vital role in many important processes such as heterogeneous catalysis, where reactant molecules chemically adsorb on catalyst surfaces; corrosion, involving surface chemical reactions; surface reactions and electrochemical processes; and in gas sensors, where selective adsorption of gases on solid surfaces enables detection.

13.3 CHEMISORPTION ON METALS

Chemisorption on metals involves forming strong chemical bonds (covalent or ionic) between gas-phase adsorbate molecules and surface metal atoms, primarily occurring on transition metals. Unlike physisorption, chemisorption involves electron transfer or sharing between the adsorbate and metal atoms. Chemisorption is a highly specific, typically irreversible, and exothermic process that acts as the crucial first step in catalytic reactions.

13.3.1 Nature of Chemisorption on Metals

In chemisorption, the adsorbate forms strong chemical bonds with surface metal atoms which is highly specific, involves activation energy, forms a monolayer, usually irreversible and is accompanied by high heat of adsorption (ΔH = 80 – 420 kJ mol^{-1}). On metal surfaces, chemisorption generally occurs due to interaction between the valence electrons of the adsorbate, and the partially filled d-orbital of transition metals.

13.3.2 Mechanism of Chemisorption on Metals

Chemisorption on metals begins when gas molecules from the bulk phase move toward and reach the metal surface. This transport occurs by diffusion through the gas phase until the molecules come into contact with the exposed surface atoms of the metal. Once the molecules approach the surface, they may first experience weak attractive forces such as van der Waals interactions. At this stage, a temporary and weakly bound state similar to physisorption may be formed. As the molecule remains near the surface, sufficient activation energy allows stronger interaction between the adsorbate and the surface metal atoms. This leads to the formation of true chemical bonds (covalent or ionic) in nature. The transition from weak physical attraction to strong chemical bonding involves an energy barrier, and once crossing an energy barrier, a stable chemisorbed layer is formed on the metal surface.

Chemisorption on metals can occur in two distinct ways:

(i). Associative chemisorptions: Molecule remains intact while forming a bond with the metal surface. For example, carbon monoxide adsorbs on nickel without breaking its internal bond.

Example: Carbon monoxide on nickel.

$$CO + Ni \longrightarrow CO—Ni$$

(ii). Dissociative chemisorptions: Molecule first breaks into atoms, and these atoms then form bonds with the surface. This type of adsorption is very common on transition metals due to their partially filled d-orbitals, which facilitate bond breaking and formation.

For example: H_2 or O_2 on Pt surface.

$$H_2 \longrightarrow 2H \quad \text{(adsorbed)}$$

$$O_2 \longrightarrow 2O \quad \text{(adsorbed)}$$

13.3.3 Factors Affecting Chemisorption

Various factors affecting chemisorptions are:

(i). Nature of the metal: Transition metals (like Fe, Ni, Pt, Pd) show strong chemisorption.

(ii). Nature of the adsorbate molecule: Molecules like H_2, O_2, CO, NO chemisorb easily and reactive gases show higher chemisorption.

(iii). Temperature: Chemisorption increases with temperature initially (due to activation energy) and at very high temperature, desorption occurs.

(iv). Surface area: Finely divided metals show greater chemisorptions and more active sites on metals, results in greater adsorption.

13.3.4 Importance of Chemisorption on Metals

Chemisorption on metals plays a vital role in surface chemistry and many industrial applications, as it constitutes the primary step in numerous catalytic and surface reactions. Its greatest importance lies in *heterogeneous catalysis*, where reactant molecules first become chemically adsorbed on the metal surface. During this process, the bonds within the molecules may dissociate, producing an activated state that assist surface reactions. The reaction products are then released by desorption from the surface.

Several important industrial processes rely on chemisorption, including the Haber process for ammonia synthesis on iron, hydrogenation reactions over nickel or palladium, and oxidation reactions on platinum catalysts. Chemisorption is also involved in surface reactions such as metal oxidation and corrosion, where gases like oxygen chemically interact with metal surfaces. The effectiveness of a metal catalyst depends largely on the strength and nature of chemisorption. If adsorption is too weak, reactants will not be sufficiently activated; whereas if it is too strong, the active sites may become blocked, resulting in catalyst poisoning. Additionally, chemisorption is important in applications such as gas sensing, electrochemical processes, and surface modification techniques.

Therefore, understanding chemisorption on metals is essential for explaining catalytic behavior, optimization of industrial processes, and studying various surface phenomena.

CHECK YOUR PROGRESS

Q1. Define Chemisorption.
Q2. Chemisorption on metals involves mainly which type of forces?
(a). Van der Waals forces
(b). Hydrogen bonding
(c). Strong chemical bonding
(d). Dipole–dipole interaction
Q3. Chemisorption on metals is usually:
(a). Multilayer adsorption
(b). Monolayer adsorption
(c). Independent of surface
(d). Completely reversible

13.4 CHEMISORPTION ON SEMICONDUCTING AND INSULATING OXIDES

Chemisorption on semiconducting and insulating oxides plays an important role in heterogeneous catalysis, gas sensing, corrosion, photocatalysis and surface reactions. Unlike metals, where free electrons are available for bonding, *oxides* have localized electronic structures and specific surface **defect**s that influence chemisorption behavior. Semiconducting and insulating oxides (e.g., ZnO, TiO_2, Fe_2O_3, Al_2O_3, SiO_2, MgO) possess ionic or partially ionic crystal structures, surface metal cations (M^{n+}), surface oxygen anions (O^{2-}), surface hydroxyl groups (–OH) and lattice defects (oxygen vacancies, interstitials) which act as **active sites** for chemisorption.

