Bachelor of Science
(B.Sc.- PCM)

Solutions, Phase equilibrium, Conductance, Electrochemistry & Functional Group Organic Chemistry -II
(DBSPCO301T24)

Self-Learning Material
(SEM-III)

Jaipur National University
Centre for Distance and Online Education

Established by Government of Rajasthan
Approved by UGC under Sec 2(f) of UGC ACT 1956
&
NAAC A+ Accredited

Jaipur National University

Course Code: DBSPCO301T24
Solutions, Phase equilibrium,
Conductance, Electrochemistry &
Functional Group Organic Chemistry-II

TABLE OF CONTENT

EXPERT COMMITTEE

Prof. R. S. Lokhende
Department of Life Sciences
Jaipur National University, Jaipur

Prof. Purnima Nag
Department of Basic Sciences
Jaipur National University, Jaipur

COURSE COORDINATOR

Dr. Urvija Garg
Department of Life Sciences
Jaipur National University, Jaipur

UNIT PREPARATION

Unit Writers

Dr. Azhar Ullah Khan
Department of Life Sciences
JNU, Jaipur
Unit:1-7

Ms Annu Yadav
Department of Life Sciences
JNU, Jaipur
Unit:8-14

Assisting & Proof Reading

Dr. Sunil K Sharma
Department of Life Sciences
JNU, Jaipur

Editor

Prof. Ruby Singh
Department of Life Sciences
JNU, Jaipur

COURSE INTRODUCTION

This comprehensive course provides an in-depth exploration of key topics in advanced chemistry, focusing on solutions, phase equilibrium, conductance, and electrochemistry, alongside an in-depth study of organic compounds including carboxylic acids, amines, diazonium salts, amino acids, and carbohydrates.

The course is divided into 14 units. Each Unit is divided into sub topics.

In this course students will learn about the nature of solutions, including solute-solvent interactions, solubility, and factors influencing solubility such as temperature and pressure. Concentration terms (molarity, molality, and normality) and their applications will be covered.

The Phase Equilibrium covers the principles of phase transitions and equilibrium, including phase diagrams and the phase rule. Students will explore how systems reach equilibrium between different phases (solid, liquid, gas) and how external changes affect these systems.

Conductance covers the basics of electrical conductance in solutions, focusing on the role of ions in conducting electricity. Students will differentiate between strong and weak electrolytes based on their dissociation in water.

In the electrochemistry students will study oxidation-reduction reactions, electrode potentials, and the Nernst equation, which relates cell potential to the concentration of reactants and products.

The course describe the properties, synthesis and chemical properties of carboxyl group (-COOH), its acidic nature, and the influence of substituents on acidity.

In the section amines and diazonium salts students will learn about the preparation and reactivity of diazonium salts, including their role in synthesizing azo dyes and other aromatic compounds.

Students will study the classification of carbohydrates into monosaccharides, disaccharides, and polysaccharides, along with their structural and functional roles.

We hope you enjoy the course. Please attempt all the assignments and exercises given at the end of each chapter.

Course Outcomes:

After completion of this course, a student will be able to

1. Understanding of the nature of solutions, including solute-solvent interactions, solubility, and concentration measures.
2. Able to interpreting phase diagrams and applying the phase rule to predict the behavior of systems at equilibrium.
3. Illustrate the structures of carbohydrates, including monosaccharides, disaccharides, and polysaccharides.
4. Describe the structure, properties and reactions of carboxylic acids, amines and diazonium salt.
5. Understanding of the structure of amino acids, including their classification as essential or non-essential, and their role in protein synthesis.
6. Analyze the structures of carbohydrates, including monosaccharides, disaccharides, and polysaccharides.

Acknowledgements:

The content we have utilized is solely educational in nature. The copyright proprietors of the materials reproduced in this book have been tracked down as much as possible. The editors apologize for any violation that may have happened, and they will be happy to rectify any such material in later versions of this book.

Unit - 1

Solution

Objective:

- Categorize mixtures of liquids.
- Differentiate Ideal and non-ideal solution.
- Describe the steps involved in steam distillation.
- Explain Roults law.
- Define mixture that freezes.
- Specify the freezing mixture.

1.1 Introduction: A homogenous molecular mixture of two or more substances is called a solution. The mixture's component that is present in lesser amounts is referred to as the solute, while the component that is present in higher amounts is referred to as the solvent. For instance, a homogenous solution in water is produced when a lesser quantity of sugar (solute) is combined with water (solvent). In this solution, the sugar molecules are evenly distributed among the water molecules. Similar to this, ions of salt (Na^+,Cl^-) scattered in water make up a solution of salt (Na^+ Cl^-) in water.

1.2 Solution Concentration:

The quantity of solute contained in a specific volume of solution is known as the solution concentration or amount of the solute present in a unit volume of solution is the usual way to express concentration.

$$\text{Concentration} = \frac{\text{Quantity of solute}}{\text{Volume of solution}}$$

Dilute solution is a mixture in which the solute concentration is relatively low. Concentrated solution refers to a highly concentrated solution.

1.3 Methods of Communicating Concentration

The concentration of a solution can be expressed in a number of ways:

(a) Mole fraction

(b) Percent by weight

(c) Molarity

(d) Molality

(f) Normality

1.3.1 Percent by Weight: It represents the solute's weight as a percentage of the solution's total weight. Than,

$$\%\,\text{by weight of solute} = \frac{\text{Wt.of solute}}{\text{Wt.of solution}} \times 100$$

Question: If 1.75 grams of NaCl dissolve in 5.85 grams of water, what is the percentage of NaCl by weight?

Answer:

$$\text{Wt. of solute (NaCl)} = 1.75\,\text{g}$$
$$\text{Wt. of solvent } (H_2O) = 5.85\,\text{g}$$
$$\therefore \quad \text{Wt. of solution} = 1.75 + 5.85 = 7.60\,\text{g}$$

Hence concentration of NaCl % by weight

$$= \frac{1.75}{7.60} \times 100$$
$$= \mathbf{23.0}$$

1.3.2 Mole Fraction: Solute and solvent are the two components that make up a simple solution. The ratio between the amount of solute and the total amount of solute plus solvent is known as the mole fraction, or X, of the solute. Than,

$$X_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Moles of solute + Moles of solvent}}$$

If n represents moles of solute and N number of moles of solvent,

$$X_{\text{solute}} = \frac{n}{n + N}$$

Notice that mole fraction of solvent would be

$$X_{\text{solvent}} = \frac{N}{n + N}$$

Mole fraction is unitless and

$$X_{\text{solute}} + X_{\text{solvent}} = 1$$

Question: In a hydrochloric acid and water solution, which contains 36% HCl by weight, find the mole fraction of HCl.

Answer:

The solution contains 36 g of HCl and 64 g of H_2O

$$\text{Number of Moles of HCl} = (36\,\text{g HCl})\left(\frac{1\text{mol HCl}}{36.5\text{g HCl}}\right)$$
$$= 0.99$$

$$\text{Number of Moles of } H_2O = (64\,\text{g } H_2O)\,\frac{1\text{mol } H_2O}{18\text{gm of } H_2O}$$
$$= 3.55$$

$$X_{HCl} = \frac{\text{moles of HCl}}{\text{moles of HCl} + \text{moles of } H_2O}$$

$$= \frac{0.99}{3.55 + 0.99} = \mathbf{0.218}$$

1.3.3 Molarity: Amount of moles of solute in one liter of solution is known as molarity, or M for short. If V liters are the volume and n is the moles number solute,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume in litres}}$$

or

$$M = \frac{n}{V\,(\text{in litres})}$$

Molarity calculation: If the volume V (in liters) and the number of moles of solute (n) are known, the molarity of a solution can be computed using the formula (1). The solute can be converted to moles when its molecular weight (MW) is known and its amount is given in grams:

$$n = x\text{ g} \times \frac{1\text{mol}}{MW\text{ g}}\text{ mol}$$

Substituting in expression (1)

$$M = x\text{ g} \times \frac{1\text{mol}}{MW\text{ g}} \times \frac{1}{V}$$

Question: When 75.5 g of pure KOH are dissolved in 540 ml of solution, what is the molarity of the resulting mixture?

Answer:

$$\text{Molecular mass of KOH} = 39.1 + 16.0 + 1.0$$
$$= 56.1$$

Calculation of moles of KOH:

$$75.5\text{g KOH} \times \frac{1\text{mol}}{56.1\text{g}} = 1.35\text{mol}$$

Calculation of volume in litres :

$$540\text{ml} \times \frac{1\text{litre}}{1000\text{ml}} = 0.540\text{ litres}$$

Calculation of Molarity : $M = \frac{n}{V}$

Thus the solution is **2.50 M.**

1.3.4 Molality: The amount of solute moles in per kilogram of solvent is known as a solution's 'Molality' (symbol m).

$$\text{Molality}\,(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}}$$

Question: When 5.0 g of toluene (C_7H_8) is dissolved in 225 g of benzene (C6H6), what is the molality of the resulting solution?

Answer:

Calculation of number of moles of solute :

$$\text{Molecular mass of toluene} = 12 \times 7 + 1 \times 8 = 92$$

$$\text{No. of moles 5 g of toluene} = \frac{5}{92} = 0.0543$$

$$\text{Mass of solvent in kg} = \frac{225g}{1000} = 0.225\text{kg}$$

$$\text{Molality} = \frac{\text{No.of moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.0543}{0.225}$$
$$= 0.24\text{m}$$

1.3.5 Normality: The number of equivalents of solute per litre of a solution is known as the normalcy of the solution (symbol N).

Question: A solution of 5g NaCl is made in 1000 g of water. Assuming the volume of the solution is equal to that of the solvent, determine the molarity, molality normality and mole fraction of solute if the density of resultant solution is 0.997 g per ml.

Answer:

$$\text{Number of moles of NaCl} = \frac{\text{Mass of NaCl}}{\text{Molecular mass NaCl}}$$

$$= \frac{5}{58.5} = 0.0854$$

By definition,

$$\text{Molality} = \frac{\text{No. of moles of solute} \times 1000}{\text{Mass of solvent in grams}}$$

$$= \frac{0.0854}{1000} \times 1000 = \mathbf{0.0854\,m}$$

$$\text{Volume of the solution} = \frac{\text{Mass of solution in grams}}{\text{Density in gm per ml}}$$

$$= \frac{1000 + 5}{0.997} = 1008\,\text{ml}$$

$$= \mathbf{1.008\ litre}$$

Now $$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{0.0854}{1.008} = \mathbf{0.0847\,M}$$

and $$\text{Normality} = \frac{\text{Number of gramequivalents of solute}}{\text{volume of solution in litres}}$$

$$= \frac{0.0854}{1.008} \qquad [\because \text{Mol mass of NaCl} = \text{Eq. wt. of NaCl}]$$

$$= \mathbf{0.0847\ N}$$

To calculate mole fraction of the solute

$$\text{No. of moles of water in 1000 ml} = \frac{1000}{18} = 55.5$$

[? 1 ml of Water = 1 g of water]

$$\text{Total number of moles} = \text{No. of moles of solute} + \text{No. of moles of solvent}$$
$$= 0.0854 + 55.5$$
$$= 55.5854$$

$$\text{Mole fraction of NaCl} = \frac{\text{No. of moles of NaCl}}{\text{Total moles}}$$
$$= \frac{0.0854}{55.5854}$$
$$= \mathbf{1.536 \times 10^{-3}}$$

1.4 Liquid-Liquid Mixture:

Another term for liquid-liquid mixtures is "solution of liquid in liquid." A solution consists of a solvent and a solute, where both are in the liquid phase and volatile when combined in a liquid-liquid mixture. The kind and nature of the intermolecular forces between molecules determine the properties of these mixtures. Characteristics such as surface tension, refractive index, viscosity, and vapor pressure depend on several factors. These mixtures are divided into three categories based on how well two liquids mix:

1.4.1 Immiscible liquid–liquid mixture: These combinations consist of two liquids that form a layer between them because they are insoluble in one another. There is no interference with the individual liquid's qualities by these liquid mixtures. Oil in water, kerosene in water, and benzene in water are a few examples.

1.4.2 Partially miscible mixture: Two layers form in these liquid mixtures because the liquids have limited solubility in each other or are immiscible. The miscibility of these liquid mixtures typically increases with temperature. For instance, consider the systems of water with nicotine, phenol, and triethylamine as illustrations.

1.4.3 Fully miscible mixture: Two liquids in these combinations are totally soluble in one another in any ratio. Take the ethanol-water and benzene-acetone systems, for instance. These combinations fall into two categories: non-ideal liquid mixtures, also known as non-ideal solutions, and ideal liquid mixtures, also known as ideal solutions.

1.5 Ideal Liquid Mixtures:

Ideal solutions are another name for these mixes. Every component in an ideal solution complies with Raoult's law at every concentration and temperature. Enthalpy of mixing (ΔHmix = 0) and volume of mixing (ΔVmix = 0) are zero for a perfect solution. This indicates that the total volume of the two liquids being mixed equals the final volume of the solution. The interaction between A and B in an ideal solution is identical to the interaction between the constituents A and B. When a constituent is present in its pure form, its molar volume is equal to its partial molar volume in an ideal solution. For instance, n-butyl chloride and n-butyl bromide, benzene and toluene, n-hexane and n-heptane, and carbon tetrachloride and chloroform.

1.5.1 Raoult's Law:

'Raoult's law' states that the partial pressure of a volatile liquid component in a solution, at any temperature, is equal to the mole fraction of that specific component present in the mixture times the vapour pressure of the pure component. Consider binary combination made up of the volatile liquids A and B. Let P_A and P_B represent the two liquids' partial pressures, and let x_A and x_B represent their mole fractions. Therefore, in line with Raoult's law:

$$P_A = x_A P_A^{o} \qquad \text{and} \qquad P_B = x_B P_B^{o}$$

where the pure liquids A and B's respective vapour pressures are represented by P o and P o. If every ingredient in a mixture follows Raoult's law at every temperature and concentration, the solution is considered perfect. The vapour pressure curve for a perfect solution is shown in Figure 1.1.

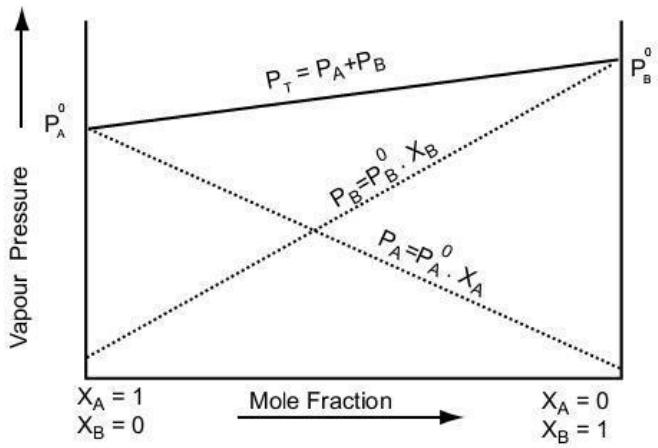


Figure 1.1 Vapour pressure curve for an ideal solution

Raoult's law does not apply when the components of a mixture influence the intermolecular forces or when a compound is formed through component interaction. A liquid's vapour pressure is the amount of pressure that a vapor at a specific temperature exerts when it is in equilibrium with a liquid in a closed container. Let's figure out what an ideal solution's vapour pressure is. The sum of the partial pressures of two liquids, A (P_A) and B (P_B), is the total vapour pressure of a solution (P).

$$P = P_A + P_B = x_A P^{\circ} + x_B P_B^{\circ}$$

1.6 Non- Ideal Solution:

Real solutions or non-ideal liquid mixtures are other names for non-ideal solutions. A solution is considered non-ideal if it deviates from Raoult's law across the whole concentration and temperature range. These solutions' vapour pressures differ from one another and from the pressure determined by applying Raoult's law. In this case, the volume and enthalpy of mixing do not equal zero. As opposed to A-A and B-B (individual components), the force between A and B in these solutions is different. The two categories of non-ideal solutions are those that exhibit a positive deviation (the vapor pressure obtained is higher than the estimated vapour pressure using Raoult's law) and those that show a negative deviation (the calculated vapour pressure obtained is lower than the calculated vapour pressure using Raoult's law).

1.6.1 A 'non-ideal solution' exhibiting positive deviation

The A-B interaction in the component A and B solution is not as strong as the A-A and B-B interactions. Because of this, the solution's vapour pressure is higher than Raoult's expected pressure. There is a positive enthalpy of mixing. Examples are carbon tetrachloride and toluene, ethanol and hexane, acetone and carbon disulphide, and carbon tetrachloride and benzene. The positive deviation curve is shown in Figure 1.2.

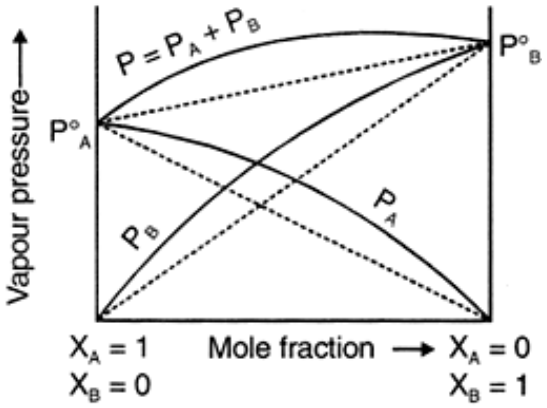


Figure- 1.2: 'Non-ideal solution' showing positive deviation

1.6.2 A 'non-ideal solution' exhibiting negative deviation

The interaction between A-B in the solution of components A and B is stronger than the interaction between A-A and B-B. In this case, the vapour pressure of a solution is lower than Raoult's expected pressure. Mixing has a negative enthalpy. For instance, phenol and aniline, acetone and water, acetic acid and pyridine, and chloroform and benzene. The curve with negative deviation is depicted in Figure 1.3.

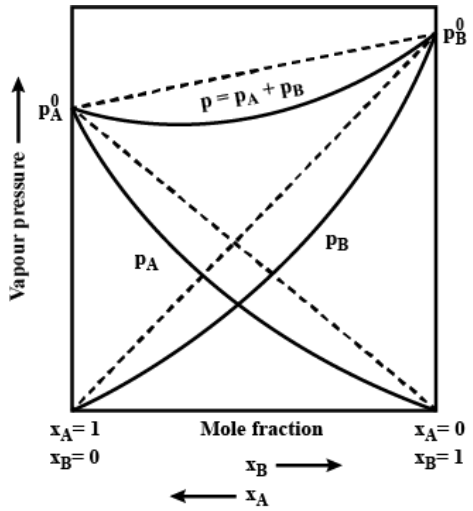


Figure 1.3 'Non-ideal solution' showing positive deviation

1.7 Immiscible Liquids, Steam Distillation:

Liquids that are insoluble in one another are known as immiscible liquids. Kerosene in water and oil in water are two examples. Condensation comes after evaporation in the distillation process. **Steam Distillation:** In this steam is passed into a round-bottom flask holding the impure organic

liquid during the steam-distillation process. Since the organic liquid is volatile, we can use steam distillation to remove impurities from it. Steam distillation is the process of distillation carried in a steam current. This method is frequently used to purify organic liquids (like aniline) that are immiscible with water and volatile in the steam. After adding nonvolatile impurity-containing water to the impure organic liquid, it is heated and steam is introduced.

Steam rising from the boiling mixture and the vapour of the organic liquid enter the condenser. One layer of the distillate collected in the receiver is made up of pure organic liquid, and the other layer is made up of water. Using a separatory funnel, the pure liquid layer is extracted and further purified.

Theory of Steam distillation: As temperature rises, the vapor pressure of a liquid increases. The temperature at which the vapor pressure equals the atmospheric pressure is known as the liquid's 'Boiling point'. Each component of a mixture of two immiscible liquids exerts its own vapour pressure as though it were acting independently.At that temperature, the sum of the individual vapour pressures (p1, p2) equals the overall vapour pressure over the mixture (P).

$$P = p_1 + p_2$$

Therefore, when the total vapour pressure P equals the atmospheric pressure, the mixture will boil at that temperature. The mixture of two liquids will have a lower boiling point than either of the pure components because P > p1 or p2.

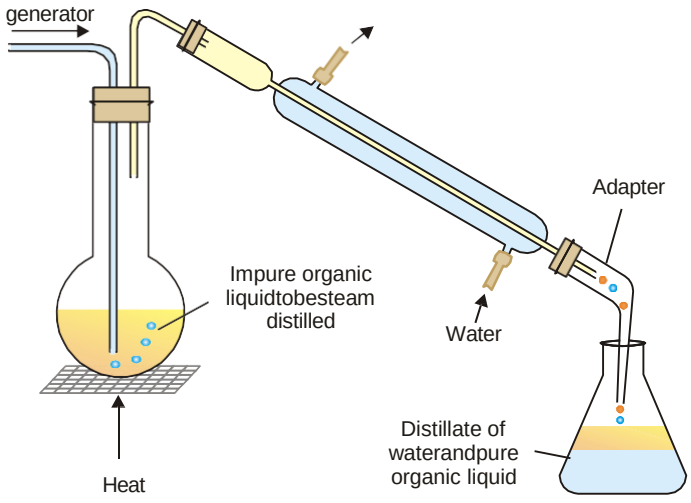


Figure 1.4 **Steam Distillation**

In the steam distillation process, an organic liquid (boiling point 100°C) is mixed with water, causing the organic liquid to boil at a temperature below 100 degrees Celsius. For example, aniline (phenylamine), which normally boils at 184°C, distills at 98°C when steam is used.

1.8 Freezing Mixture:

A combination of ice and salt that lowers the system's temperature is known as a freezing mixture. A combination of sodium chloride and ice, sodium nitrate and ice, ammonium chloride and ice, and ammonium nitrate and ice are a few examples. Let's talk about how these combinations cause the system's temperature to drop: When salt is put to ice, some of the salt dissolves in the water that is created when the ice melts, creating three phases that are in touch with one another: solution, ice, and salt. All three phases are in equilibrium at eutectic temperature. The temperature drops as a result of the heat needed for the melting of ice and the dissolution of salt.

1.8.1 Acetone-dry ice: This freezing mixture is composed of acetone-dry ice. We know that dry ice is solid CO2. This combination is frequently employed in laboratories to lower the system's temperature. When dry ice is put to acetone in a sealed container, it sublimates—converts from solid to vapor—and absorbs heat from the acetone, resulting in a sharp drop in temperature. Acetone freezes at a temperature of -95 oC. The freezing point of acetone can be reached by adding a significant amount of dry ice. Acetone and dry ice are also combined to create the cooling bath that is utilized in the lab.

Summary: We are able to learn about the several kinds of solutions that are categorized according to their miscibility as well as the steam distillation procedure that is utilized to purify impure organic liquids.The vapour pressure of a component in a solution at a specific temperature is determined by multiplying its mole fraction in the solution by its vapour pressure when it is in its pure condition, according to Raoult's law .A two-component solution is considered ideal if all of its components follow Raoult's law under all conditions, including pressure and temperature. If any of the parts deny Raoult's law, then it is not ideal.A solution containing a nonvolatile solute will experience a relative decrease in vapour pressure equal to the solute's mole fraction in the mixture.