13.4.1 Chemisorption on Semiconducting Oxides

Semiconducting oxides such as ZnO, TiO_2, SnO_2, Fe_2O_3, and NiO show characteristic chemisorption behavior due to their intermediate electrical conductivity. Unlike metals, these solids do not possess a large number of free electrons; instead, they contain a limited number of charge carriers (electrons in *n-type* and holes in *p-type* semiconductors). Therefore, chemisorption on semiconducting oxides is closely associated with electron transfer between the adsorbate and the solid surface.
When a gas molecule approaches the surface of a semiconducting oxide, it may either accept electrons from or donate electrons to the solid. As a result, chemisorbed ionic species are formed on the surface. For example, oxygen molecules adsorbed on an *n-type* semiconductor can capture electrons from the conduction band:

$$O_2 + e^- \longrightarrow O_2^-$$

$$O_2^- + e^- \longrightarrow 2O^-$$

The removal of electrons from the conduction band leads to the formation of a *depletion* layer near the surface. This causes a decrease in electrical conductivity in *n-type* semiconductors (ZnO, TiO_2, SnO_2). Conversely, adsorption of reducing gases such as CO or H_2 may return electrons to the semiconductor, increasing its conductivity.
In *p-type* semiconductors (NiO, CuO), the effect is opposite. Adsorption of electron-accepting gases increases hole concentration and hence increases conductivity.

Effect on Electrical Properties:
Chemisorption significantly modifies electrical conductivity.
(a). *n-type Semiconductors*:

- Majority carriers electrons
- Oxygen chemisorption removes electrons
- Conductivity decreases

When a reducing gas (e.g., CO, H_2) reacts:

$$CO + O^-(ads) \longrightarrow CO_2 + e^-$$

Electrons are released back to the conduction band, resulting in an increase in conductivity.
This principle is used in **gas sensors**.
(b) *p-type Semiconductors*:

- Majority carriers holes
- Oxygen adsorption increases hole concentration
- Conductivity increases

Thus, adsorption behaviour differs between n-type and p-type oxides.
Chemisorption on semiconducting oxides is greatly influenced by factors such as surface defects, oxygen vacancies, temperature, and the nature of the adsorbate. Defects and vacancies serve as active sites for adsorption. This type of chemisorption is of great practical importance in the working of semiconductor gas sensors, where changes in electrical resistance are used to detect and measure gas concentrations.
Thus, chemisorption on semiconducting oxides involves chemical bonding accompanied by charge transfer, leading to significant changes in the electrical properties of the material.

Factors Affecting Chemisorption on semiconducting oxides:

(i). Temperature
(ii). Surface area
(iii). Crystal structure
(iv). Presence of dopants
(v). Nature of adsorbate
(vi). Partial pressure of gas

13.4.2 Chemisorption on insulating Oxides

Chemisorption on insulating oxides is an important topic in surface chemistry, heterogeneous catalysis, corrosion, and gas-solid reactions. Insulating oxides such as SiO_2, Al_2O_3, MgO, CaO, Ga_2O_3 and ZrO_2 possess wide band gaps and very low

electrical conductivity. Unlike metals, they do not have free electrons; therefore, chemisorption on these surfaces mainly occurs through surface functional groups and defect sites.

Nature of Insulating Oxide Surfaces:

The surface of insulating oxides is characterized by **s**urface metal cations (M^{n+}) which act as Lewis acid sites; Surface oxygen anions (O^{2-}) which act as Lewis base sites**;** Surface hydroxyl groups (-OH) which are formed by adsorption of water and Defect sites that carry oxygen vacancies, steps.

Because of these surface species, insulating oxides show acid-base type chemisorption rather than metallic bond-type adsorption.

Mechanism of Chemisorption on Insulating Oxides:

Chemisorption generally occurs by:

(i) Acid-Base Interaction:

According to the Lewis acid-base concept, the surface metal ions (M^{n+}) act as Lewis acids and surface O^{2} or -OH groups act as Lewis bases.

Example:

$$NH_3 + M^{n+} \longrightarrow M^{n+}.\,NH_3$$

Here, NH_3 (a Lewis base) donates an electron pair to the metal cation.

Similarly,

$$CO_2 + O_2^{-} \longrightarrow CO_3^{2-}$$

CO_2 (acidic oxide) reacts with surface O^{2-} to form carbonate species.

(ii) Formation of Surface Complexes:

Adsorbate molecules form surface complexes or surface compounds.

Example: (a). Adsorption of HCl on Al_2O_3 forms surface chloride species.

(b). CO_2 on MgO forms surface carbonate.

(iii) Hydroxyl Group Involvement:

Most insulating oxides are hydroxylated in the presence of moisture:

$$M\text{-}O\text{-}M + H_2O \longrightarrow 2M\text{-}OH$$

These -OH groups participate in hydrogen bonding or dissociative chemisorption.

Example:

$$H_2O \longrightarrow H^{+} + OH^{-}$$

Factors Affecting Chemisorption on Insulating Oxides:

Chemisorption on insulating oxides is influenced mainly by:

(i). Acid-base character of oxide: Acidic oxides (SiO_2, Al_2O_3) preferentially adsorb basic molecules (NH_3, amines). Basic oxides (MgO, CaO) preferentially adsorb acidic gases (CO_2, SO_2). Amphoteric oxides (Al_2O_3, ZnO) can adsorb both acidic and basic species.

(ii). Surface hydroxyl groups: Most oxide surfaces become hydroxylated in the presence of moisture.

$$M\text{-}O\text{-}M + H_2O \longrightarrow 2M\text{-}OH$$

Surface -OH groups act as Brønsted acid or base sites, participate in hydrogen bonding and promote dissociative adsorption. Higher surface hydroxyl concentration generally increases chemisorption.

(iii). Surface area and porosity: Greater surface area, more available active sites lead to higher chemisorption

(iv).Temperature: At low temperature → adsorption may be slow, Increasing temperature → rate of chemisorption increases (activation energy required) and Very high temperature → desorption may occur.
(v). Nature and pressure of adsorbate: Small, polar, and reactive molecules adsorb more strongly.
(vi). Moisture Content: Humidity significantly affects oxide surfaces.

- **Comparison with Chemisorption on Metals:**

Feature	**Metals**	**Insulating Oxides**
Type of interaction:	Electron transfer / metallic bonding	Acid-base interaction
Active sites:	Free electrons	Surface ions & -OH groups
Role of band structure:	Important	Wide band gap (no free electrons)
Specificity:	Moderate	Highly specific

Chemisorption on insulating oxides plays a significant role in surface chemistry, catalysis, environmental science, and materials technology.

W CHECK YOUR PROGRESS

Q4. Give two examples of each semiconducting and insulating oxides.
Q5. How does chemisorption on semiconducting oxides differ from metals?

13.5 ELECTRICAL ASPECTS OF SURFACE CHEMISTRY

When a solid surface comes into contact with a gas or liquid phase, electrical phenomena arise as a result of formation of surface charge. These electrical effects play a crucial role in adsorption, catalysis, corrosion, electrochemistry, colloidal stability, and sensor technology.
The origin of electrical properties at surfaces is mainly due to:

- Non-uniform distribution of charges at the surface
- Ionization or dissociation of surface functional groups
- Selective (preferential) adsorption of ions
- Presence of structural defects in the solids
- Charge transfer occurring during chemisorption

Thus, surfaces are not electrically neutral at the microscopic level; instead they often carry net positive or negative charge.
Surface charge may arise due to ionization of surface groups, preferential adsorption of ions, and isomorphous substitution reaction mechanism.
When a charge develops at a surface, an electrical potential difference arises between surface and bulk.

(i). Surface Potential (ψ):
It is the electrical potential developed at the surface due to charge separation.
(ii). Work Function (Φ):
It is the minimum energy required to remove an electron from the surface of a solid to vacuum.
Therefore, adsorption can **increase** work function (electron-withdrawing adsorbate) and decrease work function (electron-donating adsorbate). This change provides evidence for charge transfer during chemisorption.

13.6 ELECTRICAL DOUBLE LAYER AND ZETA POTENTIAL

When a solid surface comes into contact with a liquid phase (especially an electrolyte solution), electrical charges develop at the interface. This occurs due to ionization of surface groups, preferential adsorption of ions, or structural imperfections in the solid. As a result, the surface acquires either a positive or negative charge.
However, electrical neutrality must be maintained. Therefore, oppositely charged ions from the solution are attracted toward the charged surface. This leads to the formation of a structured region of charges near the interface known as the *Electrical Double Layer* (EDL).

13.6.1 Formation of Electrical Double Layer (EDL)

An Electrical Double Layer (EDL) forms at the interface of a charged surface (solid, electrode, or colloid) and a liquid electrolyte, where surface charges attract opposite ions. This structure maintains electroneutrality and typically develops through ion adsorption, ion hydration, or surface charge modification.
The EDL consists of:

1. Inner compact layer (Stern layer): firmly adsorbed counter-ions.
2. Outer layer (Diffuse layer): loosely distributed counter-ions extending into the bulk solution.

To understand EDL, let us consider the formation of silver iodide (AgI) sol from the double decomposition reaction:

$$AgNO_3\,(aq) + NaI\,(aq) \longrightarrow AgI\,(s) + NaNO_3\,(aq)$$

The negatively charged surface of AgI particle attracts the positive ions (Na^+) and repels the negative ions (NO_3^-). As a result, the positive Na^+ ions tend to form a compact layer in the vicinity of the potential determining I^- ion layer called **stern layer**. The influence of the surface charge decreases with distance and so does the number of ions with that at a certain distance of the particle, the concentration of Na^+ ions equals the concentration of NO_3^- ions and a state of electroneutrality prevails. The diffuse layer between the stern layer and electrically neutral part of the system is called **Gouy-Chapman layer** (Diffuse layer). The region in which influence of the charge is appreciable is known as **Electrical Double Layer** is shown in **Figure 13.1.**

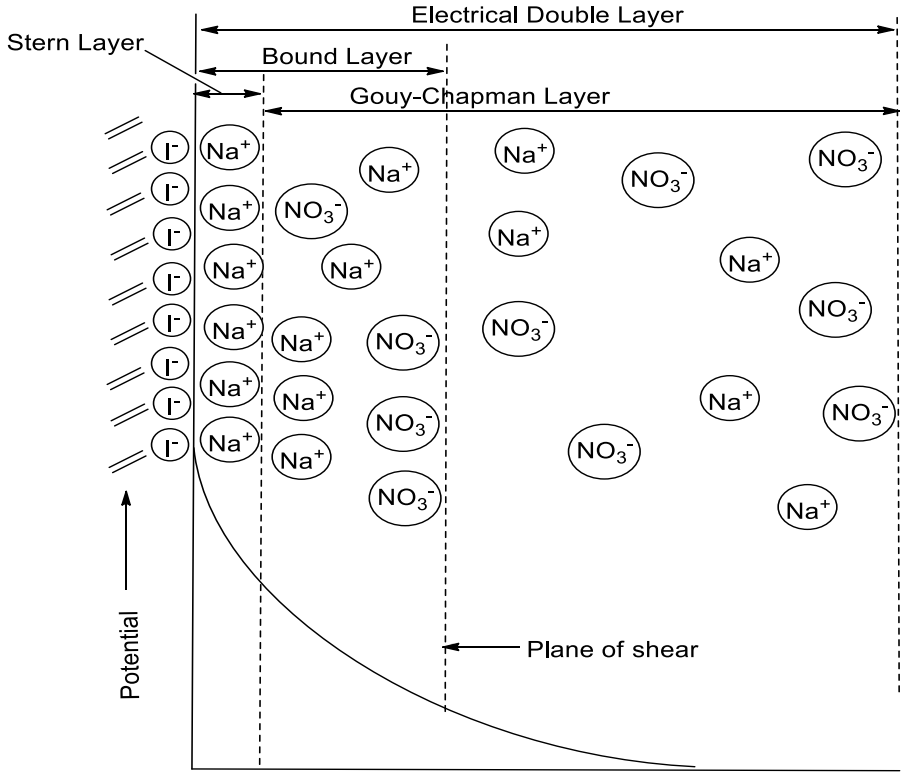


Figure 13.1: The electrical double layer (EDL) in colloidal system.

A more detailed study about this topic will discuss in Semester-II.