Keywards

Solution:A homogeneous mixture of two or more substances that has an equal distribution of solutes and solvents is called a solution.

Solute:A solute is a material that dissolves in a solution. It usually exists in smaller amounts than the solvent.

Solvent: A solvent is the material that dissolves a solute to create a solution. Usually, it is more prevalent than the solute.

Solubility: The most solute that may dissolve in a solvent at a specific temperature and pressure is known as solubility; this is commonly stated as grams of solute per 100 grams of solvent.

Concentration: Solute concentration in a specific volume of solvent or solution. It can be expressed in mass percent, molality, or molarity, among other units.

Ideal Solution: An ideal solution would be one in which every component's vapor pressure is exactly proportionate to its mole fraction in the solution, and it would also completely follow Raoult's law.

Non-Ideal solution: An ideal solution is one that follows Raoult's law exactly; a non-ideal solution deviates from it because of interactions between molecules of the solute and solvent, such as positive or negative deviations from the law between the solute and solid.

MCQ:

1. What is known as the molarity?

(A) One kilogram of the solution

(B) One liter of the solvent

(C) One liter of the solution

(D) One kilogram of the solvent Answer (C)

2. Methods that can be used to separate organic liquids that are immiscible with water and steam volatile.

(A)Fractional distillation

(B) Steam distillation

(C) Evaporation

(D) Distillation Answer: (B)

3. 30. In a solution containing 46 g of ethyl alcohol and 36 g of H_2O, the mole fraction of ethyl alcohol is

(A) 1/3

(B) 2/3

(C) 1/2

(D) 3/4 Answer: (A)

4. In 250 milliliters of the solution, 38.49 grams of H2SO4 are dissolved. What will be its molarity?

(A) 1.5 M

(B) 0.5 M

(C) 1.0 M

(D) 2.0 M Answer (D)

Short question:

1. Define freezing mixture.
2. Explain theory of steam distillation.
3. State Roult's Law.
4. Differentiate Ideal and Non-ideal solutions.
5. Explain why solution deviate from ideal behavior.

Unit - 2

Azeotropes and Distribution Law

Objectives:

- Understand the basic concept of Solvent extraction
- Differentiate lower and upper consolute temperature.
- Classify the methods of solvent extraction
- Know about the azeotropes.

2.1 Introduction: Another name for azeotropes is constant boiling mixtures. It is described as mixtures with the same composition in the vapor and solution phases. Fractional distillation is a challenging method for separating the components of these combinations. The characteristic boiling point of azeotropes is either greater (deviation positive) or lower (deviation negative) than that of any of its constituents. Minimum boiling azeotropes are azeotropes with a positive deviation. Take nitric acid and water, for instance. Maximum boiling azeotropes are azeotropes with a negative deviation.

2.2 The following are some features of azeotropes:

2.2.1 Constant Boiling Point: Because azotropes boil at a constant temperature, the vapor that is created during the distillation process has the same chemical makeup as the liquid. Azeotropes are distinguished from other mixtures whose boiling points change depending on the composition by this property. Azeotropes are categorized as having a minimal boiling point (positive azeotrope) or a maximum boiling point (negative azeotrope). In contrast to negative azeotropes, which have a boiling point higher than any of the pure components, positive azeotropes have a boiling point lower than any of the pure components.

2.2.2 Constant Composition: The boiling point of zeotropes is determined by their unique composition. The composition of the pure components is not the same as this composition. Stated differently, the proportion of each component in the liquid and vapor phases is the same.

2.2.3 Distillation Limitation: Because azeotropes cannot be split into pure components by straightforward distillation, they provide a problem in distillation procedures. To separate the components, further methods such pressure swing distillation or azeotropic distillation are frequently needed.

2.2.4 Zeotropic mixes: Azeotropes are a subclass of zeotropic mixes, which are made up of substances whose compositions in the liquid and vapor phases are not dictated by simple ratios of their constituent parts. These mixtures do not follow Raoult's law.

Examples: Ethanol-water (95.6% ethanol by volume, boiling at 78.2°C) and hydrochloric acid-water (20.2% hydrochloric acid by mass, boiling at 108.6°C) are two common instances of azeotropes.

2.3 Azeotropes : Maximum Boiling Azeotropes (HCl-H_2O):

The mixture consists of two components. Its maximum boiling point demonstrates the minimal volatility of the system. The boiling temperature versus composition curve for the HCl-H2O system is shown in Figure 2.1.

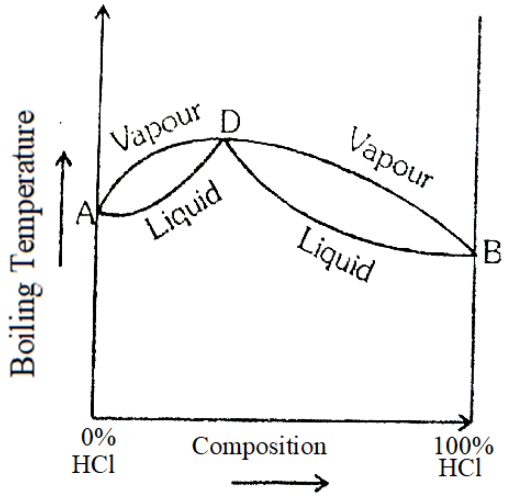


Figure2.1Boilingtemperatureversuscompositioncurveof HCl-H_2Osystem

The boiling point of HCl is –85^{o}C, while pure water boils at 100^{o}C. Point D indicates that the combination that makes up the azeotrope comprises 20.24% HCl and boils at 108.5 ^{o}C and 1 atm pressure. The distillate is water when a solution with less than 20.24% HCl is subjected to distillation. Figure 2.1 by AD illustrates this.Since the residue that is left over in this instance contains a combination with the same composition (20.24% of HCl solution in water), we are unable to extract the pure HCl. According to BD, if a solution containing more than 20.24% HCl is distilled, the filtrate is made up of pure HCl. In this instance, the residue with the same composition allows us to recover pure HCl.

2.4 Minimum Boiling Azeotropes (Ethanol-water System): Water and ethanol make up the two components of this system. Point C illustrates the boiling point of the azeotropic mixture of water and ethanol, which occurs at 78.13^{o}C and atmospheric pressure one. 95.6% of the mixture is ethanolic solution in water. The boiling temperature versus composition curve for the C_2H_5OH-H_2O system is shown in Figure 2.2.

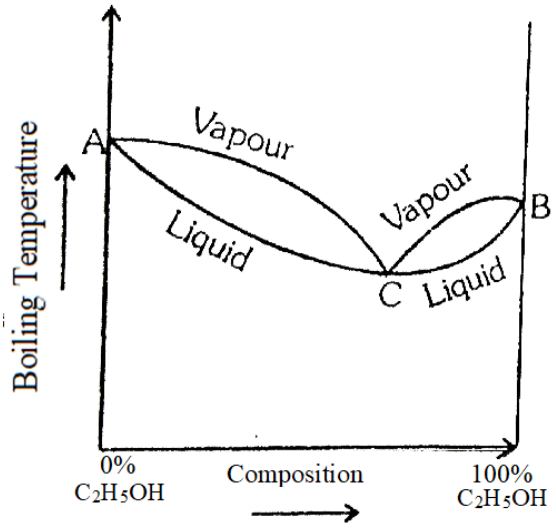


Figure- 2.2; Boiling-temperature-versus-composition-curve-of-C_2H_5OH-H_2O system

As demonstrated by AC in Figure 2.2, when a solution with a composition of 95.6% ethanol and 96% pure water is subjected to distillation, the residue is made up of pure water and the distillate is composed of 95.6% ethanol. In the second scenario, ethanol (95.6%) and pure ethanol separate if the solution with a composition of 95.6% ethanol and pure ethanol is subjected to distillation, as indicated in Figure 2.2 by BC.

2.5 Partially Miscible Liquids:

These two layers are made of a liquid mixture that is somewhat soluble in one another. Temperature affects how miscible these liquid combinations are. A total miscibility of two partially miscible liquid mixes is reached at a specific temperature. The term "critical solution temperature" or "consolute temperature" refers to this temperature.

There are many liquids that are recognized to dissolve in one another, but only to a limited degree, such as ‘Ether and Water’. Water dissolves approximately 6.5% of ether, while ether dissolves approximately 1.2% of water. They are only partially miscible because of their low

mutual solubilities. Two layers, one of a saturated ether in water solution and the other of a saturated water in ether solution, are created when equal quantities of ether and water are shaken together. Conjugate solutions are these two solutions. Of particular relevance is the effect of temperature on the mutual solubility of these conjugate solution combinations.

As an illustration, consider the water-phenol, water-triethylamine, and nicotine systems. Each of these systems will be discussed individually:

2.6 Phenol Water System: The curve depicting the miscibility of phenol and water can be found in Figure 2.3. The conjugate solution on the left side of the parabolic curve shows the percentage of phenol dissolved in water at different temperatures. Phenol becomes more soluble at higher temperatures. The other conjugate solution layer, which indicates the percentage of water in phenol, is shown by the right hand side of the curve. With rising temperatures, phenol's solubility in water also rises. On the system's temperature-composition curve, the two solution curves converge at the maxima. This point here relates to a temperature of 65.8°C and a 33% phenol content. As a result, the two conjugate solutions combine, become identical, and only one layer remains at a specific maximum temperature and this 65.8^0C temperature at which this occurs is called the critical solution temperature. A system's critical solution temperature is one of its distinguishing characteristics. The upper critical solution temperature is present in this system.

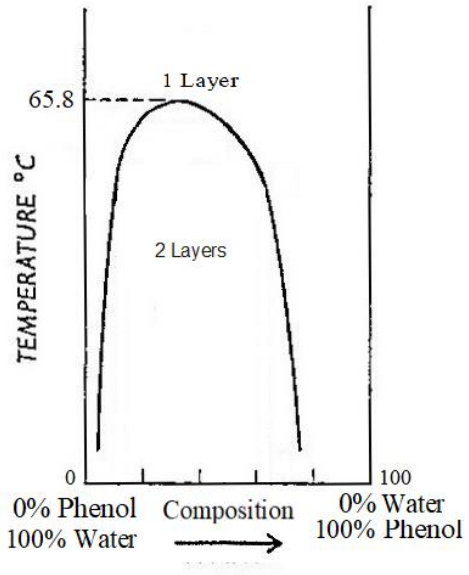


Figure- 2.3; Phenol–water system

The CST values of a few other liquid pairs that behave similarly to the phenol-water system are listed below, along with the proportion of the first component indicated in brackets.
(i) Cyclohexane-Methanol (49°C ; 29)
(ii) Hexane-Aniline (59.6°C ; 52)
(iii) Methanol with carbon disulfide (49.5°C, 80)

2.7 Tri-ethylamine-water system:

The solubility curves for triethylamine in water are shown on the left side of the curve and water in triethylamine on the right. In contrast to the phenol-water system, this system's solubilities diminish as temperature rises. At or below 18.5°C, the two conjugate solutions totally combine. This is known as critical solution temperature or lower consulate temperature. Similar to the last example, any point above the horizontal line denotes system heterogeneity (two layers), whereas any position below it denotes total homogeneity (one layer). As a result, at 10°C, an equi-component combination (50–50) will be perfectly miscible, but at 50°C, two layers will separate. The critical solution temperature is lower for these systems.

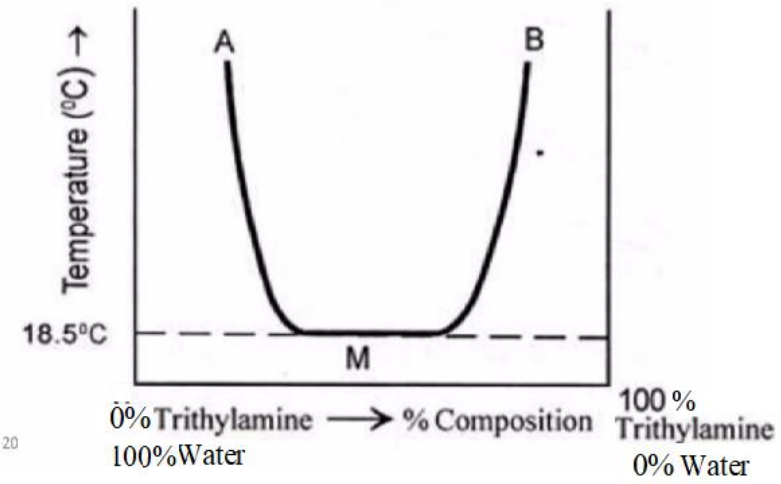


Figure- 2.4; Triethylamine-watersystem

The following lists common examples of this system, along with the % of the first component and lower critical solution temperatures.
(1) Water with Diethylamine (43°C ; 13)
(2) Water and 1-Methylpiperidine (48°C ; 5)

2.8 Nicotin-water system: Systems of this sort behave as though they were a hybrid of the preceding two. Normal temperature causes nicotine and water to be perfectly miscible; nevertheless, when the temperature rises, the two liquids' mutual solubility declines and eventually returns to miscibility. Stated differently, there is an increase in mutual solubility within specific temperature ranges when the temperature is lowered or raised. As a result, the system shows two critical solution temperatures: an upper one at 208°C and a lower one at 60.8°C, along with a closed solubility curve. When pressure is applied to this system, the upper critical temperature progressively drops and the lower critical temperature steadily rises until they eventually equalize. Currently, the liquids are miscible at all temperatures.

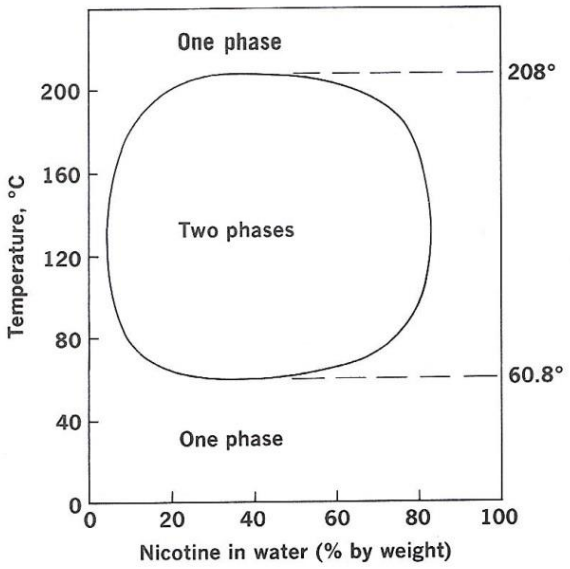


Figure-2.5: Nicotine-water system

2.9 Lower and Upper Consolute temperature:

The temperature at which two partially miscible liquids become completely miscible is known as the consolute temperature, or critical solution temperature. There are two consolute temperatures: the ‘Lower consolute temperature and the ‘Upper consolute temperature’. In the phenol-water system, the temperature at which these liquids become fully miscible is 65.8°C, which represents the upper consolute temperature. The trimethylamine-water system, on the other hand, exhibits the lowest critical solution temperature.

2.10 Effect of Impurity on Critical solution temperature:

One of a system's distinguishing characteristics is its consolute temperature, which is influenced by minute impurity concentration First, the miscibility (decreases) of the impurity will be affected if it is soluble in any of the liquids, rising the upper consolute temperature and lowering the lower consolute temperature. For instance, in a phenol-water system, the presence of sodium chloride as an impurity elevates the 'upper consolute temperature'.

In the second circumstances, if the impurity is soluble in both liquids, it increases the miscibility of the two liquids, thereby diminishing the 'upper consolute temperature' and increasing the 'lower consolute temperature'. For example, in a phenol-water system, the presence of sodium salt (soap) decreases the upper consolute temperature.

2.11 Nernst distribution law:

Separate layers are formed in a beaker containing two immiscible solvents, A and B. Solute X, which is soluble in both solvents, is now added and split or distributed between them. Solvent A to B and B to A are the paths taken by X molecules. At last, a dynamic balance is achieved. When two solvents are in equilibrium, the rate at which X molecules move from one to the other is balanced.

$$\frac{\text{Concentration of K in A}}{\text{Concentration of K in B}} = \text{a Constant}$$

The distribution of various solutes among various suitable pairs of solvents was investigated by Nernst (1891). The generalization he provided controls how a solute is distributed across two non-miscible solvents. This is known as either Nernst's Partition law or Distribution law, or just Nernst's Partition law.

According to the Nernst statement, "if a solute at constant temperature X distributes itself between two immiscible solvents A and B then X is in the same molecular form in both these solvents.

$$\frac{\text{Concentration of K in A}}{\text{Concentration of K in B}} = K_D$$

When C_1 represents the solute concentration in solvent A;

C_2 represents the solute concentration in solvent B.

'Nernst's Distribution law' may be written as

$$\frac{C_1}{C_2} = K_D$$

K_D is known as distribution coefficient or partition coefficient

Two non-miscible liquids shaken with a solute will, at equilibrium, cause the solute to become saturated in both solvents. Since concentration is also represented by solubility, the Distribution Law is also expressed as

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

where the solute's solubilities in the two solvents are represented by $S1$ and $S2$.

Thermodynamic derivation of Nernst Distribution:

Assume that there is a solute X in contact with two immiscible solvents, A and B. Let us now assume that the solute has a chemical potential of $\mu 1$ in solvent A and $\mu 2$ in solvent B. Two phases' chemical potentials will also be equivalent when they are in equilibrium.

Sothat,

$$\mu_1 = \mu_2 \qquad \ldots\ldots\ldots\ldots(1)$$

Since $$\mu = \mu^o + RT \ln a \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where, μ^o is the chemical potential of the pure state and a is the activity.

Therefore, $\mu_1 = \mu^o{}_1 + RT \ln a_1$ for Phase 1……………………….(3)

$\mu_2 = \mu^o{}_2 + RT \ln a_2$ for Phase 2…………………… .(4)

$$\mu^o{}_1 + RT \ln a_1 = \mu^o{}_2 + RT \ln a_2$$

Or

$$\mu^o{}_1 - \mu^o{}_2 = RT \ln a_1/a_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Given that R is a gas constant. The conventional chemical potentials $\mu^o{}_1$ and $\mu^o{}_2$ are both constant at constant temperature. Consequently,

$$\frac{a_1}{a_2} = constant \quad (at\ constant\ temperature) \qquad \ldots\ldots\ldots(6)$$

Henry's law, which states that activity is proportional to mole fraction, is followed in every phase since the solutions behave optimally due to their dilute nature.

$$\frac{a_1}{a_2} = \frac{k_1 \varkappa_1}{k_2 \varkappa_2} = cons\ (at\ constant temperature) \quad \ldots\ldots(7)$$

For each solute in the two phases, $k1$ and $k2$ are the Henry's law constants, and $\chi 1$ and $\chi 2$ are the mole fractions of the solute in each phase.

$$\frac{\varkappa_1}{\varkappa_2} = constant\ (at\ constant\ temperature) \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

The ratio of mole fractions to concentrations is nearly equal because of the dilution of the solutions. so,

$$\frac{\varkappa_1}{\varkappa_2} = \frac{c_1}{c_2} = cons(at\ constant\ temperature) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

Therefore, at equilibrium, if a chemical is present in two phases that are in touch with one another,

$$\frac{c_1}{c_2} = constant\ (at\ constant\ temperature) = K_D \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (10)$$

Equation 10 is known as Nernst Distribution Law.

Limitations of Distribution Law:

The distribution law can only be valid if there are two crucial conditions met:

1. There must be a constant temperature
2. There must be comparable molecules in contact with one another in both phases.

Furthermore required are the subsequent prerequisites:

3. It is a diluted set of liquids.
4. The solute does not change the mutual solubility of the two liquids, which are either mutually insoluble or only somewhat soluble (such as benzene and water).

Application of Nernst Distribution Law:

1. To determine equilibrium constant of same reaction by partition method.
2. In Solvent extraction
3. To determine solubility of a solute in a solvent
4. To determine the extent of association or dissociation of a solute in a solvent.

2.12 Solvent Extraction: Also Known as Liquid-liquid extraction.

The process of moving a material from one solvent to another, known as solvent extraction, is based on the difference in the distribution coefficient or solubility of the two immiscible or poorly soluble solvents.

.

It's a technique for quantitatively separating substances. This transfers the solute from the original solvent into the extracting solvent when the extracting solvent and solute-containing solution are agitated together. The extracting solvent separates into a layer and includes the solute of interest when the stirring is stopped.

In contrast methods of separation, it provides a more effective separation than chemical precipitation, as well as a higher degree of selectivity and quicker mass transfer than the ion exchange approach.

Compared to distillation, solvent extraction has a number of benefits, including low energy consumption, high production capacity, continuous operation, quick action, and ease of automation.

Commonly used solvent extraction techniques are ethyl acetate, diethyl ether, dichloromethane and chloroform etc.

2.12.1 Uses of Solvent extraction:

Solvent extraction is utilized in the production of biodiesel, vegetable oil, and perfumes.

It is also employed in the process of nuclear reprocessing, which is the process of recovering plutonium from irradiated nuclear fuel so that it can be used again as nuclear fuel.

2.12.2 Solvent characteristics:

- It is important that the liquid to be extracted and the solvent mix thoroughly.

- It is not acceptable for the solvent to react with the solute or be miscible with the other ingredients in the mixture.
- In order to facilitate easy evaporation following collection, the solvent's boiling point should be sufficiently low—far below the solute's melting point.
- Its coefficient of temperature should be favorable.

2.12.3 Factor affecting solvent extraction:

a. Masking agents: These are chemical substances that prevent the extraction of undesirable metal ions from metal ions that are of interest.

b. Modifier: The compounds known as modifiers are those that, when introduced to the aqueous phase, make the solute more soluble in the organic solvent that will be used for extraction. Typically, solvent extraction modifies the usage of high molecular weight alcohols.

c. Oxidation state: The oxidation state of a metal ion can be altered by conducting a redox reaction with the appropriate reagent.

d. pH: The metal complex's charge and stability are impacted by pH. The ideal pH for extracting metal ions is the one at which the metal ion complex is most neutral and stable.

e. Salting effect: Metal ions can occasionally be extracted from the aqueous phase and transferred to the organic phase by the high concentration of salt.The solubility of metal complexes in the organic phase is enhanced by salt by raising the ionic strength of the aqueous phase.

f. Synergistic agents: These are reagents that boost extraction efficiency when applied to the organic phase. They attach themselves to the metal complex and increase its solubility in the organic phase.

2.12.4 Solvent extraction techniques:

Batch extraction

Continuous extraction

Countercurrent extraction

Batch extraction techniques: This is the most basic and often applied technique. It involves shaking two ‘immiscible layers’ to extract the solute until equilibrium is reached, then allowing the layers to settle before sampling. A separatory funnel is the most often utilized tool for

carrying out a batch extraction; this is frequently used in small-scale chemical laboratories. A large distribution ratio can also be advantageously used with batch extractions.

Countercurrent extraction: Fractionation is the main application for extraction by continuous countercurrent distribution, which is the third general kind. Because of the differences in densities of the fluids in contact, separation is accomplished via a continuous countercurrent approach.

The denser phase enters vertical columns from the top and moves downward, while the less dense phase enters from the bottom and moves upward.

The values of the solute's distribution ratio and the separation factors of interfering materials will be the primary factors determining the choice of technique to be used.