13.6.2 Zeta Potential (ζ)

Zeta potential is defined as the potential difference between the surface of the tightly bound layer (plane of shear) and the electroneutral region of the solution. It is located at the shear plane and it determines the stability of colloidal systems. It represents the potential difference between the dispersion medium (bulk solution) and the stationary layer of fluid attached to the particle.
Zeta potential plays a major role in formulation of paints, pharmaceuticals and food colloids.

13.7 MEASUREMENT OF ZETA POTENTIAL AND COLLOIDAL STABILITY

Zeta potential (ζ) measurement determines the electrical charge at a particle's surface, indicating colloidal stability by measuring particle repulsion or attraction. It is measured indirectly through electrokinetic phenomena. The main methods are electrophoresis, electro-osmosis, streaming and sedimentation potential. Among them electrophoresis is most widely used.

1. Electrophoresis:
It works on the principle that when an electric field is applied to a colloidal dispersion,

charged particles move toward the oppositely charged electrode, thereby positively charged particles move towards cathode negatively charged particles move towards anode. The velocity of particle movement is called electrophoretic mobility (μ) and is given by:

$$\boldsymbol{\mu} = \frac{\boldsymbol{v}}{\mathbf{E}}$$

Where:
v = particle velocity
E = applied electric field
zeta potential (ζ) is calculated using *Henry's* equation:

$$\zeta = \frac{3\eta\mu}{2\epsilon f(\mathrm{K_a})}$$

Also, for aqueous medium (Smoluchowski approximation):

$$\zeta = \frac{\eta\mu}{\varepsilon}$$

Where:
η = viscosity of medium
Ɛ = dielectric constant
μ = electrophoretic mobility
Procedure:
In this method a dilute colloidal sample is placed in a cell, electrodes apply a known electric field; the particle velocity is measured optically, mobility is calculated and finally zeta potential (ζ) is determined using appropriate equations shown above.
Advantages: It is a rapid and accurate method of measurement and it is suitable for nano-sized particles.
Modern and advance instrumentation used are: Electrophoretic Light Scattering (ELS), Laser Doppler Velocimetry (LDV) and Phase Analysis Light Scattering (PALS).

2. Electroosmosis:
If the solid surface is fixed and liquid moves under an applied electric field, the phenomenon is called electroosmosis. In this method of measurement, the liquid flow rate is measured and zeta potential (ζ) is calculated using electroosmotic mobility. This method is used mainly for porous materials, membranes and capillaries.

13.7.1 Colloidal Stability

Colloidal stability refers to the ability of dispersed particles in a colloidal system to resist aggregation, keeping the mixture uniform over time. It is primarily achieved by overcoming attractive van der Waals forces through mechanisms like electrostatic repulsion (zeta potential) or steric hindrance (polymer/surfactant layers). This is well explained by **DLVO** theory (Derjaguin-Landau-Verwey-Overbeek Theory). According to this theory, there is a balance between the repulsive interactions between the charges of the electrical double layers on neighbouring particles and the attractive van der Waals interactions between the molecules in the particles.
General stability criteria:

Zeta potential (mV)	Stability of colloid
0 to ± 5 mV	Rapid coagulation
± 10 to ± 20 mV	Incipient instability
± 30 mV	Moderate stability
± 40 mV or more	Good stability

Thus,

- High zeta potential (≥ ± 30 mV) : Strong repulsion leads to Stable colloid
- Low zeta potential (< ± 10 mV): Particles aggregate results coagulation and flocculation occurs

W CHECK YOUR PROGRESS

Q6. What is zeta potential?

2 13.8 LET US SUM UP

- Chemisorption is a specific type of adsorption in which adsorbate molecules form strong chemical bonds (covalent or ionic) with the surface atoms of a solid. Unlike physisorption, it involves high heat of adsorption, usually forms a monolayer, requires activation energy, and is generally irreversible. Chemisorption plays a crucial role in heterogeneous catalysis, corrosion, gas sensing, and electrochemical processes.
- On metal surfaces, especially transition metals (Fe, Ni, Pt, Pd) due to partially filled d-orbitals, chemisorption occurs through electron transfer or sharing due to partially filled d-orbitals, and may proceed via associative or dissociative mechanisms. Important industrial processes such as the Haber process, hydrogenation reaction, oxidation reaction etc depends on chemisorption as the initial step.
- In semiconducting oxides (ZnO, TiO_2, SnO_2, NiO etc), chemisorption involves charge transfer between the adsorbate and the semiconductor, leading to changes in electrical conductivity; this principle is widely used in gas sensors.
- In insulating oxides (SiO_2, Al_2O_3, MgO, ZrO_2 etc), chemisorption mainly occurs through acid-base interactions involving surface metal cations, oxygen anions, and hydroxyl groups, and is strongly influenced by surface defects and hydroxylation. This principle has major role in surface chemistry, catalysis, environmental science etc.
- The development of surface charge gives rise to important electrical properties such as surface potential (ψ) and work function (Φ). When a charged surface comes into contact with an electrolyte solution, an Electrical Double Layer (EDL) is formed, consisting of a compact Stern layer and a diffuse Gouy-Chapman layer.
- The potential at the slipping plane, known as zeta potential (ζ), is a key parameter that determines colloidal stability. Zeta potential is measured using electrokinetic methods such as electrophoresis and electro-osmosis.

- According to the DLVO theory, colloidal stability results from a balance between electrostatic repulsion and van der Waals attraction, and higher magnitude ζ values (≥ ± 30 mV) indicate greater stability of the colloidal system.
- Understanding these concepts is essential in catalysis, materials science, electrochemistry, and nanotechnology.

K 13.9 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: Chemisorption is a type of adsorption in which the adsorbate molecules are held on the surface of a solid by the formation of strong chemical bonds (covalent or ionic).

Answer to Q2: (C). Strong chemical bonding

Answer to Q3: (b). Monolayer adsorption

Answer to Q4: Semiconducting oxides: ZnO, TiO_2
Insulating oxides: SiO_2, Al_2O_3

Answer to Q5: Chemisorption on semiconducting oxides differs from metals primarily in the mechanism of charge transfer, the role of surface defects, and the effect of the adsorption on the material's bulk electronic properties.

Answer to Q6: Zeta potential (ζ) is the potential difference between the dispersion medium and the slipping plane of a particle.

O 13.10 FURTHER READING

- K.L. Kapoor. *A Textbook of Physical Chemistry, Vol. V.* Mc Graw Hill (India)
- B.R. Puri, L.R. Sharma, Madan S. Pathania. *Principles of Physical Chemistry*
- D.J. Shaw. *Colloid and Surface Chemistry*. Taylor and Francis.
- P.W. Atkins. *Physical Chemistry*. Oxford University Press.
- A.W. Adamson, A.P. Gast. Physical Chemistry of Surfaces. Wiley Interscience.

M 13.11 MODEL QUESTIONS

Q1. Explain chemisorption on metal surfaces with examples.
Q2. Discuss chemisorption on semiconducting and insulating oxides with suitable examples.
Q3. Describe electrical double layer (EDL) and its significance.
Q4. Explain the measurement of zeta potential (ζ) and its role in colloidal stability.

UNIT 14: MECHANISM OF HETEROGENEOUS CATALYSIS

UNIT STRUCTURE

14.1 Learning Objectives
14.2 Introduction
14.3 Kinetics of Heterogeneous Catalysis
14.4 Mechanism of Heterogeneous Catalysis
14.5 Langmuir-Hinshelwood Model
14.6 Eley-Rideal Model
14.7 Unimolecular Surface Reactions
14.8 Bimolecular Surface Reactions
14.9 Let Us Sum Up
14.10 Answers to Check Your Progress
14.11 Further Reading
14.12 Model Questions

14.1 LEARNING OBJECTIVES

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

- understand the fundamental concepts of heterogeneous catalysis.
- understand the mechanism of heterogeneous catalysis.
- explain the kinetics of surface-catalysed reactions.
- describe the Langmuir-Hinshelwood model and Eley-Rideal model.
- differentiate between unimolecular and bimolecular surface reactions.
- apply kinetic models to catalytic systems.

14.2 INTRODUCTION

Heterogeneous catalysis involves reactions where the catalyst and reactants exist in different phases, usually a solid catalyst and gaseous or liquid reactants. In this type of catalysis, the catalyst provides an active surface on which the reaction takes place without itself being consumed. Many large-scale industrial processes are based on heterogeneous catalysis, including the Haber-Bosch process for ammonia production, the Contact process for manufacturing sulphuric acid, and Catalytic Cracking in petroleum refining etc.

The catalytic mechanism generally consists of three main steps: adsorption of reactant molecules onto the catalyst surface, reaction between the adsorbed species at active sites, and desorption of the formed products from the surface. A clear understanding of the kinetics and reaction mechanism is crucial for effective catalyst design, process optimization, and improved performance in industrial applications.

A systematic understanding of kinetics and mechanism is essential for catalyst design, improvement of activity and selectivity, optimization of operating conditions, and

efficient industrial application. This unit therefore provides both theoretical foundation and practical insight into the mechanistic aspects of heterogeneous catalysis.

14.3 KINETICS OF HETEROGENEOUS CATALYSIS

The study of kinetics of gaseous reactions on solid surfaces has become one of the most important research tools in chemistry.

The kinetics of heterogeneous catalysis differs from homogeneous reactions because:

(i). Reaction occurs on surface active sites.
(ii). Adsorption equilibrium plays a major role.
(iii). Surface coverage affects reaction rate.

The kinetics of heterogeneous catalysis involves **07** sequential steps as follows:

(i). External Diffusion: Reactants move from the bulk fluid to the external surface.
(ii). Internal Diffusion: Reactants diffuse into catalyst pores.
(iii). Adsorption: Reactants bind to active sites on the surface.
(iv). Surface Reaction: Adsorbed molecules react to form products.
(v). Desorption: Products leave the catalyst surface.
(vi). Internal Diffusion: Products move out of pores.
(vii). External Diffusion: Products move to the bulk fluid.

Key factors include:

- Surface area: Larger surface areas allow for more adsorption and faster reactions.
- Temperature: Increases rates according to the Arrhenius equation.
- Active Sites: The number of available active sites dictates the maximum rate.
- Catalytic efficiency.

Rate Expression

For many catalytic reactions:

$$\text{Rate} = k\theta$$

Where

k = rate constant

θ = surface coverage

14.4 MECHANISM OF HETEROGENEOUS CATALYSIS

Heterogeneous catalysis involves a reaction between reactants and a catalyst present in different phases, usually gaseous or liquid reactants interacting with a solid catalyst. The reaction occurs at the surface of the solid catalyst and proceeds involving five stages: diffusion, adsorption, reaction, desorption, and product diffusion. Understanding the mechanism is essential for explaining reaction rates, selectivity, and catalytic efficiency.

The mechanism of heterogeneous catalysis typically consists of the following steps:

1. *Diffusion of Reactants*:
Reactant molecules first diffuse from the bulk phase (gas or liquid) to the external surface of the catalyst. In porous catalysts, they may further diffuse into the internal pores to reach active sites.
2. *Adsorption*:
Reactant molecules become attached to active sites on the catalyst surface. Adsorption may be Physisorption (weak van der Waals forces) or Chemisorption (strong chemical bonding).

$$A + S \rightleftharpoons AS$$

Where,
S = vacant surface site
AS = adsorbed species
3. *Surface Reaction*:
The adsorbed molecules react on the surface to form product molecules. This stage involves intermediates. The adsorbed species undergo chemical transformation on the surface. This may occur either between two adsorbed species (explained by the *Langmuir-Hinshelwood model*), or between an adsorbed species and a gas-phase molecule (explained by the *Eley-Rideal model*).
4. *Desorption*:
After formation, product molecules detach from the catalyst surface:

$$PS \rightleftharpoons P + S$$

The active site (S) becomes free again and can participate in another catalytic cycle.
5. *Diffusion of Products*:
The desorbed products diffuse away from the catalyst surface into the bulk fluid.

W CHECK YOUR PROGRESS

Q1. Define heterogeneous catalysis.
Q2. What do you mean by rate-determining step?