2.12.4 Qualities that are necessary for an extractant

- To be particular about the necessary metal.
- The capacity to remove the metal at the appropriate pH or acidity.
- The high solubility of metal organic species in the organic phase and the ease with which a complex with the target metal can form.
- The metal's ease of extraction from the organic phase.
- It needs to remain steady during the main solvent extraction steps.
- A large-scale laboratory preparation is required.
- To achieve reasonable extraction and stripping rates.
- Extractant regeneration for large-scale, cost-effective recycling systems.
- No emulsion formation is present.

2.12.5 Application of solvent extraction:

1. Calculating iron levels
2. Measurement of blood lead levels
3. Analytical, biochemical, and pharmacological chemists use it in the pharmaceutical sector.
4. Other uses include determining the amount of copper in alloys like steel
5. Determining the amount of uranium, and using organic chemists to separate and purify organic substances.

Summary: Azeotropes are mixtures of liquids that boil at a steady temperature while keeping their composition unchanged in the vapor and liquid phases. The separation operations are complicated by this special quality.Based on their behavior, zeotropes can be divided into three categories: lowest boiling, maximum boiling, and heterogeneous varieties. To create separation tactics that work, it is essential to understand the type of azeotrope.The distribution law, sometimes referred to as the equilibrium law or partition law, specifies how a solute is distributed between two immiscible phases, usually a solvent and a solute. It provides a quantitative link between the solute concentrations at equilibrium in each phase.

Keywards:

Azeotropes: A mixture of two or more liquids that is difficult to separate using traditional methods because it keeps a consistent boiling point and vapor composition throughout the distillation process.

Entrainer: A third ingredient added to an azeotropic mixture to change the vapor-liquid equilibrium and make azeotropic distillation easier.

Minimum Boiling Azeotrope: A form of azeotrope in which, at the same temperature, the mixture's vapor pressure is higher than that of either pure component, resulting in a boiling point that is lower than either component's.

Maximum Boiling Azeotrope: A form of azeotrope in which, at a given temperature, the mixture's vapor pressure is lower than that of either pure component, leading to a boiling point that is higher than either component's.

Solvent extraction: In order to isolate or purify a solute from a complicated mixture, a solute is frequently transported from one phase—typically a liquid phase—to another—typically a solvent phase. This process is known as solvent extraction.

MCQ

1. A liquid mixture that is ……..miscible makes up the phenol-water system.

(A) completely

(B) Partialy

(C) Not

(D) None Answer (B)

2. Another name for consolute temperature is ……..temperature.

(A) Congruent

(B) Incongruent

(C) Critical solution

(D) None Answer (C)

3. The water-triethylamine system has a ……..constant temperature.

(A) Higher

(B) Lower

(C) Constant

(D) Zero Answer (B)

4. Azotropic mixture another name is……..

(A) Constant Boiling

(B) Constant melting

(C) Immiscible liquids

(D) Miscible liquids

Answer (A)

5. The solution temperature of the phenol-water system is …….by adding NaCl.

(A) Increases

(B) Decreases

(C) Remains same

(D) Become zero

Answer (B)

Short Answer Questions:

1. Explain the concept of solvent extraction.

2. Discuss phenol water system.

3. Define Azeitropes.

Unit -3

Phase Equilibrium

Objectives:

- A system is made up of components that are divided by boundaries and have various physical (and occasionally chemical) characteristics
- Three concepts are typically used to explain the equilibrium between various components or phases. Law of Mass action, The Clapron Equation and Phase Rule .
- Draw different component phase digrams

3.1 Phase Rule

An essential overview trade that deals with the behavior of heterogeneous systems is the phase Rule. Phase rule can be used to forecast, through a diagrammatic representation, the quality of the response of a heterogeneous system in equilibrium to variations in temperature, pressure, and concentration. This relationship was first discovered in 1874 by an American physicist J. Willard Gibbs. (**Gibb's Phase Rule)** It may be stated mathematically as:

$$F=C-P+2$$

Where F = Degree of freedom

C = Component

P = Number of phase of the system

Sum of the number of phase& degree of freedom of any system in equilibrium is greater than the number of component by 2.

3.2 Phase: According to definitions, a phase is any homogenous, physically distinct portion of a system that is separated mechanically from other parts of the system and is surrounded by a surface.

Or

A phase is any physically separate and homogeneous portion of a heterogeneous system that is isolated from other parts of the system and has consistently the same physical and chemical properties.

A homogenous system is one that has just one phase in it. And Heterogeneous systems are those that have two or more phases.

Example

- A mixture of gas – one phase
- Water system – one phase
- H_2O (l) ⇌ H_2O(s) – two phase
- H_2O (s) ⇌ H_2O (l) ⇌ H_2O (g) - three phase
- $CaCO_3$ ⇌ $CaO + CO_2$ - two solid and one gas phase.
  (solid)(solid)(gas)

3.3 Component

The minimum number of separately variable constituents mandatory to express the composition of each phase either directly or in terms of a chemical equation is known as the number of components of an equilibrium system.

Example

- H_2O (s) ⇌ H_2O (l) ⇌ H_2O (g) - One component
- Sr ⇌ Sm ⇌ S_l⇌ Sg - One component
- Mixture of O_2 and N_2 – Two component
- Sodium chloride solution – Two component
- Decomposition of Calcium carbonate
  $CaCO_3$ ⇌ $CaO + CO_2$

Three phase – two solid and one gas. Although system has three component but they are not independent to each other any of these two can be independent variable. Thus out of three two component may be selected to express the composition of any phase. Thus number of component in the system are two.

3.4 Degree of Freedom

Degree of freedom (F) is the bare minimum of independently variable that must be provided in order to fully define a system, such as temperature, pressure, and phase concentration.

If F = 0 the system is known as non-variant (in-variant) system

F = 1 uni-variant (mono variant) system

F = 2 bi-variant system

Example

1. H_2O (l) ⇌ H_2O(s)

There P = 2, C = 1

$F=C-P+2$

= 1-2+2

F = 1 (Uni-variant system)

2. H_2O (s) ⇌ H_2O (l) ⇌ H_2O (g)

There P = 3, C = 1 , F = 1-3+2

F = 0 (Non-variant system)

3.5 Deviation of Phase Rule:

Suppose you have a heterogeneous system with P phases and C components in equilibrium. We need to figure out how many variables in this system need to be arbitrarily fixed in order to fully define it, or how many degrees of freedom it has. Both temperature and pressure are constants since they determine the system's condition. On the other hand, the number of phases affects concentration factors. In order to define the composition of each phase it is necessary to specify the concentration of $(C - 1)$ constituents of each phase, the concentration of the remaining component being determined by difference. For P phases, therefore, the total number of concentration variables will be $P(C-1)$ and these along with the two variables mentioned above *viz.*, temperature and pressure, make the to total number of the variables of the system equal to $[P (C-1) + 2]$.

The partial molal free energy of any component in one phase of a system is equal to the partial molal free energy of that same constituent in all other phases when the system is in equilibrium, according to thermodynamic theory. One equation may be written among the variables if there is

one component in two phases, and two equations can be written if there is one component in three phases because the partial molal free energy of the constituents of a phase is a function of the temperature, pressure, and (C–1) concentration variables. In general, therefore, when *P*phasesarepresent,(*P*–1)equationsareavailableforeachcomponentandforCcomponents,the total number of equations or variables areC (P – 1).

The quantity of unknown variables, or degrees of freedom (F), will be as follows since the number of equations and variables equals one.

F = No. of variables – Number of equations

$$=[P\,(C-1)+2]-[C\,(P-1)]$$

$$=PC-P+2-PC+C$$

$$=C-P+2$$

$$F=C-P+2$$

3.6 One component system:

For one component system C = 1

Phase rule is given by- F = C- P + 2

F = 1 – P + 2

F = 3- P

If P = 1	**P = 2**	**P = 3**
F = 3-1	**F = 3-1**	**F = 3-1**
F = 2	**F = 1**	**F = 0**
(Bi Variant System)	**(Uni-Variant)**	**1. (Non Variant)**

For one component system maximum phase = one

Maximum number of degree of freedom = two

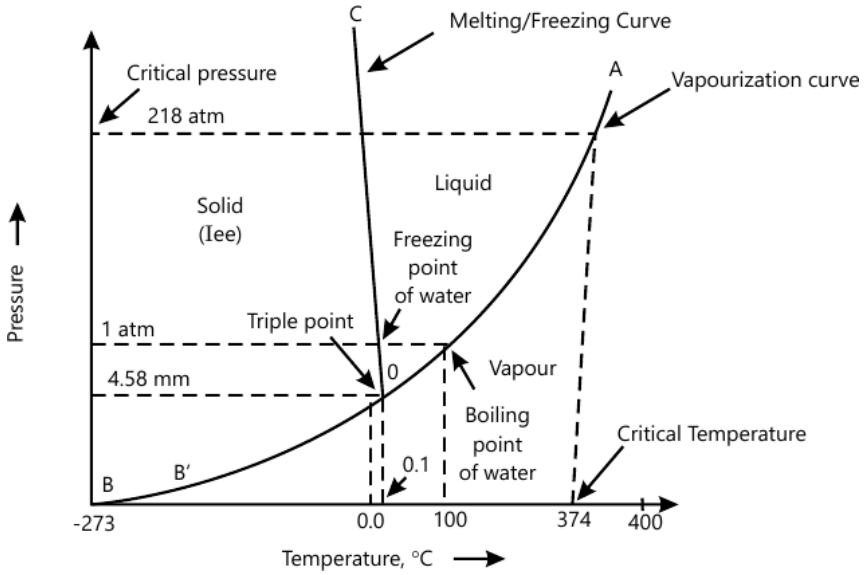
Which is temperature and pressure

Conclusion

Phase diagram can be expressed by two axis temperature and pressure.

Maximum three phase remain in equilibrium

3.6.1 One component water system



This diagram consist of -

- One component system
- Phase 3 H_2O (s) , H_2O (l) and H_2O (g)
- Curve 3 OA, OB and OC
- Area AOC (Liquid), AOB (Gas), BOC (Solid)
- Point – O (Triple point)

1. 1.Curve

a. Curve OC- (Melting or Fusion Curve)

H_2O (s)⇌ H_2O (l)

P = 2, C = 1 F = C-P +2 = 1-2+2 = 1

- Degree of freedom is one
- It indicates the effect of pressure / temperature at which the solid (ice) and liquid (water) can coexist in equilibrium.
- As pressure increases, line OC is angled toward the pressure axis, indicating that ice melts at a lower temperature.

b. **Curve OA (Vapour pressure curve)**

H_2O (l) ⇌ H_2O (g)

P = 2, C = 1 F = C-P +2 = 1-2+2 = 1

- Water and vapour coexist in equilibrium along this curve in two phases.
- The curve depicts the water's vapour pressure at various temperatures.
- The curve OA ends at A, the critical point (374º C, 218 atm), where there is only one phase remaining since the liquid and vapour can no longer be distinguished from one another. This point is referred to as the critical point.
- Critical point means the highest temperature at which the liquid can exist, when vapour pressure is 1 atm .the corresponding temperature is the boiling point 100º C of water. Critical point is the characteristic property of the pure substance.

c. **Curve OB (Sublimation curve of ice)**

H_2O (l) ⇌ H_2O (g)

P = 2, C = 1, F = C-P +2 = 1-2+2 = 1 (univariant)

It show the vapour pressure of solid ice at different temperature at the lower limit the curve OB terminate at absolute zero where no vapour exists

2. **Areas**

The conditions of temperature and pressure that allow for the stable existence of any one of the three phases—ice, water, or vapour—are represented by the AOC, AOB, and BOC areas. It is necessary to include both temperature and pressure in order to fully describe the system at any point in the region.

P = 1 , C = 1 F = C-P +2 = 1-1+2 = 2 (Bivariant)

Point O (Triple point)

H_2O (s) ⇌ H_2O (l) ⇌ H_2O (g)

P = 3 , C= 1 , F = C-P +2 = 1-3+2 = 0 (Non variant)

Temperature = 0.00098º C, Pressure 4.58 mmHg

The curve OC, OA & OB meet at point O this point is known as triple point. At this point three phase (solid, liquid & vapour) are in equilibrium therefore it is known as triple point.

Thus if either temperature or pressure is changed one of the three phase would disappear and only two phases will remain in equilibrium.

Metastable Curve (super cooled water vapour)

The liquid below the 'freezing point' is in the super cooled state which is not quite stable is known as metastable state. Water doesn't always freeze at 0 oC, thus it can be cooled below that temperature if the container holding the water and vapor is spotless and dust-free.

The curve OA' represent the metastable equilibrium.On slight disturbance the supercool water at once changes to solid ice vapour pressure of super cooled water is higher than the vapour pressure of ice.

3.6.2 Sulphur system:

Polymorphism -Polymorphism refers to a substance's existence in several crystalline forms with distinct physical characteristics.

Transition temperature – the temperature at which one form changes into another at a given pressure is known as transition temperature.

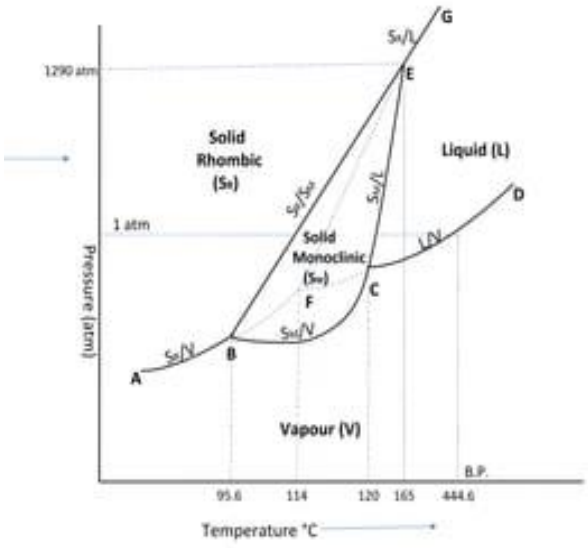
Sr ⇌ Sm

Temperature 95.6 º C

Polymorphic forms which can undergo reversible transformation into one another at transition temperature are said to be **enantiotropic** and phenomenon is known as enantiotropy

When polymorphic forms do not undergo reversible transformations into one another is known as monotropic and phenomenon is known as monotropy.

Example- diamond can be converted into graphite under suitable condition of temperature and pressure but the reverse is not possible.



This diagram consist of -One component system

- Four phase
    1. Rhombic Sulphur Sr (solid)
    2. Monoclinic Sulphur Sm (solid)
    3. Liquid Sulphur Sl (Liquid)
    4. Vapour Sulphur Sv (vapour)
- Four Area ABG (Sr), BEC (Sm), GECD (Sl), ABCD (Sv)
- Six curves AB, BC, CD, BE, CE, EG
- Three triple point B, C, E

A. **Area -** single phase are ABG (Sr) – solid

BEC (Sm)- solid

GECD (Sl)- liquid

ABCD (Sv)- vapour

P = 1 , C = 1 F = C-P +2 = 1-1+2 = 2 (Bivariant)

It is necessary to include both temperature and pressure in order to fully describe the system at any point in the region.

B. **Curves -** Curve AB – sublimation curve $Sr \rightleftharpoons Sv$

Curve BC – Vapour pressure curve $Sm \rightleftharpoons Sv$

Curve CD – Vapour pressure curve $Sl \rightleftharpoons Sv$

Curve BE – Transition Curve $Sr \rightleftharpoons Sm$

Curve CE – Fusion curve of Sm $Sm \rightleftharpoons Sl$

Curve EG – Fusion curve of Sr, $Sr \rightleftharpoons Sl$

P = 2, C = 1,

F = C -P +2

= 1- 2+ 2 = 1 (univariant)

C. **Triple point -** P = 3 , C= 1

F = C- P +2

= 1- 3+ 2 = 0 (Non variant)

Point B $Sr \rightleftharpoons Sm \rightleftharpoons Sv$, Temperature 95.6 ° C, Pressure – 0.006 mm

Point C Sm ⇌ Sl ⇌ Sv , Temperature 120 º C, Pressure – 0.04 mm

Point E Sr ⇌ Sm ⇌ Sl , Temperature 165 º C, Pressure – 1290 atm

D. Metastable equilibrium- Sr ⇌ Sm (very slowly)If Sr is heated rapidly, it is possible to pass well above the transition temperature without obtaining Sm. tn that case there are three phase (Sr, Sl, Sv) exist only. The phase diagram like that of water system, will consist three curve, one triple point and three area. The dashed curve BF, CF & FE represent the equilibrium Sr/Sv, Sl/Sv, Sr/Sl respectively at metastable triple point F the three Sr, Sl, oor Sv in equilibrium at 114 º C.

3.7 Two component system

For two component system C = 2,

F= C-P+2

2-1+2 = 3

This means three variable are need to be specified in order to describe the condition of the phase. (3 variable – pressure, temperature and concentration) a set of 3 coordinate axis at right angle to each other would be required to represent this relation graphically.

However, in practice a simple plain diagram with two variable only is considered, the third variable is kept constant.

Since, effect of P on solid – liquid equilibrium is negligible such system in which only solid & liquid phase are considered are known as condensed system

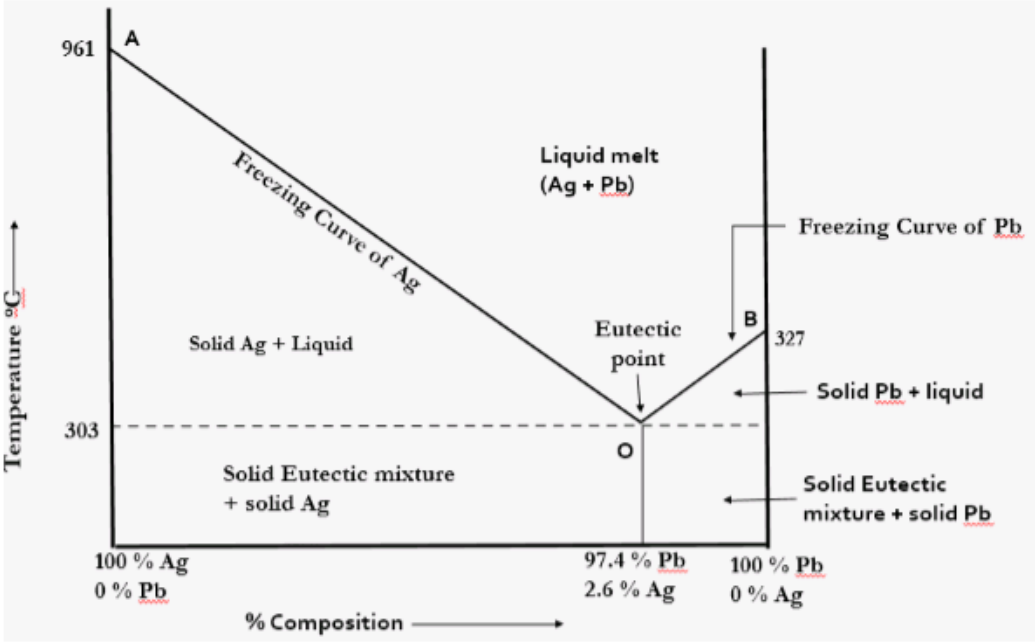
F' = C-P+1 (Reduced phase rule)

A. The two component are not miscible in the solid state and form Eutectic Mixture
B. The two component form a stable compound with Congruent melting point
C. The two compound form a compound with incongruent melting point

Under atmospheric pressure, temperature and concentration in condensed systems are often measured experimentally. In this situation, the degree of freedom is lowered by one, therefore we can express the 'Reduced Phase Rule' as

$$F' = C - P + 1$$

where the system's remaining degrees of freedom are indicated by F'. For a two-component condensed system with solid and liquid components, the reduced phase rule makes more sense to use.



3.7.1 The two component are not miscible in the solid state and form Eutectic Mixture : Silver – Lead system

This diagram consist-

4 phase – solid Ag, Solid Pb, Solution of molten Ag & Pb, Vapour

2 Component

Pb & Ag are immiscible in the solid state & do not combine.

Molten Ag & Pb mix together in all proportion to give a simple homogeneous solution

The lead – silver system is an example of simple eutectic system in which the pure components alone separate as solid phase on cooling a molten mix.

The boiling point of Ag & Pb being considerable high the vapour phase is practically absent consequently the pressure can have no effect on the system. Thus Ag-Pb system is a condensed system with three phase.

From Diagram

- The point A represent the melting point 961ºC of pure Ag and point B represent the melting point of pure Pb 321 ºC
- Addition of Ag lowers the M.P. of Pb along BO thus-
- Curve BO represent Freezing point curve of Pb
- Curve AO represent freezing point curve of Ag (addition of Pb to pure Ag lowers the M.P of Ag along curve AO)
- **Curve**

  AO – Ag (s) ⇌ Liquid

  BO – Pb (s) ⇌ Liquid

  Phase = 2 , Component = 2

  Reduce Phase Rule = F' = C-P+1 = 2-2+1

  F' = 1 (Monovariant System)
- **Eutectic point O**

  Two curved The condition under which three phase solid Ag, solid Pb, and molten are in equilibrium is represented by the point where AO and BO meet, which is common to both curves.

  Ag (s) ⇌ Pb (s) ⇌ Liquid

  P = 3, C= 2,

  Reduce Phase Rule = F' = C-P+1 = 2-3+1

  F' = 0 (Nonovariant System)

  Temperature 303 ºC composition "Ag 2.6%", " Pb 97.4%" are fixed point O which is known as Eutectic point .

Eutectic point - The term "Eutectic point" refers to the lowest temperature at which a liquid can coexist in balance with solids A and B.

Eutectic temperature- the temperature at eutectic point

Eutectic composition- the composition at eutectic point

Eutectic mixture: a solid mixture of these two component systems with the lowest freezing point of any component mixture that is conceivable (mixture of Pb & Ag at eutectic point)

If the temperature is raised above eutectic temperature the solid phase silver & lead will disappear. If temperature is low ered below eutectic temperature only solid silver & lead will exist where solution phase is not exist.

- **Area**
- **Above AOB -** molten **(Ag & Pb)** Homogeneous liquid solution where P =1, C=2, F' = 2-1+1 = 2
- **Below AO- Solid Ag+ Solution (Pb/Ag) , P= 2, C=2, F'= 2-2+1 = 1**
- **Below BO- Solid Pb + Solution (Ag/Pb), P= 2, C=2, F'= 2-2+1 = 1**
- **Area below Te- solid Pb and solid Ag , P= 2, C=2, F'= 2-2+1 = 1**

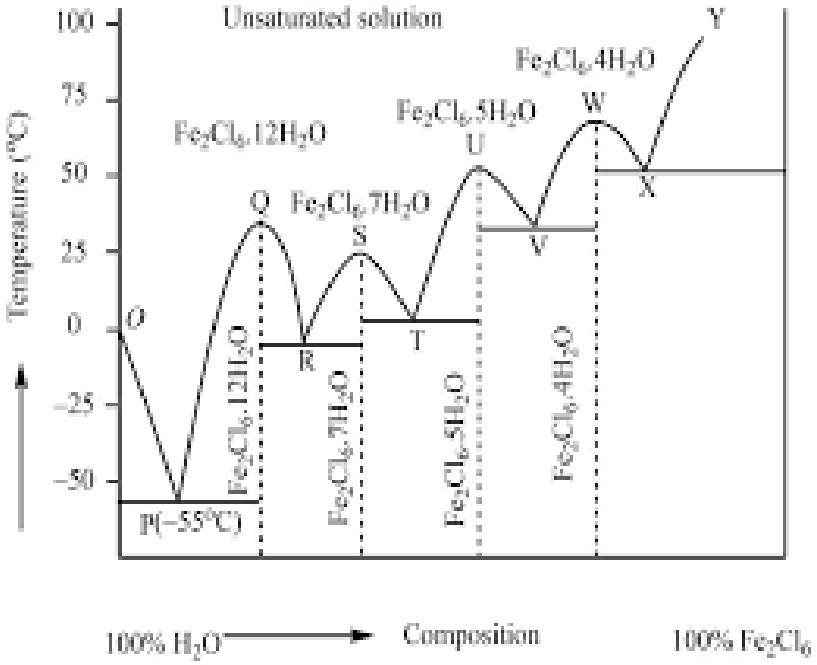
Desilverisation of lead –– The phase diagram is used in the separation of Ag from Pb in Pattinson's Process for the Desilverisation of Argentiferous Lead: Lead with Argentifice. To make the system consist exclusively of the liquid phase, denoted by point x in the figure, the argentiferous lead, which contains a very small percentage of Ag (.10%), is first heated to a temperature much over its melting point. Let it cool while it's there. The melt's temperature will decrease along the xy line. Pb will start to crystallize out and the solution will contain a progressively greater proportion of silver as soon as point y is achieved.

The system will move along the line YC as more cooling occurs. Lead is regularly removed with ladles as it separates out over time. Up to point O, where the percentage of Ag increases to 2.6, the melts keep getting richer and richer in Ag. Hence, 2.6% of this melt can now be found in the original argentiferous lead, which may have had 0.1% of Ag initially.

3.7.2 The two component form a stable compound with Congruent melting point($FeCl_3$-H_2O System): The temperature at which compound AB's liquid phase and solid phase have the same composition at the maximum point on the freezing point curve is referred to as the compound's congruent melting point.

At point D, there is only one component in the system because the composition of the two phases is the same. As a result, it is not variable.

F=C–P+1=1–2+1= 0



This provides an example of a 2-component system in whichthe two component form a stable compound with congruent melting point. It is a composite system made of several simple eutectic systems.

The system consist-

- Two component system (Fe_2Cl_6 and H_2O)
- Seven phase condensed system (4 solid , ice, anhydrous ferric chloride and solution)
- Ferric chloride(Fe_2Cl_6)forms four stable crystalline hydrates ($Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$, $Fe_2Cl_6.4H_2O$)
- Formation of stable compound
- It appears to be made of several simple eutectic diagram
- Four congruent melting point
- Five eutectic point
- Six curve

- The vapour phase is disregarded and the system Fe2Cl6/H2O is regarded as condensed because all temperature and concentration measurements are performed at atmospheric pressure.

1. Point O – Freezing point of H_2O (0 ºC) at this point Ice ⇌H_2O
2. Curve OP- on adding $FeCl_3$ freezing temperature of water decreases and curve OP is obtained along the curve- Ice ⇌ solution, P = 2, C= 2, F'= 2-2+1 = 1 (uni variant)
3. Point P (First Eutectic Point)- on adding $FeCl_3$ along OP curve freezing point temperature decreases regularly & at point P solid $Fe_2Cl_6.12H_2O$ separate out as a new phase $Fe_2Cl_6.12H_2O$ ⇌ Ice ⇌solution , P= 3, C= 2, F' = 2-3+1 = 0
4. Curve PQ- on further addition of $FeCl_3$& heating, ice disappears and it follow the PQ path which is called the solubility curve of $Fe_2Cl_6.12H_2O$.
   $Fe_2Cl_6.12H_2O$ ⇌solution , P = 2, C= 2, F'= 2-2+1 = 1 (uni variant)
5. Point Q (Congruent melting point) – on more addition of $FeCl_3$ the point Q is reached which rise in temperature and at Q, solid and liquid has same composition and is regenerated as the congruent melting point of $Fe_2Cl_6.12H_2O$
   $Fe_2Cl_6.12H_2O$ ⇌solution , P = 2, C= 1, F'= 1-2+1 = 0 (non variant)
6. Curve QR – on continue addition of ferric chloride the depression of freezing point of $Fe_2Cl_6.12H_2O$ takes place till R is achieved. QR is the melting point curve for $Fe_2Cl_6.12H_2O$.

Congruent melting point		
Point	**Congruent m.p.**	**Hydrate**
C	37º	$12H_2O$
E	32.5º	$7H_2O$
G	56º	$5H_2O$
I	73.5º	$4H_2O$

Eutectic Point	Temperature	Phases in Equilibrium
P	–55°	ice,$12H_2O$,solution
R	27.4°	$12H_2O$,$7H_2O$,solution
T	30°	$7H_2O$,$5H_2O$,solution
V	55°	$5H_2O$,$4H_2O$,solution
X	66°	$4H_2O$,Fe_2Cl_6,solution

There are two components and three phases in the system at each of these eutectic positions. Using the reduced phase rule formula, we've

$$F=C–P+1=2–3+1= 0$$

The system is nonvariant in this sense.

Summary: The phase rule can be used to qualitatively forecast how changes in temperature, pressure, and concentration will affect a heterogeneous system that is in equilibrium. The different phases of the phase diagram can be shown as areas. Three phases in equilibrium: one phase, two phases by line, and three phases by point. For equilibrium circumstances of state of matter, allotropy, enantiotropy, monotropy, and metastable equilibrium have been explained.

Key wards:

Phase: A consistent chemical composition and physical characteristics that define a physically separate form of matter.

Equilibrium: The state of having equal amounts of conflicting forces or influences.
Phase diagram: Phase diagrams are a type of graphic depiction that illustrate how a substance's equilibrium conditions vary depending on temperature and pressure.
Triple Point:the unique combination of temperature and pressure that occurs when a substance in thermodynamic equilibrium exists in its three phases: solid, liquid, and gas.

Critical point: The point on a phase diagram known as the critical point is reached when a substance's liquid and gas phases are identical in density and cannot be separately identified.

MCQ:

1. What is degree of freedom for water at triple point?

(A) 0

(B) 3

(C) 2

(D) 4 Answer (A)

2. The line that divides the regions of (Liquid + Solid) and (Solid) must be a portion of

(A) Tie-Line

(B) Solidus

(C) Liquidus

(D) Solvus Answer (B)

3. The greatest number of phases that can coexist in equilibrium in a system with one component is:

(A) 1

(B) 2

(C) 3

(D). 4 Answer (C)

4. The Phase rule can be represented as follows in expressions of the number of phases (P), components (C), and degrees of freedom (F):

(a) P + C = F + 2

(b) F = P + C – 2.

(c) P + F equals C + 2

(d) P - F equals C + 2. Answer (iii)

5. The point C in the benzene-naphthalene system phase diagram is referred to as the:

(i) Eutectic Point

(ii) Congruent Point

(iii) Triple Point

(iv) Critical Point Answer (i)

Short Answer:

1. Provide definitions for the terms phase, components, and degree of freedom.
2. Explain what you mean when you say "desilverization." (The Pattinson Method)
3. Talk about the water system's phase diagram.
4. Go over the sulfur system's phase diagram.
5. Describe the Phase rule and provide the sources for it.

Unit - 4

Electrolyte Conductance and Ionic Mobility

Objectives:

- Understand the concepts of conductance, conductivity
- Explore the variation of conductivity with dilution for weak and strong electrolytes.
- Familiarize with Kohlrausch's law of independent migration of ions.
- Understand the concept of ionic mobility

4.1 Introduction

In the realm of electrochemistry, understanding the conductance of electrolytes is paramount. Conductance, expressed as conductivity, is a measure of a solution's ability to conduct electricity. In this chapter, we delve into the intricacies of conductance, including its relationship with dilution for both ‘weak and strong’ electrolytes, the ‘Kohlrausch law’ of independent transference number, migration of ions, experimental determination methods such as the Hittorf and Moving Boundary methods. Additionally, we explore the concept of ionic mobility and its significance in electrolyte behavior.

4.2 Conductivity and Conductance

Conductivity (κ) is the measure of a solution's ability to conduct electricity, and it is inversely related to resistance. It is expressed in siemens per meter (S/m). Conductance (G) is the reciprocal of resistance and is given by the equation $G = 1/R$, where R is resistance. For a solution with electrodes of unit area separated by unit distance, conductance equals conductivity.
In general, the concentration and mobility of ions within a solution affect its conductivity. High conductivity is a result of strong electrolytes, such as strong acids and bases, totally dissociating into ions. Weak electrolytes, on the other hand, only partially separate into ions, leading to a significantly lower conductivity.

4.2.1 Equivalent Conductivity

Equivalent conductivity (Λ) is a measure of the conductivity of an electrolyte solution containing one equivalent of the electrolyte. An equivalent of an electrolyte is the amount that provides or reacts with one mole of electrons during electrolysis. It is expressed in siemens per meter per equivalent ($S \cdot m^2 \cdot eq^{-1}$).

The equivalent conductivity of an electrolyte solution can be intended using the equation:

$\Lambda = \kappa / c$

Where:

- κ is the conductivity of the solution
- Λ is the equivalent conductivity,
- c is the concentration of the electrolyte in moles per cubic meter (mol/m^3).

Equivalent conductivity is useful for comparing the conductivities of electrolytes at different concentrations or dilutions. It helps in understanding the contribution of individual ions to the overall conductivity of the solution.

4.2.2 Molar Conductivity

Molar conductivity (Λ_m) is the conductivity of a solution containing one mole of the electrolyte dissolved in a certain volume of the solution. It is expressed in siemens per meter per mole ($S \cdot m^2 \cdot mol^{-1}$). Molar conductivity is calculated using the equation:

$\Lambda_m = \Lambda / n$

Where:

Λ_m is the molar conductivity,

Λ is the equivalent conductivity,

n is the number of moles of the electrolyte present in the solution.

Molar conductivity is particularly useful for comparing the conductivities of different electrolytes, as it normalizes the conductivity with respect to the number of moles of the electrolyte present.

4.2.3 Variation of Conductivity with Dilution

The conductivity of a solution generally increases with dilution for both strong and weak electrolytes. This increase can be attributed to the decrease in the concentration of ions due to dilution, which reduces the chances of ion-ion interactions hindering ion mobility. For strong electrolytes, the increase in conductivity with dilution is significant as they dissociate almost completely, whereas for weak electrolytes, the increase is less pronounced due to partial dissociation.

- **Strong Electrolytes:**

Strong electrolytes separate totally into ions as liquefy in a solvent. For example, strong acids like Hydrochloric acid (HCl) and strong bases like Sodium Hydroxide (NaOH) dissociate into H^+ and Cl^- or Na^+ and OH^- ions, respectively.

As the concentration of a strong electrolyte solution decreases through dilution, the number of ions per unit volume decreases. However, since strong electrolytes dissociate completely, the concentration of ions decreases proportionally to the dilution. Thus, the conductivity of the solution remains high even with dilution because there are still a significant number of ions available to carry the electrical charge.

In summary, the conductivity of strong electrolyte solutions decreases slightly with dilution due to the decrease in ion concentration, but it remains relatively high compared to weak electrolyte solutions.

- **Weak Electrolytes:**

These electrolytes partially dissociate only into ions when dissolved in a solvent. Examples include weak acids like acetic acid (CH_3COOH) and weak bases like ammonia (NH_3). As the concentration of a weak electrolyte solution decreases through dilution, the extent of dissociation also decreases. At higher concentrations, more molecules of the weak electrolyte are in close proximity to each other, leading to more ion-pair formations and fewer free ions in solution. However, as the solution is diluted, the distance between molecules increases, reducing the likelihood of ion-pair formation and allowing more molecules to dissociate into ions. Consequently, the conductivity of the solution increases with dilution for weak electrolytes.

- **Comparison:**

The variation in conductivity with dilution for strong and weak electrolytes can be summarized as follows:

- For strong electrolytes, conductivity decreases slightly with dilution due to the decrease in ion concentration, but it remains relatively high.
- For weak electrolytes, conductivity increases with dilution due to increased dissociation and the generation of more free ions.

Understanding the behavior of conductivity with dilution is crucial in various fields such as electrochemistry, chemical engineering, and environmental science, where the properties of electrolyte solutions play a significant role in processes and applications

4.3 Kohlrausch Law of Independent Migration of Ions

According to Kohlrausch's law, an electrolyte's molar conductivity at infinite dilution is equal to the sum of the molar conductivities of each of its ions. Mathematically, it is expressed as:

$\Lambda^\circ = \Sigma\lambda^\circ_i$

Where Λ° is the molar conductivity at infinite dilution, and λ°_i is the molar conductivity of the ith ion.

This law provides a theoretical basis for understanding how ions migrate independently in solution, irrespective of the presence of other ions.

4.4 Transference Number and Experimental Determination

Transference number (t_i) is a measure of the fraction of the total current carried by an individual ion species in an electrolyte solution during electrolysis. It provides valuable information about the mobility and contribution of different ions to the overall conductivity of the solution. Transference numbers are typically denoted as t_+ for cations and t_- for anions. The sum of the transference numbers of all ions in the solution is always equal to 1.

There are several experimental methods used to determine transference numbers, two of the most common being the Hittorf method and the Moving Boundary method.

4.4.1 Hittorf Method

The Hittorf method, also known as the migration or transport number method, relies on the principle that during electrolysis, the migration rates of ions towards the electrodes are different due to their varying mobilities. By measuring the changes in concentration of ions near the electrodes over time, the transference numbers of individual ions can be determined.

The steps involved in the Hittorf method are as follows:

1. **Preparation of Cells**: Two identical cells, each containing the same electrolyte solution, are set up. One of the cells is used for the anode, and the other is used for the cathode.
2. **Electrolysis**: A constant current is passed through both cells for a specific duration of time.
3. **Analysis of Concentration Changes**: After electrolysis, samples are collected from near the anode and cathode in both cells. The concentrations of ions in these samples are then analyzed using suitable analytical techniques, such as titration or spectroscopy.
4. **Calculation of Transference Numbers**: The change in concentration of each ion species near the anode and cathode is determined. From these changes, the transference numbers (t_+ and t_-) of the cations and anions can be calculated using appropriate mathematical formulas.

4.4.2 Moving Boundary Method

The Moving Boundary method, also known as the cell method or the Ostwald method, is based on the observation of the movement of ions in a cell containing a concentration gradient of the electrolyte. This method is particularly suitable for determining transference numbers in solutions with high conductivities.

The steps involved in the Moving Boundary method are as follows:

1. **Preparation of Cell**: A cell with two compartments separated by a semi-permeable membrane or a porous plug is set up. The electrolyte solution with a concentration gradient is placed in one compartment, while a non-conducting solution or a reference electrode is placed in the other compartment.

2. **Application of Electric Field**: A voltage is applied across the cell, creating an electric field that drives the migration of ions.
3. **Observation of Boundary Movement**: Over time, the boundary between the two solutions moves, indicating the migration of ions. The rate of movement of the boundary is measured experimentally.
4. **Calculation of Transference Numbers**: Using appropriate mathematical relationships, the transference numbers of individual ions can be calculated from the rates of movement of the boundary.

Both the Hittorf and Moving Boundary methods provide reliable means of determining transference numbers, allowing for a better understanding of ion behavior in electrolyte solutions. These experimental techniques are essential tools in various fields, including electrochemistry, chemical engineering, and materials science, where the behavior of ions in solution is of paramount importance.

4.5 Ionic Mobility

The capacity of ions to flow through a solution when subjected to an electric field is known as ionic mobility. It is a fundamental property that plays a crucial role in various electrochemical processes, including electrolysis, electroplating, and electrochemical cell reactions. Ionic mobility is influenced by factors such as the charge and size of the ion, the viscosity and temperature of the solvent, and the presence of other ions in the solution.

4.5.1 Factors Affecting Ionic Mobility:

1. **Ion Charge:** The magnitude of the charge on an ion directly affects its mobility. Generally, ions with higher charges experience stronger interactions with the surrounding solvent molecules and other ions, resulting in lower mobility. For example, divalent ions (e.g., Ca^2+, Mg^2+) typically have lower mobility compared to monovalent ions (e.g., Na^+, Cl^-).
2. **Ion Size:** The size of the ion also influences its mobility. Larger ions experience greater resistance from the solvent molecules and the surrounding medium, leading to lower

mobility. Conversely, smaller ions can move more freely through the solution and exhibit higher mobility.

3. **Solvent Viscosity:** The viscosity of the solvent affects the mobility of ions by influencing the resistance encountered by the ions as they move through the solution. Higher viscosity impedes ion movement, resulting in lower mobility. Solvents with lower viscosity facilitate faster ion mobility.
4. **Temperature:** Temperature has a significant impact on ionic mobility. Generally, higher temperatures increase the kinetic energy of ions and solvent molecules, leading to enhanced ion mobility. As a result, ionic conductivity tends to increase with temperature.
5. **Concentration and Presence of Other Ions:** The concentration of ions in the solution and the presence of other ions can affect ionic mobility through ion-ion interactions and ion-solvent interactions. In concentrated solutions, ion-ion interactions may hinder ion mobility, whereas dilution can reduce these interactions and enhance mobility.

4.5.2 Measurement of Ionic Mobility:

Ionic mobility can be measured experimentally using techniques such as conductivity measurements, electrophoresis, and nuclear magnetic resonance (NMR) spectroscopy.

1. **Conductivity Measurements:** Ionic mobility can be indirectly determined by measuring the electrical conductivity of an electrolyte solution. The conductivity is related to the mobility of ions through the solution under an applied electric field.
2. **Electrophoresis:** Electrophoresis is a technique that involves applying an electric field to a solution containing charged particles (ions or molecules). The movement of the particles under the influence of the electric field allows for the determination of their mobility.
3. **Nuclear Magnetic Resonance Spectroscopy:** NMR spectroscopy can be used to study the motion of ions in solution by analyzing the relaxation times of nuclear spins. Changes in relaxation times in the presence of an electric field provide information about ion mobility.

4.5.3 Applications of Ionic Mobility:

Ionic mobility plays a critical role in various fields, including:

Electrochemistry: Ionic mobility governs the rate of ion transport in electrochemical reactions, influencing processes such as electrolysis, battery operation, and corrosion.

Analytical Chemistry: Electrophoresis techniques utilize ion mobility to separate and analyze ions based on their mobility differences, enabling applications such as DNA sequencing and protein analysis.

Materials Science: Understanding the mobility of ions in solid-state electrolytes is essential for the development of advanced materials for applications in fuel cells, sensors, and electronic devices.

Summary

In the vast landscape of electrochemistry, understanding the behavior of electrolytes is crucial. This summary aims to encapsulate the intricate concepts surrounding conductance, Kohlrausch's Law, transference number, and ionic mobility, shedding light on their significance and applications. Conductance, the measure of a solution's ability to conduct electricity, serves as a gateway to comprehending the underlying mechanisms of electrolytes. It quantifies the ease with which ions move through a solution under the influence of an electric field. Conductivity, closely related to conductance, represents the conductance per unit distance and unit area. These parameters play a pivotal role in elucidating the electrical properties of electrolyte solutions, offering insights into their behavior at different concentrations and dilutions. At the heart of electrolyte behavior lies Kohlrausch's Law, a fundamental principle that unveils the independent migration of ions in solution. This law states that the molar conductivity of an electrolyte at infinite dilution is the sum of the individual molar conductivities of its ions. Kohlrausch's Law serves as a guiding light, providing a theoretical framework for understanding ion behavior and enabling precise calculations in various electrochemical processes. Transference number emerges as a beacon in the realm of electrolytic studies, offering valuable insights into ion transport phenomena. It represents the fraction of the total current carried by an individual ion species in an electrolyte solution. Ionic mobility, the hallmark of ion transport, encapsulates the essence of electrolyte behavior. It encompasses a myriad of factors, including ion charge, size, solvent viscosity, temperature, and ion concentration.

Keywords:

- **Conductance:** The ability of a solution to conduct electricity, measured in siemens (S).
- **Conductivity:** The conductance of a solution per unit distance, often denoted as κ, measured in siemens per meter (S/m).
- **Equivalent Conductivity:** The conductance of a solution containing one equivalent of an electrolyte is denoted as Λ and measured in (S·m^2·eq^-1).
- **Molar Conductivity:** The conductance of a solution containing one mole of an electrolyte,
- **Kohlrausch Law:** At infinite dilution, the molar conductivity of an electrolyte equals the sum of the molar conductivities of its ions
- **Transference Number:** The fraction of the total current carried by an individual ion species in an electrolyte solution.

MCQs:

1. What is the measure of a solution's ability to conduct electricity?

   A) Conductivity

   B) Concentration

   C) Viscosity

   D) Density

   Answer: A)

2. Which law says that the ‘molar conductivity’ of an electrolyte at infinite dilution is the sum of the individual molar conductivities of its ions?

   A) Avogadro's Law

   B) Ohm's Law

   C) Boyle's Law

   D) Kohlrausch Law

   Answer: D)

3. What is the fraction of the total current carried by an individual ion species in an electrolyte solution?

   A) Conductivity

   B) Molar Conductivity

C) Transference Number

D) Equivalent Conductivity

Answer: C)

4. Which experimental method involves measuring the change in concentration of ions near the electrodes during electrolysis?

A) Hittorf Method

B) Moving Boundary Method

C) Electrophoresis

D) Conductivity Measurement

Answer: A)

5. Ionic mobility refers to the ability of ions to move through a solution under the influence of an electric field.A) Ionic Charge

B) Ionic Radius

C) Ionic Mobility

D) Ionic Concentration

Answer: C)

Short Questions:

1. Define conductance and conductivity. How are they related?
2. Explain the variation of conductivity with dilution for weak and strong electrolytes.
3. What is the Kohlrausch law of independent migration of ions? Discuss its significance.
4. Describe the Hittorf method for the experimental determination of transference numbers.
5. How does ionic mobility influence electrolyte behavior?

Unit - 5

Applications of Conductance Measurements in Analytical Chemistry

Objectives:

- Measure the conductance of weak electrolytes in solution.
- Understand the relationship between conductance and ionization in weak electrolytes.
- Understand the factors affecting solubility and solubility products.
- Calculate the ionic product of water (KwK_wKw) using conductometric data.
- Perform conductometric titrations of acid-base systems.

5.1 Applications of Conductance

In the realm of analytical chemistry, conductance measurements play a pivotal role in elucidating the properties of various chemical species. From determining the degree of ionization of weak electrolytes to unraveling the solubility products of sparingly soluble salts, conductance measurements offer a versatile toolkit for understanding the intricate interplay of ions in solution. Conductance measurements find diverse applications across various fields, ranging from analytical chemistry to materials science and beyond. Let's explore some of the key applications:

(i) Ionic Conductivity in Electrolyte Solutions

Conductance measurements are extensively used to characterize the ionic conductivity of electrolyte solutions. By measuring the electrical conductance of a solution and applying theories such as the Kohlrausch's Law of Independent Migration of Ions, researchers can determine the mobility of ions and thus understand the transport properties of electrolytes. This is crucial in fields such as electrochemistry, where electrolyte conductivity governs the performance of batteries, fuel cells, and other electrochemical devices.