14.5 LANGMUIR-HINSHELWOOD MODEL

The Langmuir-Hinshelwood (LH) model is one of the most important kinetic models used to describe heterogeneous catalytic reactions, where both reactants are adsorbed on the catalyst surface before reacting. In LH mechanism of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface.
Basic **Assumptions** of the Langmuir-Hinshelwood model as follows:

1. Adsorption on specific sites: The catalyst surface contains a fixed number of active sites.
2. Monolayer adsorption: Adsorption of reactants follows the *Langmuir adsorption isotherm*.
3. Uniform surface: All active sites are equivalent, and the heat of adsorption is constant, regardless of surface coverage.
4. Surface phenomena: Both reactants are adsorbed on the surface.

5. Surface reaction: The surface reaction between adsorbed species is slow and is the rate-determining step.
6. Desorption: Desorption of products is rapid.
7. No lateral interactions: No interaction between adsorbed molecules on neighbouring sites.

- **Derivation of Rate equation:**

Consider a bimolecular reaction:

$$\mathrm{A_{(g)} + B_{(g)} \rightarrow Product\ (P)}$$

Step 1: Adsorption

$$\mathbf{A + S} \rightleftharpoons \mathrm{A - S}$$
$$\mathrm{B + S \rightleftharpoons B - S}$$

Where, S = vacant active site

According to Langmuir adsorption isotherm:

$$\theta_A = \frac{K_A\, P_A}{1 + K_A P_A + \ K_B P_B}$$

$$\theta_B = \frac{K_B\, P_B}{1 + K_A P_A + \ K_B P_B}$$

Where,

θ = Surface area covered

K = Adsorption equilibrium constant

P = Partial pressure

Step 2: Surface Reaction (Rate Determining Step)

$$\boldsymbol{A - S + B - S \rightarrow Product}$$

Rate of reaction:

$$r = k\theta_A\theta_B$$

Substituting values of θ, the rate of the reaction (r) becomes-

$$r = \frac{k\, K_A K_B\ P_A P_B}{(1+K_A P_A + K_B P_B\ )^2} \qquad (14.1)$$

This is the general **Langmuir-Hinshelwood** rate expression.

- **Special Cases:**

1. At low pressure ($\boldsymbol{K_A P_A \ll 1\ and\ K_B P_B \ll 1}$) equation (14.1) becomes-

Denominator ≈ 1

$$r = kK_A K_B P_A P_B$$

Thus, reaction becomes **second order**.

2. At High pressure ($\boldsymbol{K_A P_A \gg 1}$, $\boldsymbol{K_B P_B \gg 1}$, surface becomes saturated, thus rate becomes independent of pressure (**Zero order** behaviour).

3. One of the reactant strongly adsorbed

If A is strongly adsorbed and B is weakly adsorbed:

Rate may show **first-order** dependence on B and **zero-order** on A.

14.6 ELEY-RIEDAL MODEL

In heterogeneous catalysis, reactions occur on the surface of a solid catalyst. Depending on how the reactant molecules interact with the surface, different mechanisms are proposed. One such mechanism is the *Eley-Rideal (ER) Model*, proposed by D. D. Eley and E. K. Rideal.

"According to this model, only one of the reactant molecules is adsorbed on the catalyst surface, while the other reactant reacts directly from the gas (or liquid) phase with the adsorbed species."

Thus in Eley-Rideal mechanism of a surface-catalysed reaction, a gas phase molecule collides with one another molecule that already adsorbed on the surface.

Assumptions of the Eley-Rideal model as follows:

1. Only one reactant is adsorbed on the catalyst surface.
2. Adsorption follows the Langmuir adsorption isotherm.
3. The second reactant reacts directly from the gas phase with the adsorbed species.
4. The surface reaction is the rate-determining step.
5. Desorption of product is rapid.

Mechanism:

Consider a reaction between gaseous molecules A and B:

$$A_{(g)} + B_{(g)} \rightarrow Product\ (P)$$

Step 1: Adsorption of A on the surface

$$\boldsymbol{A_{(g)} + S \rightleftharpoons A - S}$$

Where, S represents an active site.

Step 2: Surface reaction (rate-determining step)

$$\boldsymbol{A - S + B_{(g)} \rightleftharpoons Products + S}$$

Here, B reacts directly from the gas phase with the adsorbed A.

Derivation of Rate Expression:

From Langmuir adsorption isotherm we have:

$$\theta_A = \frac{K_A\, P_A}{1 + K_A P_A}$$

Where,

K_A = adsorption equilibrium constant for A

P_A, P_B = partial pressures of A and B

θ_A = fraction of surface covered by A

Since the surface reaction is rate determining, thus:

$$r = k\theta_A P_B$$

Substituting the value of θ_A, we get:

$$r = \frac{k\, K_A P_A P_B}{1 + K_A P_A} \qquad (14.2)$$

This is the **Eley-Rideal** rate equation**.**

- **Special Cases:**

1. At low pressure of A ($\boldsymbol{K_A P_A \ll 1}$), equation (14.2) becomes-

$$\boldsymbol{r \approx k K_A P_A P_B}$$

Rate is **first** order in both A and B.

2. At high pressure of A ($\boldsymbol{K_A P_A \gg 1}$), then

$$r \approx k P_B$$

Rate becomes **independent** of P_A and first order in P_B.

- **Comparison with Langmuir-Hinshelwood Model:**

Features	**Eley-Rideal Model**	**Langmuir-Hinshelwood Model**
Adsorption:	Only one reactant adsorbed	Both reactants adsorbed
Surface reaction:	Between adsorbed species and gas-phase molecule	Between two adsorbed species
Rate expression:	Depends on one surface coverage	Depends on both surface coverages
Applicability:	When one reactant weakly adsorbs	When both reactants strongly adsorb

W CHECK YOUR PROGRESS

Q3. State assumptions of the Langmuir-Hinshelwood model.