(ii) Quality Control in Chemical Processes

In industrial settings, conductance measurements serve as valuable tools for quality control of chemical processes. By monitoring the conductance of solutions at various stages of production, manufacturers can ensure consistency and purity of their products. For instance, in the pharmaceutical industry, conductance measurements can detect impurities or deviations from specified formulations, helping maintain product efficacy and safety.

(iii). Monitoring Water Purity and Pollution

Conductance measurements play a key role in assessing water quality and detecting pollutants. The electrical conductivity of water is influenced by the concentration of dissolved ions, which can originate from natural sources or pollution. By measuring the conductance of water samples, environmental scientists can identify contamination levels and track the effectiveness of remediation efforts. Additionally, conductivity measurements are used in water treatment plants to optimize the dosing of chemicals for disinfection and pH adjustment.

(iv). Soil Salinity Assessment in Agriculture

In agriculture, soil salinity can significantly impact crop growth and yield. Conductance measurements provide a rapid and non-destructive method for assessing soil salinity levels. By measuring the electrical conductivity of soil extracts or directly probing the soil with conductivity sensors, farmers and agronomists can identify areas with excessive salt accumulation and implement appropriate irrigation and soil management strategies to mitigate the effects of salinity on crop productivity.

(v) Process Control in Chemical Synthesis

In chemical synthesis, conductance measurements are employed for real-time process monitoring and control. By continuously monitoring the conductivity of reaction mixtures, researchers can track the progress of chemical reactions, detect the formation of by-products or intermediates, and optimize reaction conditions to maximize product yield and purity. This real-time feedback enables rapid adjustments to reaction parameters, leading to more efficient and reproducible synthesis processes.

(v). Characterization of Polymer Electrolytes

In the field of materials science, conductance measurements are utilized to characterize polymer electrolytes, which are essential components in various electrochemical devices such as lithium-ion batteries and fuel cells. By measuring the conductivity of polymer electrolyte membranes, researchers can assess their suitability for specific applications, optimize their composition and morphology, and understand ion transport mechanisms within the polymer matrix. This knowledge aids in the development of high-performance and durable electrochemical devices

5.2 Determination of Degree of Ionization of Weak Electrolytes

The determination of the degree of ionization of weak electrolytes is a fundamental aspect of analytical chemistry, crucial for explaning the behavior of acids, bases, and salts in solution.

Weak electrolytes only partially dissociate into ions when dissolved in a solvent, in contrast to strong electrolytes, which dissociate completely. Conductance measurements offer a powerful method for quantifying the degree of ionization of weak electrolytes. Let's delve into the principles and procedures involved in this determination:

5.2.1 Principles of Conductance Measurements for Weak Electrolytes

a) **Ohm's Law and Electrical Conductivity**: Ohm's law states that the current (I) flowing through a conductor is directly proportional to the voltage (V) applied across it, and inversely proportional to its resistance (R). In the context of electrolyte solutions, the electrical conductivity (κ) is a measure of the ability of the solution to conduct electricity and is defined as the reciprocal of resistance ($\kappa=1/R$).

b) **Ionic Mobility and Conductivity**: In an electrolyte solution, ions carry electrical charge and contribute to conductivity. The mobility of ions, or their ability to move under the influence of an electric field, determines the conductivity of the solution. For weak electrolytes, only a fraction of the solute molecules dissociate into ions, resulting in lower conductivity compared to strong electrolytes.

c) **Degree of Ionization (α)**: The degree of ionization of a weak electrolyte (α) is defined as the fraction of solute molecules that dissociate into ions in solution. It is typically represented as a percentage or decimal value between 0 and 1.

5.2.2 Procedure for Determining Degree of Ionization

a) **Preparation of Solutions**: Prepare solutions of the weak electrolyte at various concentrations. It is essential to accurately measure the concentrations and ensure uniform mixing of the solute in the solvent.

b) **Measurement of Conductance**: Use a conductance meter to measure the electrical conductivity of each solution. The conductance meter applies a known voltage across the solution and measures the resulting current, allowing calculation of the conductivity.

c) **Calibration and Corrections**: Calibrate the conductance meter using standard solutions of known conductivity. Apply any necessary corrections for factors such as temperature, electrode polarization, and cell geometry to obtain accurate conductance measurements.

d) **Plotting Conductivity vs. Concentration**: Plot the conductivity (κ) of the solutions against their concentration (C). For weak electrolytes, the conductivity will increase with concentration but will not reach the same levels as strong electrolytes due to partial ionization.

e) **Determination of Limiting Conductivity**: Extrapolate the plot to zero concentration to obtain the limiting molar conductivity (Λ^0) of the weak electrolyte. This represents the conductivity that would be observed if all the solute molecules were completely dissociated into ions.

f) **Calculation of Degree of Ionization**: Use the limiting molar conductivity and the conductivity of the solution at a given concentration to calculate the degree of ionization (α) using the formula:

$$\alpha = \frac{\kappa}{\Lambda^0 \times C}$$

Where:

α = Degree of ionization

κ = Conductivity of the solution

Λ^0= Limiting molar conductivity

C = Concentration of the weak electrolyte

g) **Interpretation and Analysis**: Analyze the calculated values of α\alphaα to understand the extent of ionization of the weak electrolyte at different concentrations. Compare the degree of ionization with theoretical predictions and experimental observations to validate the results.

Example 1: Find the Degree of ionization (α) if Molar conductivity at infinite dilution (Λ^0_m) for acetic acid (CH_3COOH) = 390.7 S cm^2 mol^{-1} . Conductance of a 0.01 M solution of acetic acid (κ) = 1.65 S cm^{-1}

Solution:

Calculate the molar conductivity (Λ_m) of the 0.01 M acetic acid solution:

$$\Lambda_m = \kappa \times 1000 \backslash C$$

Where C is the concentration in mol/L.

$$\Lambda_m = 1.65 \times 1000 \backslash 0.01 = 165 \text{ S cm}^2 \text{ mol}^{-1}$$

Determine the degree of ionization (α) using the ratio of the molar conductivities:

$$\alpha = \Lambda_m \backslash \Lambda^0_m$$

$$\alpha = 165 \backslash 390.7 \approx 0.422$$

So, the degree of ionization (α) of the acetic acid in the 0.01 M solution is approximately 0.422 or 42.2%.

Example 2: Find Degree of ionization if Molar conductivity at infinite dilution for formic acid (HCOOH) = 391 $\text{S cm}^2 \text{ mol}^{-1}$. Conductance of a 0.05 M solution of formic acid = 3.91 S cm^{-1}

Solution:

Calculate the molar conductivity (Λ_m) of the 0.05 M formic acid solution:

$$\Lambda_m = \kappa \times 1000 \backslash C$$

$$\Lambda_m = 3.91 \times 1000 \backslash 0.05 = 78.2 \text{ S cm}^2 \text{ mol}^{-1}$$

Determine the degree of ionization (α):

$$\alpha = \Lambda_m \backslash \Lambda^0_m$$

$$\alpha = 78.2 \backslash 391 \approx 0.20$$

So, the degree of ionization (α\alphaα) of the formic acid in the 0.05 M solution is approximately 0.20 or 20%.

5.3 Solubility and Solubility Products of Sparingly Soluble Salts

The maximum amount of a material that may dissolve in a given quantity of the solvent at a certain temperature is referred to as the substance's solubility in the solvent. Sparingly soluble salts are compounds that exhibit low solubility in a solvent, typically water. Conductance measurements offer a valuable approach to indirectly determine the solubility and solubility products of such salts. Let's delve into the principles and procedures involved:

5.3.1 Principles of Conductance Measurements for Sparingly Soluble Salts

a) **Ionic Equilibrium and Conductivity**: When a sparingly soluble salt dissolves in water, it undergoes partial dissociation into ions. The equilibrium between the dissolved ions and the undissolved solid establishes an ionic equilibrium in solution. Conductance measurements allow us to indirectly assess the concentration of ions in solution based on their contribution to the electrical conductivity.

b) **Solubility Product (Ksp)**: For a sparingly soluble salt, the equilibrium between the dissolved ions and the undissolved solid can be described by its solubility product constant (Ksp).

c) **Conductivity and Ion Concentration**: The conductivity of a solution is directly proportional to the concentration of ions present in solution. By measuring the conductivity of a solution containing a sparingly soluble salt, we can indirectly infer the concentration of the dissolved ions and, subsequently, determine the solubility and solubility product of the salt.

5.3.2 Procedure for Determining Solubility and Solubility Product

1. **Preparation of Saturated Solutions**: Prepare a series of solutions by dissolving varying amounts of the sparingly soluble salt in a fixed volume of solvent, typically water, at a constant temperature. Allow each solution to reach saturation, ensuring that no more salt can dissolve.
2. **Measurement of Conductance**: Use a conductance meter to measure the electrical conductivity of each saturated solution. The conductance meter applies a known voltage across the solution and measures the resulting current, allowing calculation of the conductivity.
3. **Calibration and Corrections**: Calibrate the conductance meter using standard solutions of known conductivity. Apply any necessary corrections for factors such as temperature, electrode polarization, and cell geometry to obtain accurate conductance measurements.
4. **Plotting Conductivity vs. Concentration**: Plot the conductivity (κ) of the saturated solutions against their concentration (C). As the concentration increases, more ions are present in solution, leading to higher conductivity.

5. **Extrapolation to Infinite Dilution**: Extrapolate the plot to zero concentration to obtain the limiting molar conductivity (Λ^0) of the ions in solution. This represents the conductivity that would be observed if the ions were completely dissociated and infinitely diluted.
6. **Calculation of Solubility Product**: Use the limiting molar conductivity and the conductivity of the saturated solution to calculate the solubility product (Ksp) of the sparingly soluble salt using the formula:

$$K_{sp} = \frac{\kappa}{\Lambda^0}$$

Where:

K_{sp} = Solubility product constant

κ = Conductivity of the saturated solution

Λ^0 = Limiting molar conductivity of the ions

7. **Interpretation and Analysis**: Analyze the calculated solubility product constant to determine the solubility of the salt and compare it with literature values. Assess the reliability and accuracy of the experimental results, considering factors such as experimental errors and deviations from ideal behavior.

Example 3: Calculate the solubility product (Ksp) of silver bromide (AgBr) if its solubility in water at 25°C is 5.0×10^{-7} mol/L.

Solution:

Write the dissociation equation for AgBr:

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

Let the solubility of AgBr be S mol/L. Since the dissociation of AgBr produces one Ag^+ ion and one Br^- ion per formula unit, the concentrations of Ag^+ and Br^- in a saturated solution are both equal to S.

Given $S=5.0\times10^{-7}$ mol/L, the equilibrium concentrations are:

$$[Ag^+]=5.0\times10^{-7} \text{ mol/L}$$

$$[Br^-]=5.0\times10^{-7} \text{ mol/L}$$

Calculate K_{sp}:

$$K_{sp} = [Ag^+][Br^-] = (5.0\times10^{-7})\,(5.0\times10^{-7})$$

$$K_{sp} = 25\times10^{-14} = 2.5\times10^{-13}$$

So, the solubility product (K_{sp}) of AgBr is 2.5×10^{-13}.

Example 4: The solubility of calcium fluoride (CaF_2) in water at 25°C is 2.2×10^{-4} mol/L. Calculate the solubility product (K_{sp}) of CaF_2

Solution:

Write the dissociation equation for CaF_2

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

Let the solubility of CaF_2 S mol/L. The dissociation produces one Ca^{2+} ion and two F^- ions per formula unit.

Given $S=2.2\times10^{-4}$ mol/L, the equilibrium concentrations are:

$[Ca^{2+}]=S=2.2\times10^{-4}$ mol/L

$[F^-]=2S=2\times2.2\times10^{-4}=4.4\times10^{-4}$ mol/L

Calculate K_{sp}:

$K_{sp} = [Ca^{2+}][F^-]^2 = (2.2\times10^{-4})\ (4.4\times10^{-4})^2$

$K_{sp} = (2.2\times10^{-4})\ (19.36\times10^{-8}) = 42.592\times10^{-12}$

$K_{sp} = 4.2592\times10^{-11}$

So, the solubility product (K_{sp}) of CaF_2 4.2592×10^{-11}

5.4 Ionic Product of Water

Water, although often considered a neutral molecule, undergoes self-ionization to a small extent, producing hydronium (H_3O^+) and hydroxide ($OH^{-)}$ ions. The ionic product of water (K_w) quantifies the concentration of these ions at equilibrium. Conductance measurements allow for the determination of K_w by measuring the conductance of pure water at various temperatures. By extrapolating the conductance to infinite dilution, one can obtain the limiting molar conductivity of water, which, in turn, facilitates the calculation of K_w. This parameter holds significance in various fields, including biochemistry, where it governs the pH of biological fluids and cellular environments.

5.5 Hydrolysis Constant of a Salt

When salts dissolve in water, they can undergo hydrolysis, resulting in the formation of acidic or basic solutions. Conductance measurements enable the determination of hydrolysis constants, which quantify the extent of hydrolysis and the resulting pH of the solution. By titrating a solution of the salt with a strong acid or base and monitoring the change in conductance, one can derive the hydrolysis constant. This information is invaluable in understanding the behavior of salts in aqueous solutions, particularly in industrial processes where precise control of pH is essential for product quality and process efficiency.

5.6 Conduct metric Titrations in Acid-Base Systems

Conduct metric titrations, a subset of volumetric titrations, rely on the measurement of electrical conductance during the titration process. In acid-base systems, conduct metric titrations offer a rapid and precise method for determining the equivalence point and the concentration of the analyte or titrant. By plotting the change in conductance against the volume of added titrant, one can identify the inflection point corresponding to the equivalence point. Conduct metric titrations are particularly advantageous in situations where visual indicators are ineffective or impractical, such as in highly colored or turbid solutions.

5.6.1 Principles of Conduct metric Titrations

i. **Conductivity and Ion Mobility:**
   - Conductivity (κ) of a solution depends on the concentration and mobility of ions.
   - Strong electrolytes (like NaCl) completely dissociate in water and have high conductivity.
   - Weak electrolytes (like acetic acid) partially dissociate and have lower conductivity.

ii. **Titration Process:**
   - During the titration, a titrant is added to a solution containing the analyte.
   - The conductivity of the solution changes as the titrant reacts with the analyte, forming products with different conductive properties.

5.6.2 Conductmetric Titration Curves

1. **Strong Acid with Strong Base:** Example: HCl (strong acid) titrated with NaOH (strong base). Initial conductivity is high due to the presence of H^+ ions (high mobility). As NaOH is added, H^+ ions are neutralized to form water ($H^+ + OH^- \rightarrow H_2O$). The conductivity decreases until the equivalence point is reached because H^+ ions are being replaced by Na^+ and Cl^- ions, which have lower conductivity. A second increase in conductivity follows the equivalency point because of the extra OH- ions from NaOH.

   Graph:

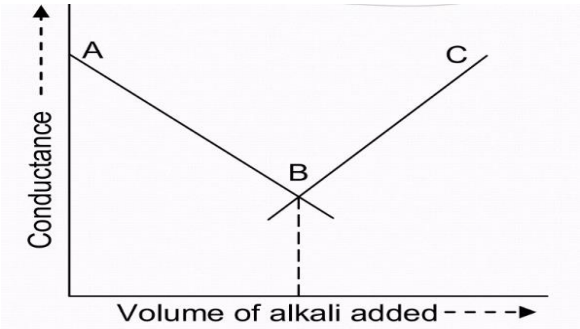


Figure-5.1: Conductmetric Titration between Strong Acid with Strong Base

2. **Weak Acid with Strong Base:** Example: Acetic acid (CH_3COOH) titrated with NaOH. Initial conductivity is low due to partial dissociation of acetic acid. As NaOH is added, H^+ ions from acetic acid are neutralized. The conductivity decreases initially and then increases after the equivalence point as excess OH^- ions are added.

Graph:

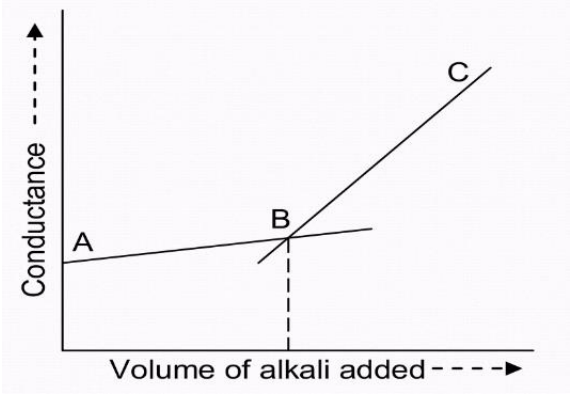


Figure-5.2: Conductmetric Titration between Weak Acid with Strong Base

3. **Strong Acid with Weak Base:** Example: HCl titrated with ammonia (NH_3). Initial conductivity is high due to H^+ ions. As NH_3 is added, H^+ ions are neutralized to form ammonium ions ($NH4^+$). The conductivity decreases up to the equivalence point and then remains relatively constant due to the buffering action of the ammonium ions.

Graph:

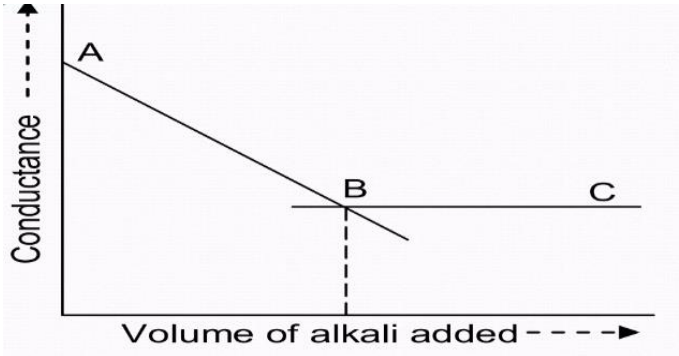


Figure-5.3: Conductmetric Titration between Strong Acid with Weak Base

4. **Weak Acid with Weak Base:** Example: Acetic acid titrated with ammonia. Initial conductivity is low. Conductivity changes gradually as the weak acid and weak base react to form water and weakly ionized salts. The conductivity curve is less pronounced compared to strong acid-base titrations.

Graph:

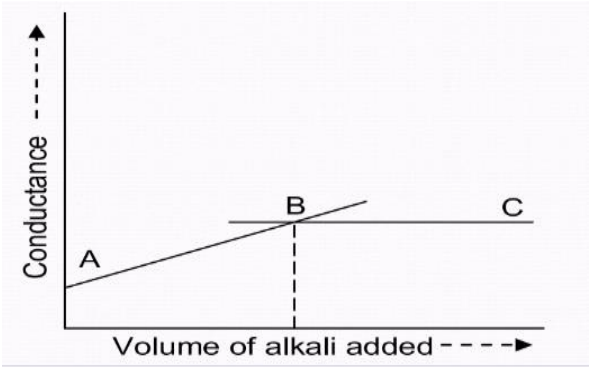


Figure-5.4: Conductmetric Titration between Weak Acid with Weak Base

Summary

Conductance measurements provide a versatile and accurate method for studying various properties of electrolytes and their solutions. This technique is particularly useful for determining the degree of ionization of weak electrolytes, calculating the solubility and solubility products of sparingly soluble salts, and measuring the ionic product of water and the hydrolysis constant of salts. Additionally, conductometric titrations offer a precise way to identify the equivalence point in acid-base titrations, making them a valuable tool in analytical chemistry. Conductometric measurements enable the determination of the degree of ionization by comparing the conductance of the weak electrolyte to that of a strong electrolyte. By measuring the conductance of saturated solutions of sparingly soluble salts, the solubility product constant (Ksp) can be calculated, providing insights into the salt's solubility behavior. Conductance measurements of pure water at various temperatures allow for the calculation of Kw, illustrating the temperature dependence of water's ionization. Conductometric titrations, especially in acid-base systems, help in accurately determining the equivalence point by monitoring the changes in conductance throughout the titration process.

Keywords:

- **Conductance**: The measure of a solution's ability to conduct electricity, dependent on ion concentration and mobility
- **Degree of Ionization:** The fraction of a weak electrolyte that dissociates into ions in solution.
- **Weak Electrolytes:** Substances that partially dissociate into ions in solution, resulting in low conductance.
- **Ionic Product of Water (Kw):** The equilibrium constant for the self-ionization of water, equal to the product of the concentrations of hydrogen ions and hydroxide ions in pure water.
- **Conductometric Titrations:** Titration method where the conductance of the solution is measured continuously to detect the equivalence point.

MCQs

1. What is the primary principle behind conductometric titrations?

    A) Color change

    B) Temperature change

    C) Change in conductance

    D) Precipitate formation

    Answer: C)

2. Which of the following is used to calculate the solubility product (KspK_{sp}Ksp) of a sparingly soluble salt?

    A) Concentration of Salt

    B) Conductance of the solution

    C) pH of solution

    D) Volume of solution

    Answer: B)

3. The degree of ionization of a weak electrolyte can be determined by measuring:

    A) Temperature

    B) Conductance

    C) Pressure

    D) Volume

    Answer: B)

4. The ionic product of water (KwK_wKw) at 25°C is approximately:

    A) 1×10−71 \times 10^{-7}1×10−7

    B) 1×10−101 \times 10^{-10}1×10−10

    C) 1×10−141 \times 10^{-14}1×10−14

    D) 1×10−41 \times 10^{-4}1×10−4

    Answer: C)

5. In a conductometric titration of HCl with NaOH, the conductivity of the solution decreases initially because:

    A) HCl is a strong electrolyte

    B) NaOH is a strong electrolyte

    C) H+ ions are neutralized by OH- ions

D) Na+ ions increase in concentration

Answer: C)

6. The hydrolysis constant (K_h) of a salt is determined using:

A) Conductometric measurements

B) Colorimetric analysis

C) Potentiometric titrations

D) Gravimetric analysis

Answer: A)

Short Answer Questions

1. Explain how conductance measurements can be used to determine the degree of ionization of a weak electrolyte.
2. Describe the steps involved in calculating the solubility product (Ksp) from conductance measurements.
3. How does temperature affect the ionic product of water (Kw)?
4. What is the significance of the hydrolysis constant (Kh) of a salt, and how is it determined using conductance measurements?
5. Outline the typical conductometric titration curve for a strong acid titrated with a strong base.

Unit - 6

Electrochemistry

Objectives

- Understand Electrochemical Cells
- Grasp the concept of the electromotive force (EMF) of a cell.
- Measure EMF: Learn methods for measuring the EMF of a cell.
- Understand the Nernst equation and its significance.
- Identify various types of electrodes.

6.1 Introduction

Electrochemistry is a branch of chemistry that deals with the inter conversion of chemical energy and electrical energy. This field is fundamental to a wide range of applications, including batteries, fuel cells, electroplating, and corrosion prevention. The primary components of electrochemical systems are cells, which can be classified into reversible and irreversible types, depending on their ability to convert energy in both directions. This chapter explores these concepts, as well as the electromotive force (EMF) of a cell, methods for measuring EMF, the Nernst equation, types of electrodes, and standard electrode potentials.

6.2 Reversible and Irreversible Cells

6.2.1 Reversible Cells

A reversible cell is an electrochemical cell that can function both as a galvanic cell (producing electrical energy from a spontaneous chemical reaction) and as an electrolytic cell (consuming electrical energy to drive a non spontaneous chemical reaction). The key characteristic of reversible cells is that the direction of the reaction can be reversed by changing the direction of the current.

6.2.2 Characteristics of Reversible Cells

Dynamic Equilibrium: The cell can reach a state of dynamic equilibrium where the forward and reverse reactions occur at equal rates.

Efficiency: Reversible cells can theoretically achieve 100% efficiency, as no energy is lost in the process.

Examples: Lead acid batteries and hydrogen oxygen fuel cells are common examples of reversible cells.

6.2.3 Irreversible Cells

In contrast, an irreversible cell is an electrochemical cell where the chemical reaction cannot be reversed by simply reversing the direction of the current. Once the reactants are converted into products, the reaction cannot spontaneously return to its original state.

6.2.4 Characteristics of Irreversible Cells

One Way Reaction: The chemical reaction proceeds in one direction and cannot be reversed under normal operating conditions.

Lower Efficiency: These cells are typically less efficient than reversible cells because energy is lost in the form of heat and other side reactions.

Examples: Disposable batteries, such as alkaline batteries and zinc carbon cells, are typical examples of irreversible cells.

6.3 Concept of EMF of a Cell

The electromotive force (EMF) of a cell, also known as cell potential or cell voltage, is the maximum potential difference between two electrodes of the cell when no current is flowing. It is a measure of the energy provided by the cell to move electrons through an external circuit.

6.3.1Factors Affecting EMF

1. Nature of Electrodes: The types of materials used for the anode and cathode can significantly influence the EMF.
2. Concentration of Solutions: The concentration of ions in the electrolyte solutions affects the cell potential.
3. Temperature: The EMF of a cell changes with temperature, as reaction kinetics and thermodynamics are temperature dependent.

4. Pressure: For cells involving gases, the pressure of the gaseous reactants and products can affect the EMF.

6.3.2 Measurement of EMF of a Cell

- **Potentiometric Method**

The most common method for measuring the EMF of a cell is the potentiometric method, which involves using a high impedance voltmeter to measure the potential difference between the two electrodes without drawing any significant current.

Steps:

1. Setup: Connect the cell to a high impedance voltmeter.
2. Measurement: Record the potential difference (voltage) displayed on the voltmeter.
3. Calibration: Ensure that the voltmeter is properly calibrated and that the reference electrode (if used) is stable.

- **Galvanic Method**

Another method involves using the cell as a power source to drive a known load and measuring the potential difference across the load. However, this method is less accurate because the cell's internal resistance and current flow can affect the measurement.

6.4 Nernst Equation

The Nernst equation provides a quantitative relationship between the EMF of an electrochemical cell and the concentrations of the reactants and products involved in the redox reactions. It is derived from the standard Gibbs free energy change for the cell reaction.

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

E = EMF of the cell

E^0= Standard EMF of the cell

R = Universal gas constant (8.314 J/mol·K)

n = Number of moles of electrons transferred in the reaction

T = Temperature in Kelvin

Q = Reaction quotient (ratio of product concentrations to reactant concentrations)

F = Faraday constant (96485 C/mol)

6.4.1 Importance of the Nernst Equation

- Predicting Cell Potential: The Nernst equation allows the calculation of the cell potential under nonstandard conditions, considering the actual concentrations of reactants and products.
- Determining Equilibrium Constant: By setting E to zero (equilibrium condition), the Nernst equation can be used to calculate the equilibrium constant for the cell reaction.
- Understanding Reaction Direction: The sign and magnitude of the cell potential indicate the spontaneity of the reaction and its direction.
- Designing Batteries: It helps in designing batteries with desired voltages by adjusting the concentrations of reactants.

6.5 Types of Electrodes

Electrodes in electrochemical cells can be broadly classified into several types based on their material and function:

- **Metallic Electrodes**: Made of metals, these electrodes participate in redox reactions by losing or gaining electrons.
  Examples: Copper, zinc, platinum electrodes.
- **Inert Electrodes**: These do not participate in the reaction but provide a surface for the reaction to occur.
  Examples: Platinum, graphite electrodes.
- **Gas Electrodes**: These involve a gas in contact with an inert metal that acts as an electrode.
  Examples: Hydrogen electrode, chlorine electrode.
- **Metal-Metal Ion Electrodes**: Consist of a metal in contact with its ion in solution.
  Examples: Copper-Copper sulfate electrode, silver-silver chloride electrode.
- **Redox Electrodes**: Involve a redox couple in solution, where both the oxidized and reduced forms are present.
  Examples: $Fe^{3+/}Fe^{2+}$ electrode.

6.5.1 Standard Electrode Potential

Measured at standard state conditions, which include 1 M concentration for solutions, 1 atm pressure for gases, and a predetermined temperature (often 298 K), the standard electrode potential (E°) is the individual potential of a reversible electrode. With respect to the standard hydrogen electrode (SHE), which has a potential of 0.00 volts, the standard electrode potential is measured.

6.5.2 Importance

- **Predicting Cell EMF**: The standard electrode potentials of the anode and cathode can be used to calculate the overall cell potential.
- Determining Spontaneity: The standard electrode potential helps predict the spontaneity of redox reactions.
- Electrochemical Series: Provides a basis for the electrochemical series, which ranks elements and compounds based on their standard electrode potentials.

Summary

Electrochemical cells can be classified as reversible or irreversible based on their ability to convert chemical energy into electrical energy and vice versa. Reversible cells can operate both as galvanic (producing electricity) and electrolytic (consuming electricity) cells, allowing for the direction of the reaction to be reversed. Irreversible cells, on the other hand, cannot reverse the chemical reaction through the application of electrical energy. The electromotive force (EMF) of a cell is the maximum potential difference between its electrodes when no current is flowing. It represents the energy available to drive the flow of electrons through an external circuit and depends on the nature of the electrodes, ion concentrations, temperature, and pressure. The EMF of a cell can be measured using a potentiometric method with a high-impedance voltmeter, ensuring minimal current flow to avoid altering the cell's potential. Another method involves using the cell to drive a known load and measuring the potential difference across it, though this is less accurate due to internal resistance effects. It is crucial for calculating the cell potential under non-standard conditions, determining equilibrium constants, and understanding reaction spontaneity. Electrodes in electrochemical cells are classified based on their material and function. These include metallic electrodes, inert electrodes, gas electrodes, metal-metal ion

electrodes, and redox electrodes. Each type serves a specific role in facilitating the electrochemical reactions.

Keywords:

- **Reversible Cell:** An electrochemical cell that can function both as a galvanic and an electrolytic cell, allowing reversible reactions.
- **Irreversible Cell:** An electrochemical cell where the chemical reaction cannot be reversed by changing the direction of current.
- **Electromotive Force (EMF):** The maximum potential difference between two electrodes of a cell when no current flows, driving electron movement.
- **Potentiometric Method:** A technique to measure EMF using a high-impedance voltmeter to minimize current flow.
- **Nernst Equation:** A formula that relates cell EMF to the concentrations of reactants and products, allowing calculation under non-standard conditions.
- **Standard Electrode Potential (E°):** The potential of a reversible electrode at standard state conditions, used to predict cell EMF and reaction spontaneity.

MCQs

1. Which of the following is a characteristic of a reversible cell?
   (A) Only operates as a galvanic cell
   (B) Only operates as an electrolytic cell
   (C) Can operate both as a galvanic and electrolytic cell
   (D) Does not involve redox reactions

   Answer: (C)

2. Which of the following is an example of an irreversible cell?
   (A) Lead-acid battery
   (B) Hydrogen-oxygen fuel cell
   (C) Alkaline battery
   (D) Nickel-cadmium battery
   Answer: (C)

3. The EMF of a cell is defined as:

(A) The current flowing through the cell

(B) The maximum potential difference between two electrodes when no current flows

(C) The resistance of the electrolyte

(D) The power output of the cell

Answer: (B)

4. Which factor does NOT affect the EMF of a cell?

(A) Nature of electrodes

(B) Concentration of solutions

(C) Shape of electrodes

(D) Temperature

Answer: (C)

5.Which method is commonly used to measure the EMF of a cell?

(A) Ammeter method

(B) Potentiometric method

(C) Ohmmeter method

(D) Galvanometer method

Answer: (B)

6. In the potentiometric method, the voltmeter used should have:

A) Low impedance

B) No impedance

C) High impedance

D) Variable impedance

Answer: C)

7. The Nernst equation relates the EMF of a cell to:

(A) The temperature of the solution

(B) The concentrations of reactants and products

(C) The surface area of electrodes

(D) The pressure of the system

Answer: (B)

Short Answer Questions

1. Define a reversible cell and provide an example.
2. Explain the concept of EMF of a cell.
3. Describe the potentiometric method for measuring EMF.
4. Write the Nernst equation and explain its significance.
5. List and briefly describe three types of electrodes used in electrochemical cells.

Unit - 7

Electrochemical Series and Thermodynamics of Electrochemical Cells

Objectives:

- Understand the Electrochemical Series:
- Learn the arrangement of elements in the electrochemical series.
- Comprehend the basic principles of thermodynamics as applied to electrochemical cells.
- Determine enthalpy change (ΔH) and entropy change (ΔS) from EMF data.
- Calculate the equilibrium constant (K) for a reaction using EMF data.

7.1Electrochemical Series

The 'Electrochemical series', also known as the activity sequence, is a listing of elements given in order of their 'Standard Electrode' potentials. This series helps in predicting the direction of redox reactions and the feasibility of electrochemical processes.

8.1.1 Significance of the Electrochemical Series

- **Predicting Reaction Spontaneity**:

Elements higher in the series are more likely to be reduced (gain electrons), while elements lower are more likely to be oxidized (lose electrons). A metal higher in the series can displace a metal ion lower in the series from its compound. (as shown in table 7.1)

- **Electrode Selection:**

Helps in selecting suitable electrodes for constructing electrochemical cells.

- **Corrosion Analysis:**

Predicts the tendency of metals to corrode; metals lower in the series are more prone to corrosion.

Table 7.1 Electrochemical Series

Elements	Electrode Reaction	E°_{red} (volts)
	Oxidised Form + ne⁻ ⟶ Reduced Form	
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	− 3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	− 2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	− 2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	− 2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	− 2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	− 2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	− 1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	− 0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	− 0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	− 0.44
	$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	− 0.41
Cd	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	− 0.40
Pb	$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	− 0.31
Co	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	− 0.28
Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	− 0.25
Sn	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	− 0.14
Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	− 0.13
H_2	$2H^+ + 2e^- \longrightarrow H_2(g)$ (standard electrode)	0.00
Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+ 0.34
I_2	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+ 0.54
Fe	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+ 0.77
Hg	$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+ 0.79
Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+ 0.80
Hg	$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+ 0.85
N_2	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$	+ 0.97
Br_2	$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+ 1.08
O_2	$O_2(g) + 2H_3O^+(aq) + 2e^- \longrightarrow 3H_2O$	+ 1.23
Cr	$Cr_2O_7^{2-} + 14H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
Cl_2	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+ 1.36
Au	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+ 1.42
Mn	$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 12H_2O(l)$	+ 1.51
F_2	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+ 2.87

Increase

(a) Tendency for oxidation to occur
(b) Power as reducing agent

(a) Tendency for reduction to occur
(b) Power as oxidising agent

Increase

7.2 Thermodynamics of a Reversible Cell

Electrochemical cells convert chemical energy into electrical energy. The thermodynamics of these cells help in understanding the energy changes during the reaction.

8.2.1 EMF and Gibbs Free Energy (ΔG)

The EMF (E) of a cell is related to the Gibbs free energy change (ΔG) of the cell reaction by the equation:

ΔG = -nFE

where:

ΔG= Gibbs free energy change (Joules)

n= number of moles of electrons transferred in the reaction

F = Faraday constant (96,485 C/mol)

E= EMF of the cell (Volts)

7.2.2 Nernst Equation

The 'Nernst equation' relates the EMF of an electrochemical cell to the concentrations of the reactants and products:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

Where:

E = standard EMF of the cell

R = gas constant (8.314 J/mol·K)

T = temperature (Kelvin)

n = number of moles of electrons

F = Faraday constant (96,485 C/mol)

Q = reaction quotient

7.2.3 Calculation of Enthalpy (ΔH) and Entropy (ΔS)

The change in enthalpy (ΔH) and entropy (ΔS) can be determined from the temperature dependence of the EMF:

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

From the Gibbs free energy change and the Nernst equation, we can write:

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

Using the temperature dependence of the cell EMF, we get:

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF}$$

Thus, entropy change can be calculated from the slope of the E vs. T plot, and enthalpy change can be calculated from ΔG and ΔS.

7.2.4 Calculation of Equilibrium Constant from EMF Data

The equilibrium constant (K) for a reaction can be related to the standard EMF of the cell:

$$\Delta G = -RT \ln K$$

Since $\Delta G^0 = -nF E^0$

$$-nF E^0 = -RT \ln K$$

Solving for K:

$$\ln K = nF E^0 / RT$$

$$K = \exp (nF E^0 / RT)$$

Thus, by measuring the standard EMF of the cell, the equilibrium constant can be calculated.

Summary

This chapter provides a detailed exploration of the electrochemical series and the thermodynamics of electrochemical cells. The electrochemical series lists elements based on their standard electrode potentials, aiding in predicting the spontaneity of redox reactions. The thermodynamic properties of electrochemical cells, including Gibbs free energy, enthalpy, and entropy, can be determined from EMF data. The Nernst equation plays a crucial role in linking the cell potential to the concentrations of the reactants and products. Furthermore, EMF

measurements allow the calculation of equilibrium constants, providing insight into the feasibility and extent of chemical reactions.

Keywords:

- **Electrochemical Series:** A list of elements arranged by their standard electrode potentials, indicating their ability to act as oxidizing or reducing agents.
- **Reversible Cell:** An electrochemical cell that can operate in both directions (forward and reverse reactions) with minimal energy loss.
- **Equilibrium Constant (K):** A number that expresses the ratio of the concentrations of products to reactants at equilibrium for a given reaction.
- **Electromotive Force (EMF):** The voltage generated by an electrochemical cell due to the redox reactions occurring within it.

MCQs:

1. The following elements has the highest standard electrode potential?
   (A) Lithium (Li)
   (B) Zinc (Zn)
   (C) Silver (Ag)
   (D) Hydrogen (H) Answer: C)
2. The standard EMF of a cell can be used to calculate which thermodynamic property?
   (A) Enthalpy change (ΔH)
   (B) Gibbs free energy change (ΔG)
   (C) Entropy change (ΔS)
   (D) Heat capacity Answer: B)
3. The Nernst equation is used to:
   (A) Calculate the equilibrium constant (K)
   (B) Determine the standard electrode potential (E°)
   (C) Relate EMF to the concentration of reactants and products
   (D) Measure the temperature dependence of EMF Answer: (C)
4. What is the relationship between Gibbs free energy change (ΔG) and the equilibrium constant (K)?

(A) \(\Delta G = RT \ln K\)

(B) \(\Delta G = -RT \ln K\)

(C) \(\Delta G = \frac{RT}{\ln K}\)

(D) \(\Delta G = -nFE\) Answer: (B)

5. Which of the following is true for a reversible cell?

(A) It cannot be used to perform work.

(B) It operates with maximum efficiency.

(C) It is always at equilibrium.

(D) It has a zero EMF. Answer: B)

6. If the EMF of a cell decreases with increasing temperature, what can be inferred about the entropy change (ΔS)?

(A) ΔS is positive.

(B) ΔS is negative.

(C) ΔS is zero.

(D) ΔS cannot be determined from this information. Answer: B)

Short Answer Questions

1. What is the significance of the electrochemical series in predicting the direction of redox reactions?
2. How can the Nernst equation be used to calculate the EMF of a cell at non-standard conditions?
3. Describe the relationship between Gibbs free energy change (ΔG) and the EMF of a cell.
4. Explain how to calculate the equilibrium constant (K) for a reaction using EMF data.
5. How can you determine the entropy change (ΔS) from the temperature dependence of the EMF?

Unit - 8

Electrochemical Methods and Potentiometric Titrations

Objectives:

- Understand Concentration Cells
- Differentiate between concentration cells with transference and without transference.
- Comprehend Liquid Junction Potential
- Understand the concept and causes of liquid junction potential.
- Determine pH Using Electrodes:
- Grasp Potentiometric Titrations:

8.1.1 Concentration Cells with Transference

In concentration cells with transference, the ions move between two half-cells, and the transference number (fraction of total current carried by a particular ion) plays a role in the EMF generated. Example

Consider a concentration cell with the following half-cells:

- Anode: Zn (s) | Zn^{2+} (0.01 M)

- Cathode: Zn (s) | Zn^{2+} (1 M)

The Nernst equation for the cell is:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[Zn^{2+}]_{anode}}{[Zn^{2+}]_{cathode}}$$

$$E = 0 - \frac{0.0591}{2} \log \frac{0.01}{1}$$

$$E = 0.02955 \log 100$$

$$E \approx 0.0591 \text{ V}$$

8.1.2 Concentration Cells without Transference

In these cells, the EMF is generated solely due to the concentration gradient, without any significant ion movement between the half-cells.

Example

For a cell without transference, such as:

- Anode: Ag (s) | Ag+ (0.001 M)
- Cathode: Ag (s) | Ag+ (0.1 M)

The Nernst equation is similar:

$$E = E^\circ - \frac{RT}{F} \ln \frac{[\mathrm{Ag}^+]_{\text{anode}}}{[\mathrm{Ag}^+]_{\text{cathode}}}$$

$$E = 0 - 0.0591 \log \frac{0.001}{0.1}$$

$$E = 0.0591 \log 100$$

$$E \approx 0.118\,\mathrm{V}$$

8.2 Liquid Junction Potential and Salt Bridge

- **Liquid Junction Potential**

This potential arises at the interface between two different electrolyte solutions due to the unequal diffusion rates of ions. It can lead to inaccuracies in EMF measurements.

- **Salt Bridge**

A salt bridge minimizes liquid junction potential by providing a pathway for ion flow, maintaining electrical neutrality. It typically contains a concentrated electrolyte solution (e.g., KCl) that does not react with the cell components.

8.3 pH Determination Using Electrodes

Hydrogen Electrode

The hydrogen electrode, often used as the standard reference, involves the reaction:

$H_2\,(g) \leftrightarrow 2H^+ + 2^{e-}$

The EMF of the cell can be related to pH as:

$$E = E^\circ - \frac{0.0591}{2} \log[\mathrm{H}^+]$$

8.3.1 Quinhydrone Electrode

The quinhydrone electrode consists of quinhydrone dissolved in the solution whose pH is to be measured. The equilibrium between quinone (Q) and hydroquinone (QH_2) depends on pH:

$$Q + 2H^+ + 2e^- \leftrightarrow QH_2$$

The electrode potential is given by:

$$E = E^\circ + \frac{0.0591}{2} \log \frac{[QH_2]}{[Q][H^2]}$$

8.4 Potentiometric Titrations

8.4.1 Acid-Base Potentiometric Titrations

In acid-base titrations, the pH of the solution is monitored using a pH electrode. The potential change is plotted against the volume of titrant added. The equivalence point is determined by the inflection point on the titration curve. Example: Titrating HCl with NaOH:

- Initial pH is low (acidic).
- pH increases gradually as NaOH is added.
- At the equivalence point, pH rapidly rises.
- Beyond equivalence, pH levels off as excess NaOH is added.

8.4.2 Oxidation-Reduction Potentiometric Titrations

In redox titrations, the potential change is monitored using a redox electrode. The titration curve plots the potential versus the volume of titrant added. The equivalence point is determined from the sharp change in potential.Example Titrating Fe^{2+} with Ce^{4+}:

- Initial potential reflects Fe^{2+} concentration.
- As Ce^{4+} is added, Fe^{2+} is oxidized to Fe^{3+}.
- At the equivalence point, all $Fe^{2+}$is oxidized, and potential rises sharply.
- Beyond equivalence, potential stabilizes at a new higher value.

Summary

This chapter delves into various electrochemical methods and their applications. It covers concentration cells, explaining the differences between those with and without transference and their mechanisms for generating EMF. The chapter also addresses the liquid junction potential, its causes, and how a salt bridge can mitigate it. It explores the determination of pH using hydrogen and quinhydrone electrodes, providing the principles and procedures for these methods. Finally, it provides a qualitative treatment of potentiometric titrations, focusing on acid-base and oxidation-reduction reactions, explaining their principles and practical applications.

Keywords:

- **Concentration Cells:** Electrochemical cells where the electrodes are the same material but immersed in solutions of different concentrations, generating EMF based on concentration gradients.
- **Transference:** The movement of ions in an electrochemical cell, contributing to the overall current.
- **Hydrogen Electrode**: An electrode used as a reference in pH measurements, involving the redox reaction of hydrogen gas.
- **Potentiometric Titrations:** Titrations in which the potential difference (voltage) of the solution is measured to determine the end point of the reaction.

MCQs

1. Which of the following best describes a concentration cell without transference?

   A) A cell where ions move between the half-cells.

   B) A cell where the EMF is generated solely due to concentration differences.

   C) A cell that uses a salt bridge to minimize liquid junction potential.

   D) A cell that generates EMF due to both concentration differences and ion movement.

   Answer: B)

2. What is the primary purpose of a salt bridge in an electrochemical cell?

   A) To generate additional EMF.

B) To maintain electrical neutrality and minimize liquid junction potential.

C) To separate the oxidation and reduction half-cells.

D) To increase the conductivity of the cell.

Answer: B)

3 The EMF of a hydrogen electrode is primarily used to measure:

A) The concentration of hydrogen ions in solution.

B) The oxidation state of metals.

C) The potential difference between two electrodes.

D) The liquid junction potential. Answer: A)

4 In a quinhydrone electrode, the redox couple involved is:

A) Quinone and hydroquinone.

B) Hydrogen and hydroxide ions.

C) Iron(II) and Iron(III).

D) Silver and silver chloride. Answer: A)

5 During an acid-base potentiometric titration, the equivalence point is determined by:

A) The initial pH of the solution.

B) The first appearance of a color change.

C) The inflection point on the pH versus volume plot.

D) The final pH after adding all the titrant. Answer: C)

6 In an oxidation-reduction potentiometric titration, the potential at the equivalence point is characterized by:

A) A gradual change in potential.

B) A sharp change in potential.

C) A constant potential.

D) A decrease in potential. Answer: B)

Short Answer Questions

1. What is a concentration cell with transference, and how does it generate EMF?
2. How does a salt bridge minimize liquid junction potential in an electrochemical cell?
3. Explain the principle of pH determination using a hydrogen electrode.
4. What role does the quinhydrone electrode play in pH determination?
5. Describe the procedure for an acid-base potentiometric titration.
6. What distinguishes an oxidation-reduction potentiometric titration from an acid-base potentiometric titration?