Q4. At high surface coverage in the Langmuir- Hinshelwood model, the reaction often shows:

(a). Second-order kinetics
(b). First-order kinetics
(c). Zero-order kinetics
(d). Third-order kinetics

Q5. The Eley-Rideal mechanism is applicable when:

(a). Both reactants strongly adsorb
(b). One reactant weakly adsorbs
(c). Catalyst surface is inert
(d). Reaction is homogeneous

14.7 UNIMOLECULAR SURFACE REACTIONS

Unimolecular surface reactions are heterogeneous catalytic reactions in which a single reactant molecule undergoes transformation after being adsorbed on the catalyst surface. In this type of reaction, the rate-determining step involves only one adsorbed species on the surface. The mechanism of the reactions generally follows the adsorption-reaction-desorption sequence. These reactions are important in many industrial processes such as decomposition, isomerization, and cracking reactions.

General Mechanism:

A unimolecular surface reaction may involve a reaction between a molecule A of the reactant and a vacant site S on the surface.

Step 1: Adsorption

$$\boldsymbol{A_{(g)} + S \rightleftharpoons A - S}$$

Step 2: Surface Reaction (Rate-determining step)

$$\boldsymbol{AS \rightarrow Products + S}$$

Here, AS represents the adsorbed species.

Rate Expression:

According to the **Langmuir-Hinshelwood** hypothesis, the rate of reaction depends on the surface coverage of the reactant.

Suppose, θ_A = fraction of surface covered by A and k = rate constant for surface reaction

Then, $r = k\theta_A$

From Langmuir adsorption isotherm we have:

$$\theta_A = \frac{K\,P_A}{1 + K\,P_A}$$

Where:

K = adsorption equilibrium constant

P_A = partial pressure of A

Thus substituting the value of θ_A, the overall rate becomes:

$$r = \frac{k\,K\,P_A}{1+K\,P_A} \qquad (14.3)$$

- **Limiting Cases:**

Two limiting cases of equation (14.3) are discussed below:

1. At low pressure, when reactant is slightly adsorbed, $(KP_A \ll 1)$ so that rate becomes

$$\boldsymbol{r = kKP_A}$$

i.e. the reaction follows **first-order** kinetics with respect to A.

2. At high pressure, when the reactant is strongly adsorbed, $(KP_A \gg 1)$ so that rate becomes

$$\boldsymbol{r = k}$$

i.e. the reaction is **zero-order** with respect to A, since the surface is saturated.

The pressure-dependence of the rate of a unimolecular surface reaction is shown in **Figure 14.1.** From the figure it is clear that at low pressure, the fraction of area covered by the molecules (or the concentration of adsorbed molecules) increases linearly with pressure and also the rate of surface reaction. In high pressure, all the sites on the surface are occupied (i.e. θ = 1) and thus the concentration of adsorbed molecules remains constant and hence reaction becomes zero-order with respect to the adsorbed molecules.

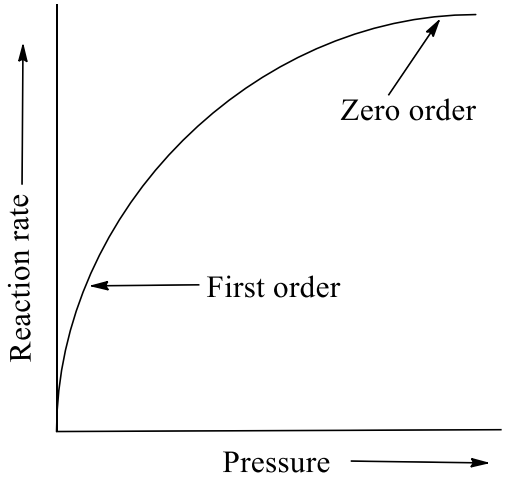


Figure 14.1: Pressure-dependence of the rate of a unimolecular surface reaction.

Characteristics of Unimolecular Surface Reactions:

Important characteristics are given below:

(a). Involvement of a Single Adsorbed Species: Only one reactant molecule is involved in the rate-determining step.

(b). Dependence on Surface Coverage: The reaction rate depends on the fractional surface coverage (θ) of the adsorbed species.

(c). Shows transition from first-order kinetics at low pressure to zero-order kinetics at high Pressure.

(d). Involvement of Active Sites: Reaction occurs only at specific active sites on the catalyst surface. The number and nature of these sites influence the reaction rate.

(e). Common in catalytic decomposition and isomerization reactions.

Examples:

Some typical unimolecular surface reactions are:

(a). Decomposition of ammonia on molybdenum:

$$2\,NH_3 \longrightarrow N_2 + 3H_2$$

(b). Decomposition of nitrous oxide on gold:

$$2\,N_2O \longrightarrow 2N_2 + O_2$$

(c). Isomerization reactions on solid acid catalysts.

14.8 BIMOLECULAR SURFACE REACTIONS

Bimolecular surface reactions are heterogeneous catalytic reactions in which two reactant molecules participate in the rate-determining step on the catalyst surface. Both reactants are generally adsorbed on the surface before undergoing reaction. These reactions are very common in industrial catalysis, including hydrogenation, oxidation, and synthesis reactions. The kinetics of such reactions commonly explained using the *Langmuir-Hinshelwood* mechanism and the *Eley-Rideal* mechanism.

Mechanism:

Langmuir-Hinshelwood Mechanism of bimolecular surface reaction:
In this mechanism, both reactants are adsorbed on the catalyst surface.

Step 1: Adsorption

$$\boldsymbol{A_{(g)} + S \rightleftharpoons A - S}$$
$$\boldsymbol{B_{(g)} + S \rightleftharpoons B - S}$$

Step 2: Surface Reaction (Rate-determining step)

$$\boldsymbol{AS + BS \rightarrow Products + 2S}$$

Rate Expression:
If θ_A and θ_B are surface coverages, then rate becomes-

$$r = k\theta_A\theta_B$$

Using Langmuir adsorption isotherm, we have

$$\theta_A = \frac{K_A\, P_A}{1 + K_AP_A + \, K_BP_B}$$

$$\theta_B = \frac{K_B\, P_B}{1 + K_AP_A + \, K_BP_B}$$

Therefore, substituting these values the rate of the bimolecular reaction becomes-

$$r = \frac{k\, K_AK_B\, P_AP_B}{(1+K_AP_A+ K_BP_B)2} \qquad (14.4)$$

- **Limiting cases:**

Let us consider the following three cases:

1. When A and B both are weakly adsorbed. In such case, $K_AP_A \ll 1\ and\ K_BP_B \ll 1$, so that the rate becomes

$$r = kP_AP_B$$

i.e. the reaction is *first-order* with respect to A and B and overall **second-order** reaction.
Example: Reaction between NO and O_2 on a glass surface.