Unit - 9

Carboxylic Acids

Objectives:

- Understanding the structure and properties of carboxylic acids.
- Exploring the reactivity of carboxylic acids in various chemical reactions.
- Differentiating between aliphatic and aromatic carboxylic acids.
- Learning synthetic methods for preparation and derivatization.
- Developing analytical skills for characterization and quantification.
- Cultivating critical thinking and problem-solving abilities through practical exercises and case studies.

9.1 Introduction

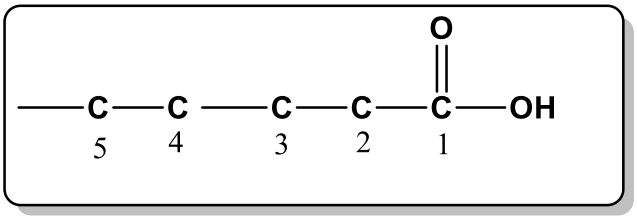
Aliphatic or aromatic compounds with at least one carboxyl group (-COOH) in the molecule are known as carboxylic acids. A carboxyl group (COOH), which is made up of a hydroxyl group (-OH) and a carbonyl group (C=O) joined to the same carbon atom, is the fundamental component of these molecules. Because of their peculiar structure, carboxylic acids have a wide range of applications due to their special qualities.

Aliphatic carboxylic acids are characterized by straight or branched carbon chains, often referred to as alkyl or alkenyl groups, with the carboxyl functional group (-COOH) attached to one end. These compounds are typically derived from saturated or unsaturated hydrocarbons and can range from simple monocarboxylic acids like formic acid (methanoic acid) to complex polycarboxylic acids such as citric acid. Aliphatic carboxylic acids are commonly found in nature as constituents of fats, oils, and waxes, where they serve roles in energy storage and biological processes.

In contrast, aromatic carboxylic acids feature an aromatic ring structure, characterized by alternating single and double bonds, with a carboxyl group attached to the ring. The most prominent example is benzoic acid, where the carboxyl group is directly attached to a benzene ring. Aromatic carboxylic acids often exhibit enhanced stability and aromaticity, imparting distinct chemical and physical properties compared to their aliphatic counterparts. They are frequently employed in the synthesis of pharmaceuticals, fragrances, and agrochemicals due to their unique reactivity and structural motifs.

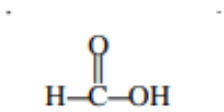
9.2 Nomenclature

Carboxylic acids have historically been named based on their sources, resulting in common names such as acetic acid (ethanoic acid) and benzoic acid. However, in accordance with IUPAC guidelines, the systematic nomenclature of carboxylic acids involves selecting the longest carbon chain containing the carboxyl group (-COOH). The suffix "-*oic* acid" replaces the "-*e*" ending of the corresponding alkane. Notably, the carbon atom of the carboxyl group is always designated as carbon 1 when numbering the chain. This systematic approach ensures clarity and consistency in naming organic compounds.

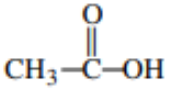


Other substituents and functional groups in carboxylic acids are numbered and named following the standard rules of nomenclature, as previously studied. This entails assigning numerical locants to the substituents in the order that gives the lowest numbers, with Greek letters or numerical locants used to indicate their positions relative to the carboxyl group.

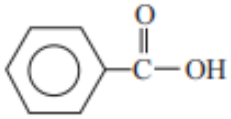
Examples



Methanoic acid (Formic acid)

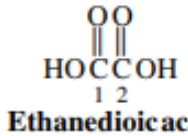


Ethanoic acid (Acetic acid)

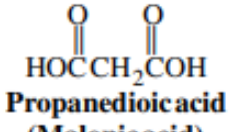


Phenylmethanoic acid (Benzoic acid)

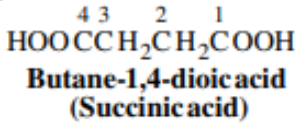
Dicarboxylic Acids: When a compound contains two carboxyl groups, the suffix "-*dioic acid*" is used, and the positions of the carboxyl groups are indicated by numerical locants separated by commas (e.g., succinic acid, butanedioic acid).



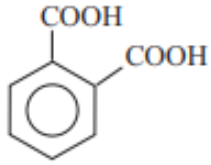
Ethanedioic acid
(Oxalic acid)



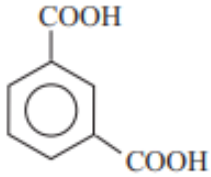
Propanedioic acid
(Malonic acid)



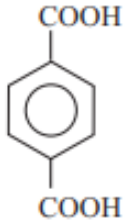
Butane-1,4-dioic acid
(Succinic acid)



***o*-Phthalic acid**
(Phthalic acid)



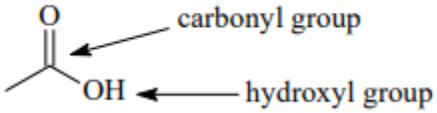
***m*-Phthalic acid**
(Isophthalic acid)

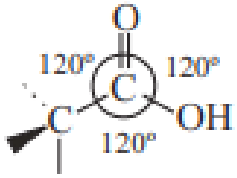


***o*-Phthalic acid**
(Terephtyhalic acid)

9.3 Structures and Physical Properties

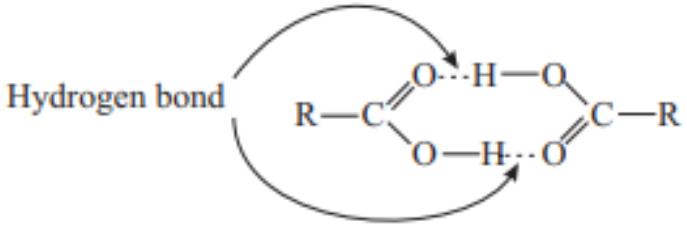
- **Molecular Structure**: The fundamental structural feature of carboxylic acids is the carboxyl group (-COOH), which consists of a carbonyl group (C=O) and a hydroxyl group (-OH) attached to the same carbon atom. This arrangement imparts a planar geometry to the carboxyl group, with the carbon atom exhibiting sp^2 hybridization. The bond angles around the carbon atom are approximately 120 degrees.





- **Hydrogen Bonding:**

Carboxylic acids exhibit hydrogen bonding due to the polarity of both the carbonyl and hydroxyl groups within their structure. Interestingly, many carboxylic acids tend to exist in a dimeric form, where two molecules of the acid are held together by two hydrogen bonds. This dimerization phenomenon is a consequence of the complementary interaction between the hydrogen bond donor (the hydroxyl group) of one molecule and the hydrogen bond acceptor (the carbonyl group) of another molecule.



Dimer of a carboxylic acid

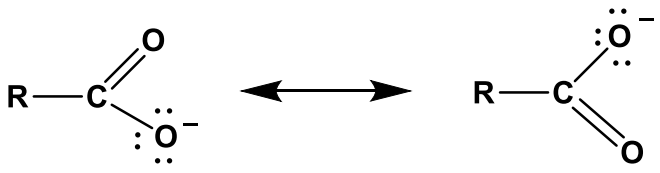
The higher melting and boiling points characteristic of carboxylic acids are primarily attributed to intermolecular hydrogen bonding. The lower molecular weight members of this group display considerable water solubility. This solubility is facilitated by the formation of hydrogen bonds between carboxylic acid molecules and water molecules, further highlighting the importance of intermolecular interactions in their physical properties.

9.4Acidity of Carboxylic Acids and its Factors Effecting

Carboxylic acids exhibit acidity due to their ability to dissociate in water. This dissociation occurs according to the following equilibrium reaction, where the carboxylic acid donates a proton (H^+) to water, forming a carboxylate ion and a hydronium ion.

Carboxylic acid **Carboxylate ion**

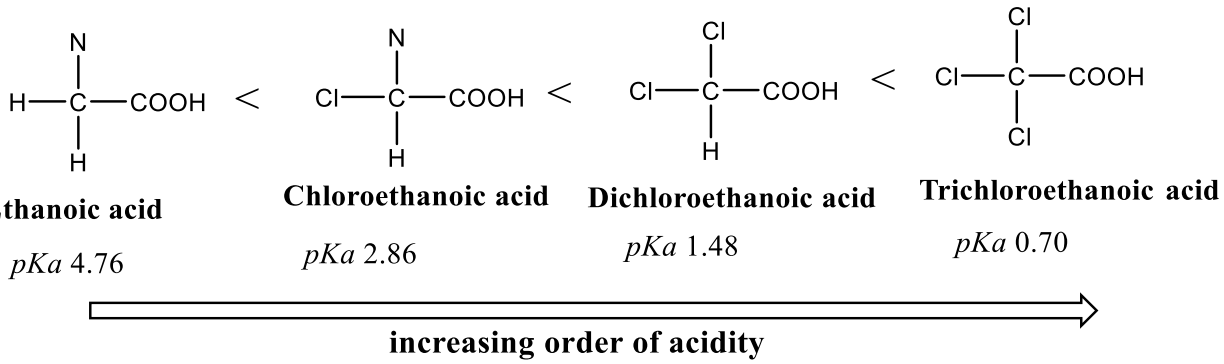
Carboxylic acids have the lower *pKa* value which indicates the greater acidic properties than comparison to alcohols. The acidity of carboxylic acids can be elucidated by considering the anion formed upon ionization. The resulting carboxylate ion, derived from the dissociation of carboxylic acids, can be depicted as a 'Resonance Hybrid' of the following two structures: [Include the structures of the resonance hybrid.]



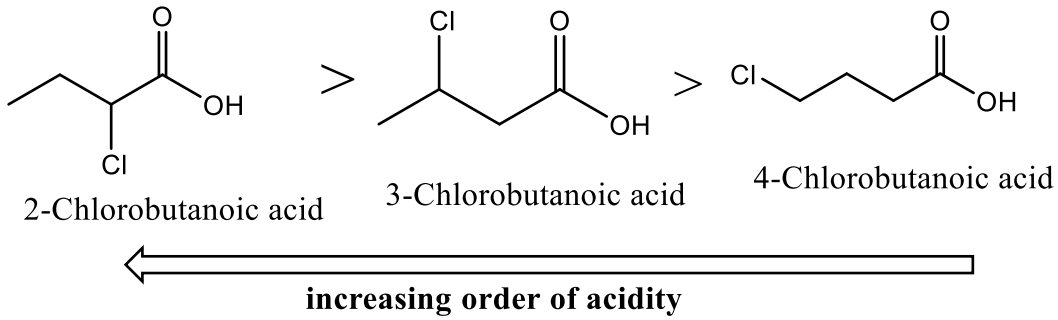
Resonance structures of Carboxylate Ion

These structures illustrate the delocalization of the negative charge over two oxygen atoms, resulting in the stabilization of the carboxylate ion. This increased stability of the carboxylate ion facilitates the release of a proton from the -COOH group, contributing to the acidic nature of carboxylic acids.

Alkyl groups, being electron-releasing in nature, hinder the release of H^+ ions, thereby diminishing acidity. Consequently, ethanoic acid exhibits lower acidity compared to methanoic acid. Hence, it can be concluded that **electron-donating** substituents decrease the acidity of carboxylic acids. Other side the **electron withdrawing** substituents such as halogens and nitro-group increases the acidity. As halogen number increases in the carboxylic acid, its acidity rises. This occurs because halogen groups facilitate the release of H^+ ions, making it progressively easier.



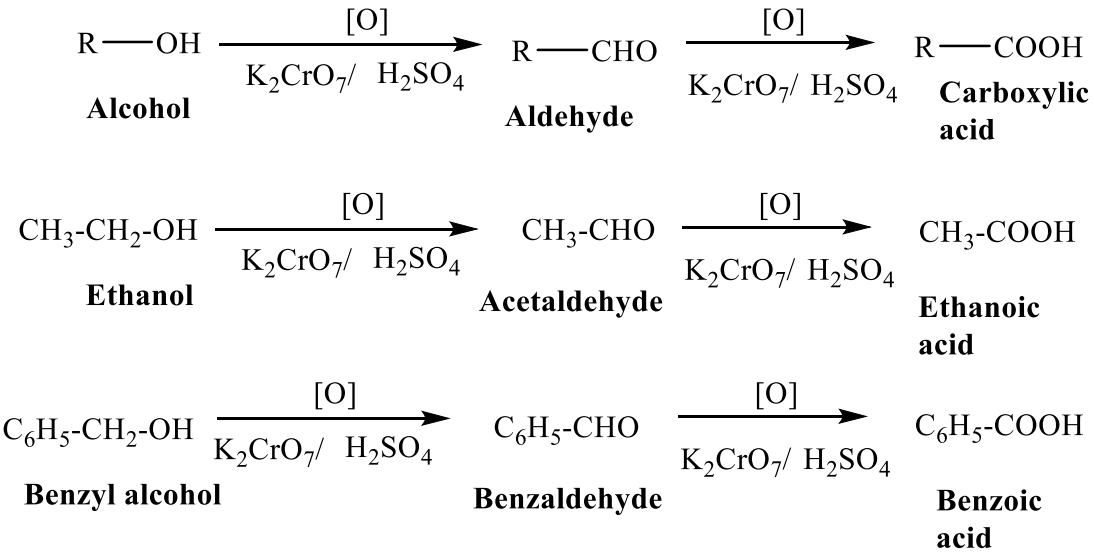
Because of the decreasing inductive effect, the acidity of carboxylic acids diminishes as the halogen group moves farther up the carbon chain. Consequently, the acidity of 2-chlorobutanoic acid (*pKa* 2.86) is more than that of 3-chlorobutanoic acid (*pKa* 4.05), which is greater yet than that of 4-chlorobutanoic acid *(pKa* 4.50).



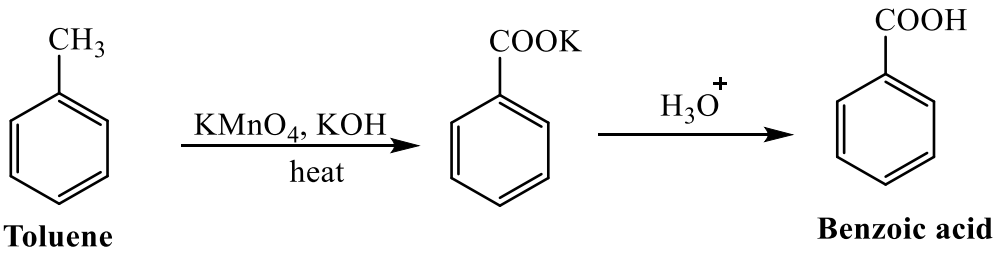
9.4 Synthesis of Carboxylic Acids

(i) Oxidation Reaction

Primary alcohols can be oxidized to form either ‘aldehydes or carboxylic acids’, depending on the reaction conditions and oxidizing agent used. Stronger oxidizing agents, such as potassium permanganate ($KMnO_4$) or chromium trioxide (CrO_3), can further oxidize primary alcohols to carboxylic acids via the formation of an aldehyde intermediate.

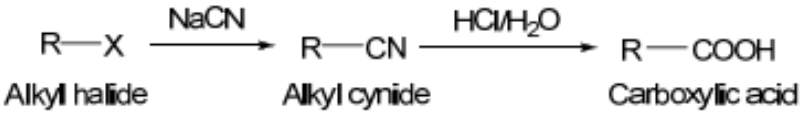


Aromatic carboxylic acids can be synthesized through the oxidation of alkylbenzenes using potassium dichromate ($K_2Cr_2O_7$) or acidic or alkaline potassium permanganate ($KMnO_4$).

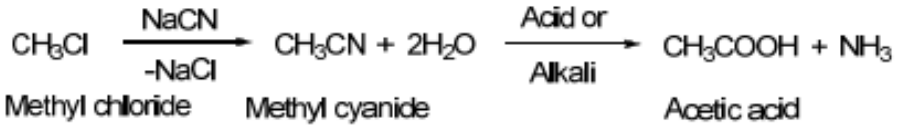


(ii) Hydrolysis Reactions

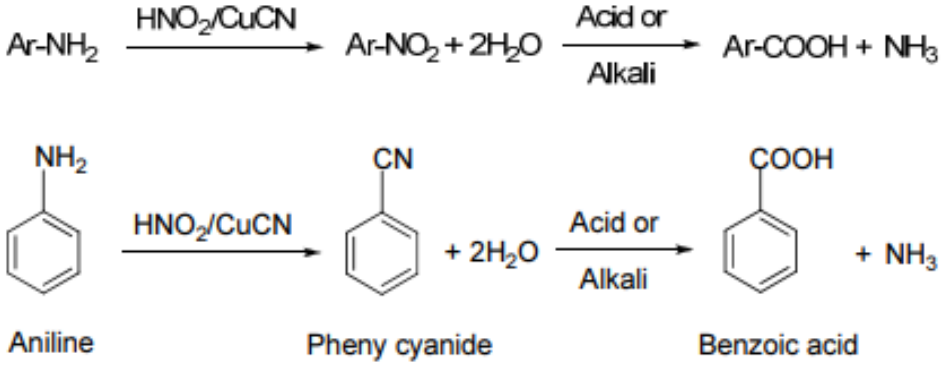
Alkyl halides undergo SN^2 displacement reactions with sodium cyanide to yield nitriles, which, upon hydrolysis, are converted into carboxylic acids. During acid hydrolysis, the cyano group undergoes a transformation into a carboxyl group facilitated by a hydrogen bond



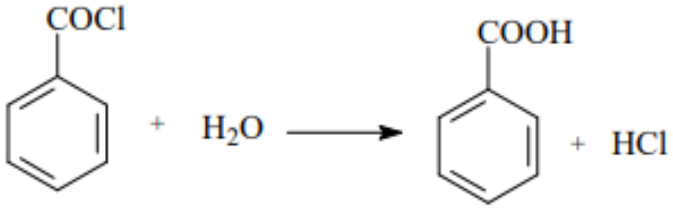
(Where, R is an alkyl group and X is a halide)



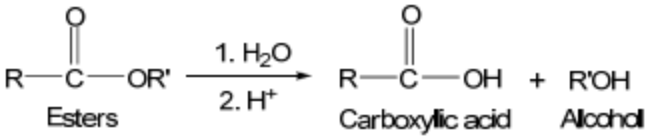
When aromatic amines react with nitrous acid, they yield aromatic nitrites, which upon acidic hydrolysis, are converted into aromatic carboxylic acids.

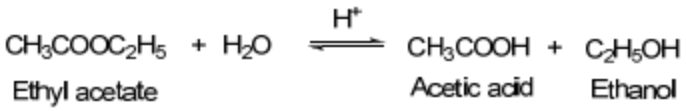


- **By the Hydrolysis of acid chlorides**

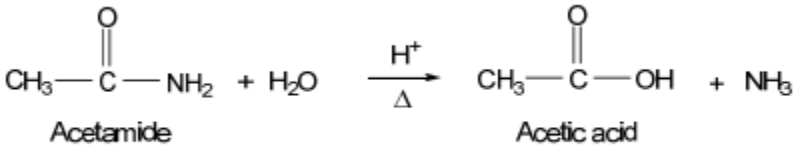


- **By the Hydrolysis of esters**





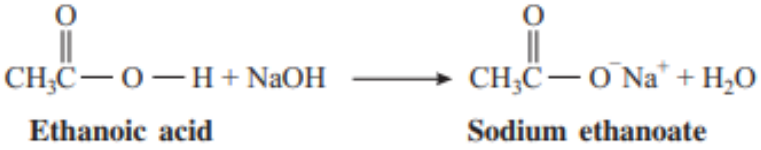
- **By the Hydrolysis of Amides**



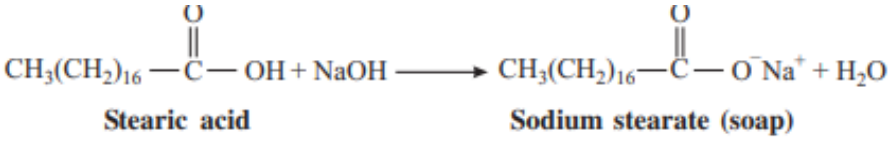
9.5 Chemical Reactions of Carboxylic Acids

- **Reaction with NaOH**

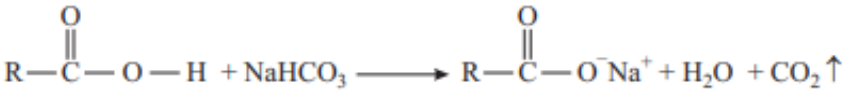
Strong bases like metal hydroxides fully deprotonate carboxylic acids to produce salts.



It's intriguing to note that soaps are sodium salts derived from long-chain carboxylic acids, commonly referred to as fatty acids.



Carboxylic acids can also undergo deprotonation by weak bases like sodium bicarbonate. In this process, they yield the sodium salt of the acid, along with carbon dioxide and water as byproducts.

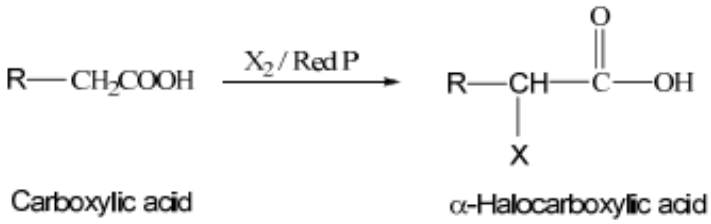


This reaction serves as a laboratory test for carboxylic acids. The observation of bubbles, indicating the liberation of CO_2 gas, upon treatment with $NaHCO_3$, confirms the presence of a carboxyl functional group in the compound.

Phenols do not exhibit this reaction because they are weaker acids compared to carboxylic acids. Consequently, this test can be utilized to distinguish between these two categories of compounds.

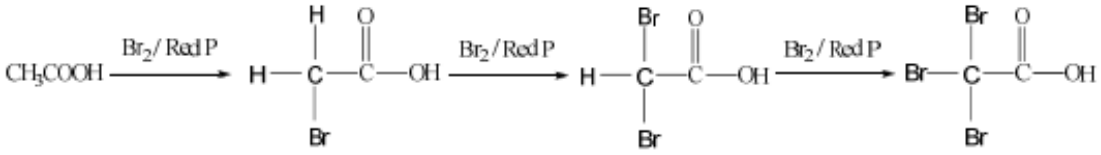
- **Hell-Volhard-Zelinski Reaction(α–halogenation of carboxylic acids)**

Carboxylic acids can undergo halogenation with bromine or chlorine in the presence of a small amount of red phosphorus to form α-halo or β-haloacids. This reaction, known as the 'Hell-Volhard-Zelinsky' reaction, involves the replacement of an α-hydrogen atom in the carboxylic acid by a chlorine or bromine atom to yield an α-halo carboxylic acid.