2. When A is adsorbed more strongly than B. In this case $K_AP_A \gg K_BP_B$, so that the rate becomes

$$r = \frac{k\, P_AP_B}{(1 + K_AP_A)2}$$

i.e. the reaction is *first-order* with respect to B, the weakly adsorbed component.
Example: Reaction between CO_2 and H_2 on platinum belongs to this category.

3. When one of the reactant is strongly adsorbed. Let A be very strongly adsorbed component, then $K_AP_A \gg K_BP_B\ and\ K_AP_A \gg 1$. Now the rate of the equation becomes-

$$r = \frac{k\, P_AP_B}{K_A^2\, P_A^2} = \, K_1\left(\frac{P_B}{P_A}\right)$$

Where $K_1 = \frac{k}{K_A^2}$, evidently the rate is **inversely** proportional to the concentration of the very strongly adsorbed component. This is expressed by saying that the reaction is inhibited by such a component.

Example: Reaction between H_2 and O_2 on platinum belongs to this category.

Characteristics of Bimolecular surface reactions:

- Two reactant molecules are involved in the rate-determining step.
- Reaction occurs on active sites of the catalyst.
- Surface coverage strongly influences rate of the reaction.
- Follows Langmuir-Hinshelwood or Eley-Rideal mechanisms.

Examples:

(a). Hydrogenation of ethylene:

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

(b). Oxidation of carbon monoxide:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

(c). Ammonia synthesis:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

W CHECK YOUR PROGRESS

Q6. What is meant by a unimolecular surface reaction?
Q7. Give one example of a bimolecular surface reaction.

2 14.9 LET US SUM UP

- This unit explains the mechanism and kinetics of heterogeneous catalysis, where reactions occur on the surface of a solid catalyst. The catalytic process involves adsorption of reactants, surface reaction at active sites, and desorption of products, along with diffusion steps.
- The kinetics of heterogeneous catalysis differs from homogeneous reactions because surface coverage, adsorption equilibrium, and active site availability significantly influence the reaction rate. The rate is often expressed in terms of surface coverage (θ), and adsorption behaviour is commonly described using the Langmuir adsorption isotherm. The rate-determining step plays a crucial role in controlling overall kinetics.
- We have discussed two major models of Heterogeneous catalysis namely:

(i). **Langmuir-Hinshelwood model** where both reactants are adsorbed before reacting. The reaction shows second-order behaviour at low pressure and zero-order behaviour at high pressure due to surface saturation.

(ii). **Eley-Rideal model** in which only one reactant is adsorbed, and the other reacts directly from the gas phase. Its rate law predicts first-order behaviour at low coverage and pressure independence of the strongly adsorbed species at high pressure.

- This unit further distinguishes between Unimolecular surface reactions, where only one adsorbed species is involved in the rate-determining step, and Bimolecular surface reactions, where two reactant molecules participate. Unimolecular reactions typically show a transition from first-order kinetics at low pressure to zero-order kinetics at high pressure. Bimolecular reactions may

follow either Langmuir-Hinshelwood or Eley-Rideal mechanisms or shows other kinetic behaviour depending on adsorption strengths.

- Overall, the unit integrates theoretical derivations, limiting cases, mechanistic interpretation, and industrial relevance, providing both conceptual clarity and practical insight into heterogeneous catalytic systems essential for explaining industrial catalytic processes.

K 14.10 ANSWERS TO CHECK YOUR PROGRESS

Answer to Q1: Heterogeneous catalysis is a type of catalysis in which the catalyst and the reactants are present in different phases, usually a solid catalyst with gaseous or liquid reactants.

Answer to Q2: The slowest elementary step in a reaction mechanism that controls the overall rate.

Answer to Q3: Basic Assumptions of the *Langmuir-Hinshelwood* model are:

(a). The catalyst surface contains a fixed number of active sites.
(b). Monolayer adsorption
(c). All active sites are equivalent, and the heat of adsorption is constant, regardless of surface coverage.
(d). Both reactants are adsorbed on the surface.
(e). The surface reaction between adsorbed species is slow and is the rate-determining step.
(f). Desorption of products is rapid.

Answer to Q4: (c) Zero-order kinetics $(since\ K_A P_A, K_B P_B \gg 1)$

Answer to Q5: (b) One reactant weakly adsorbs.

Answer to Q6: A unimolecular surface reaction is a type of heterogeneous catalytic reaction in which only one reactant molecule is involved in the rate-determining surface reaction step.

Answer to Q7: Oxidation of carbon monoxide on a platinum surface.

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

O 14.11 FURTHER READING

- K.J. Laidler. *Chemical Kinetics*. Pearson
- B.R. Puri, L.R. Sharma, Madan S. Pathania. *Principles of Physical Chemistry*
- K.L. Kapoor. *A Textbook of Physical Chemistry, Vol. V.* Mc Graw Hill (India)
- J.M.Thomas, W.J.Thomas. *Principles and Practice of Heterogeneous Catalysis*. Wiley VCH.

M 14.12 MODEL QUESTIONS

Q1. Discuss the factors affecting the kinetics of heterogeneous catalysis.
Q2. Derive the rate equation for the Langmuir-Hinshelwood mechanism.
Q3. Compare Langmuir-Hinshelwood and Eley-Rideal models.
Q4. Using Langmuir adsorption theory, account for the experimental observation that the decomposition of phosphine (PH_3) on tungsten follows first-order kinetics at low pressures and zero-order kinetics at high pressures.
Q5. Why does unimolecular surface reaction become zero-order at high pressure?
Q6. Write the rate expression of Langmuir-Hinshelwood mechanism for bimolecular surface reactions.