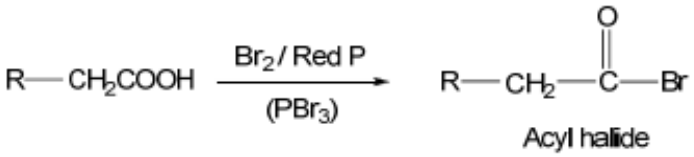
(Where, X= Cl, Br)

Example- Bromination

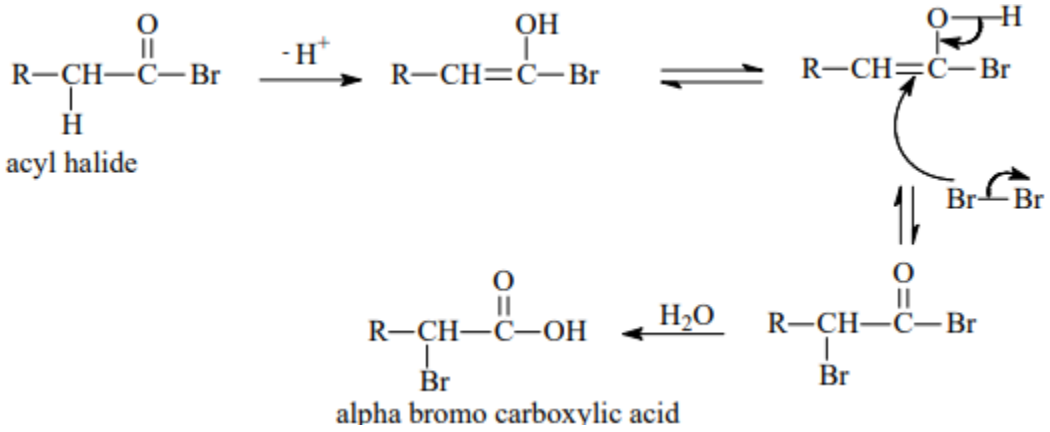


Stepwise Mechanism of HVZ

In the initial step, phosphorus reacts with bromine to produce phosphorus tri-bromide, which then converts the carboxylic acid into an acyl bromide.



In the second step the **acyl bromide** undergoes tautomerization to its enol form, which then proceeds to attack the halogen molecule, resulting in the formation of an α-halo acyl halide. Subsequent hydrolysis with water yields the final α-halo carboxylic acid product.

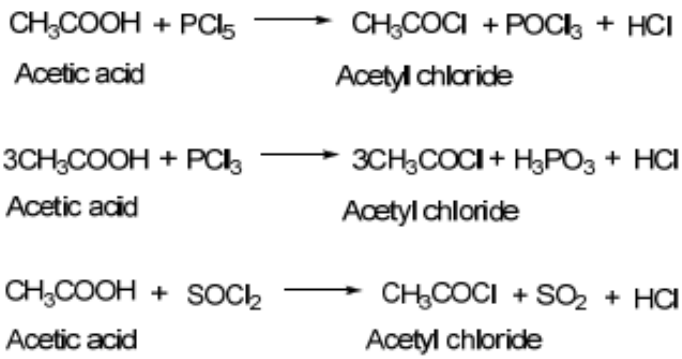


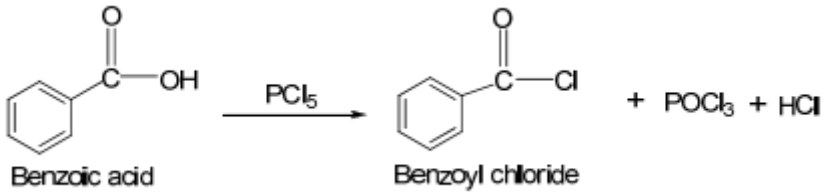
While the ‘α-bromination’ of certain carbonyl compounds like aldehydes and ketones can proceed with Br_2 under acidic conditions, this reaction typically does not occur with amides, acids and esters. This is because only aldehydes and ketones undergo ‘enolization’ to a significant extent, enabling the reaction to take place.

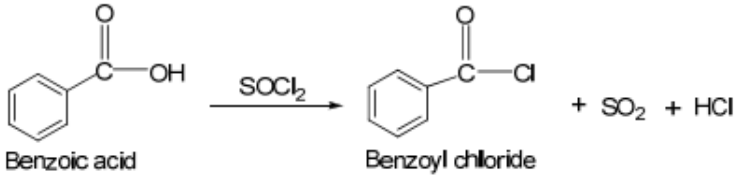
9.6 Conversion of Carboxylic acids to other derivatives

(i) Preparation of acid halides

The conversion of carboxylic acids to acid halides includes the substitution of the (-OH) of the carboxylic acid with a halogen atom (such as chlorine, bromine, or iodine). This transformation is commonly achieved through the use of reactive halogenating agents, typically thionyl chloride ($SOCl_2$) or phosphorus trichloride (PCl_3), although other reagents such as phosphorus pentachloride (PCl_5) and oxalyl chloride $(COCl)_2$ can also be employed.

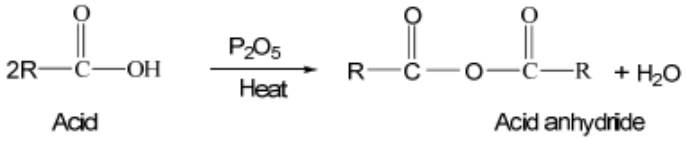


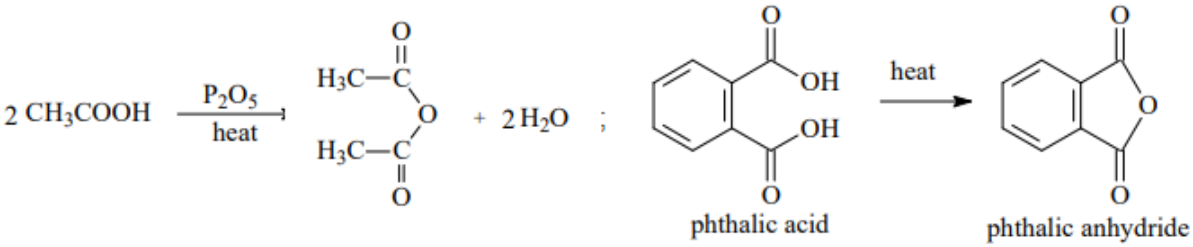




(ii) Preparation of acid Anhydrides

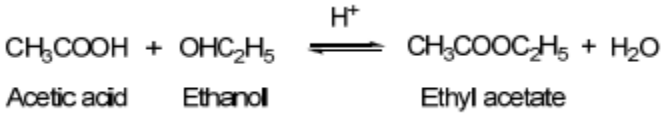
Indeed, acid anhydrides can be synthesized through the dehydration of carboxylic acids, a process where water is eliminated from adjacent carboxylic acid molecules. This reaction typically occurs in the presence of strong dehydrating agents such as phosphorus pentoxide (P_2O_5) or concentrated sulfuric acid (H_2SO_4). The dehydration of two molecules of acetic acid (CH_3COOH) using phosphorus pentoxide (P_2O_5) as a dehydrating agent can be represented as follows:



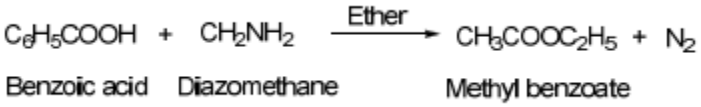


(iii) Preparation of Esters:

Carboxylic acids undergo esterification with alcohols in the presence of concentrated sulfuric acid. This reaction entails the substitution of the -OH group of the carboxylic acid with the -OR group of the alcohol or phenol and is commonly referred to as Fischer-Speier esterification. For instance, the reaction between ethanoic acid and ethanol yields ethyl ethanoate.

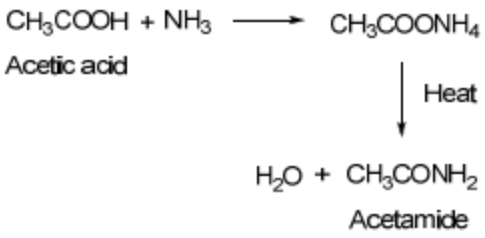


Esters can also be synthesized by treating carboxylic acids with an ethereal solution of diazomethane.



(iv) Preparation of Amides

Amides can be prepared from acids through various synthetic routes. One common method involves the direct condensation of a carboxylic acid with ammonia (NH_3) or an amine (RNH_2) in the presence of a dehydrating agent. The reaction proceeds as follows:

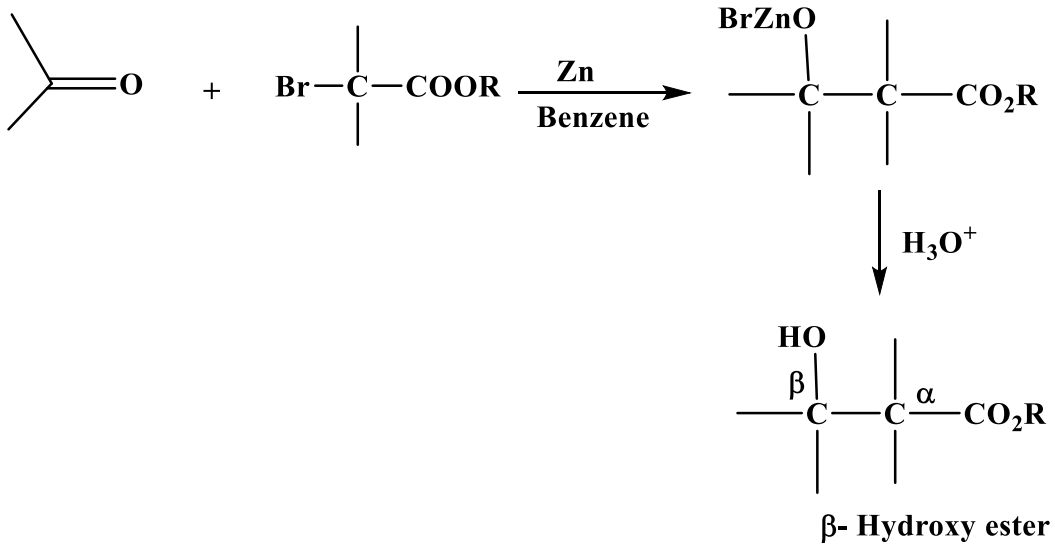


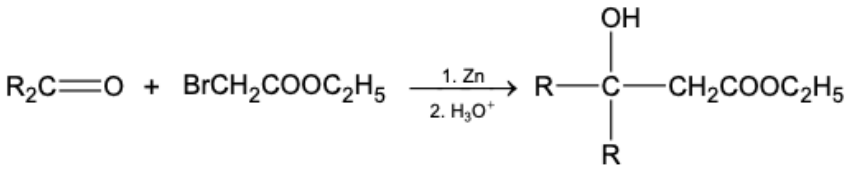
In this reaction, -OH group of the –COOH (carboxylic acid) is replaced by the -NH_2 group of the ammonia or amine, forming an amide bond (CONH) and generating water as a byproduct.

9.7 Name reaction s of Carboxylic acid and its derivatives

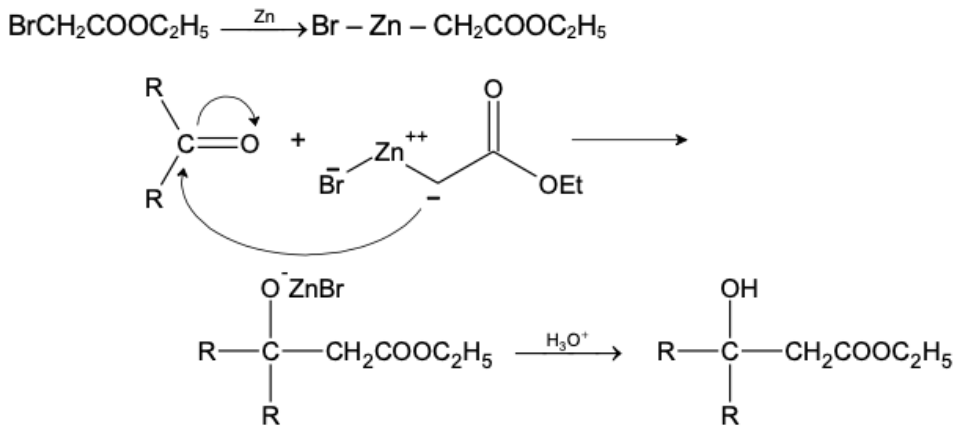
(i) Reformatsky Reaction

The Reformatsky reaction is a type of organic reaction that involves the addition of an α-haloester or α-haloketone to a carbonyl compound, typically an aldehyde or ketone, in the presence of a metal such as zinc. This reaction results in the formation of β-hydroxyesters or β-hydroxyketones. The mechanism typically proceeds through the formation of an enolate intermediate, which then reacts with the haloester or haloketone to yield the final product. The Reformatsky reaction is named after the Russian chemist Sergey Nikolaevich Reformatsky, who first reported it in 1887.



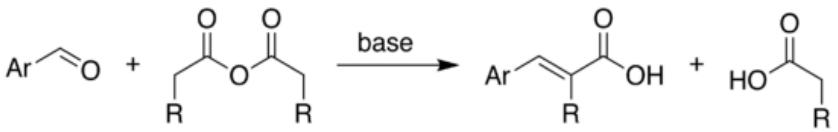


Reaction mechanism; The intermediate formed in the reaction resembles an organozinc reagent, which adds to the carbonyl group in a manner similar to a Grignard reagent.



(ii) Perkin Reaction

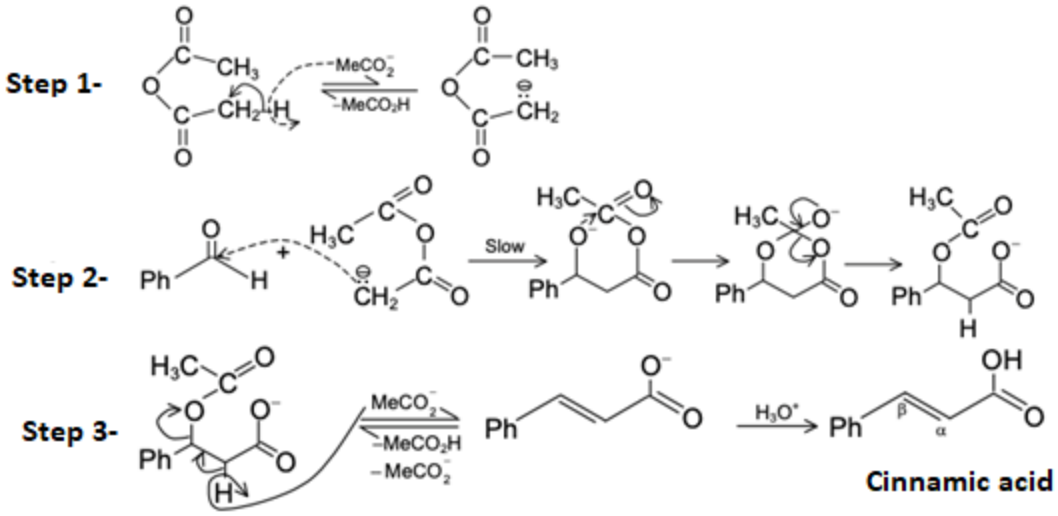
The Perkin reaction is a classic organic reaction named after its discoverer, William Henry Perkin. It involves the condensation of an aromatic aldehyde with an anhydride in the presence of an alkali catalyst, typically potassium hydroxide. The reaction leads to the formation of an α,β-unsaturated aromatic acid, known as a cinnamic acid derivative. This reaction is significant in organic synthesis for the preparation of various substituted cinnamic acids, which find applications in pharmaceuticals, fragrances, and other industries.



Reaction Mechanism

In the Perkin reaction, it is noted that the acetate ion abstracts a proton from the α-carbon of the anhydride, resulting in the generation of a carbanion. This carbanion subsequently attacks the carbonyl group of the aldehyde. The resulting product then removes a proton from the acid,

leading to the formation of an aldol-type compound. Subsequently, in the presence of hot acetic anhydride, dehydration of the aldol compound occurs.



Summary

Carboxylic acids are organic compounds distinguished by the presence of a carboxyl group (-COOH), imparting distinctive properties, synthesis routes, and chemical reactivity. These molecules exhibit weak acidity due to resonance stabilization of their carboxylate ion, with physical states ranging from colorless liquids to solids, often with pungent odors. They can be synthesized through various methods, including oxidation of primary alcohols or aldehydes, hydrolysis of nitriles, oxidative cleavage of alkenes, and the Kolbe-Schmitt reaction. Carboxylic acids partake in a variety of chemical reactions, such as acid-base reactions yielding carboxylate salts, esterification with alcohols to form esters, decarboxylation under strong heat, reaction with Grignard reagents to produce tertiary alcohols, and substitution reactions generating acid derivatives like acid chlorides, anhydrides, and amides. Understanding these properties, synthesis pathways, and reactivity is essential for their applications in organic synthesis, industrial processes, and biological systems.

Keywords

Carboxylic Acid: Organic compounds containing the carboxyl functional group (-COOH).

Acidity: Measure of how easily a compound gives up a proton (H+) from the carboxyl group.

Physical Properties: Characteristics of carboxylic acids such as melting point, boiling point, solubility, and odor.

Carboxylate Ion: Conjugate base of a carboxylic acid, formed by loss of a proton from the carboxyl group.

Condensation Reactions: Chemical reactions in which two molecules combine, usually with the loss of a small molecule such as water.

MCQ

1. Which functional group characterizes carboxylic acids?

(A) Hydroxyl (-OH) group (B) Carbonyl (C=O) group

(C) Carboxyl (-COOH) group (D) Aldehyde (-CHO) group **Answer (C)**

2. What is a common method for synthesizing carboxylic acids from primary alcohols or aldehydes?

(A) Ozonolysis (B) Hydrolysis of nitriles

(C) Reduction (D) Oxidation **Answer (D)**

3. Which of the following reactions does NOT involve the formation of carboxylic acids?

(A) Esterification (B) Decarboxylation

(C) Hydrolysis of esters (D) Reduction of carboxylic acids to alcohols

Answer (D)

4. What is the acidity of carboxylic acids primarily attributed to?

(A) Resonance stabilization of the carboxylate ion

(B) Electronegativity of the oxygen atom in the carboxyl group

(C) Presence of a hydroxyl group

(D) Inductive effect of neighboring functional groups **Answer (A)**

5. Which of the following is NOT a derivative of carboxylic acids?

(A) Acid chloride (B) Acid anhydride

(C) Aldehyde (D) Amide **Answer (C)**

Short Answer Questions

1. Explain the weak acidity of carboxylic acids, mentioning the factors contributing to their acidic nature.
2. Outline two methods for synthesizing carboxylic acids from alcohols, providing the necessary reagents and conditions for each .
3. Explain the Perkin reaction with mechanism.
4. Explain the Reformatsky Reaction with mechanism
5. Describe the a-halogenation of carboxylic acids

Unit - 10

Amines and Diazonium Salt

Objectives;

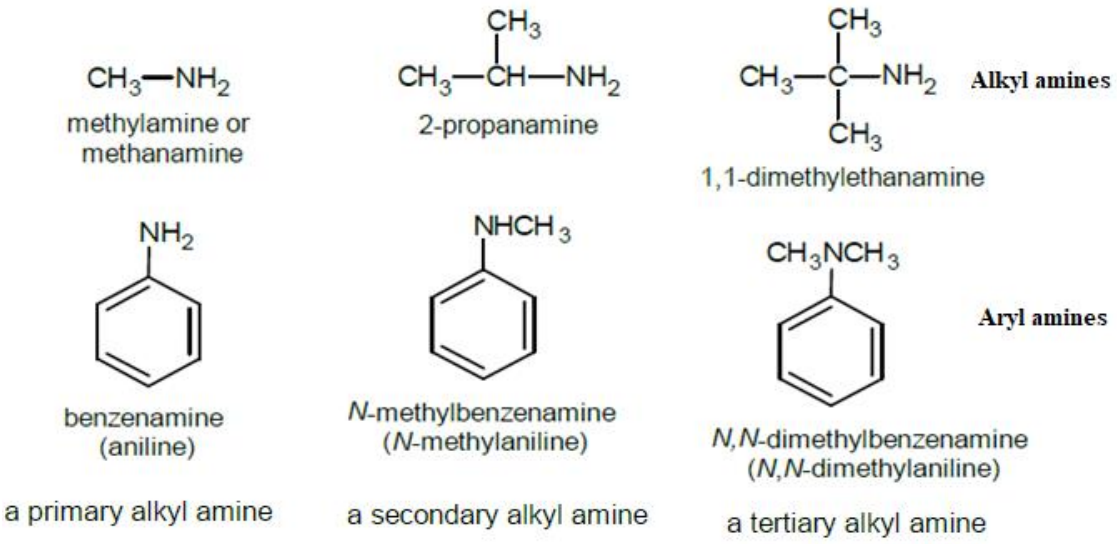
- Grasping the structural features and classification of amines.
- Exploring the physical properties and basicity of amines.
- Understanding the synthesis methods for amines, including reductive amination and Gabriel synthesis.
- Investigating the diverse reactions of amines, such as nucleophilic substitution, Hofmann elimination, and formation of imines and enamines.
- Recognizing the versatility of diazonium salts in organic synthesis, particularly in the preparation of aryl halides, phenols, and azo compounds.
- Learning about the stability and reactivity of diazonium ions.
- Understanding the applications of amines and diazonium salts in pharmaceuticals, dyes, and materials science.

10.1 Introduction

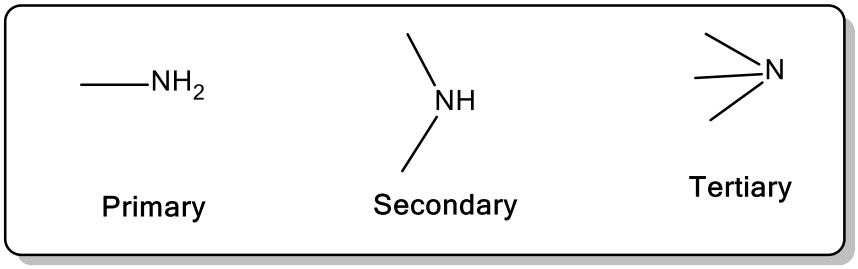
Amines constitute a significant category within nitrogen-containing organic compounds. They are characterized by the presence of one or more alkyl or aryl groups bonded to a nitrogen atom.Amines are important organic bases due to the presence of a pair of non-bonding electrons on the nitrogen atom.

Amines are categorized as primary (1^o), secondary (2^o), or tertiary based (3^o), on the quantity of alkyl or aryl groups connected to the nitrogen atom. When the nitrogen's attachments are alkyl groups, the amine is termed an alkyl amine. However, if at least one of the nitrogen atom's attachments is an aryl group, the amines are referred to as aryl amines or anilines.

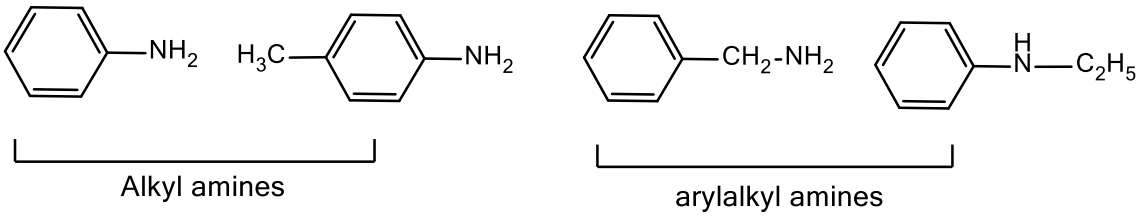
Below are examples of primary, secondary, and tertiary alkyl as well as aryl amines, along with their respective names:



The characteristic functional groups for primary, secondary and tertiary amines are:



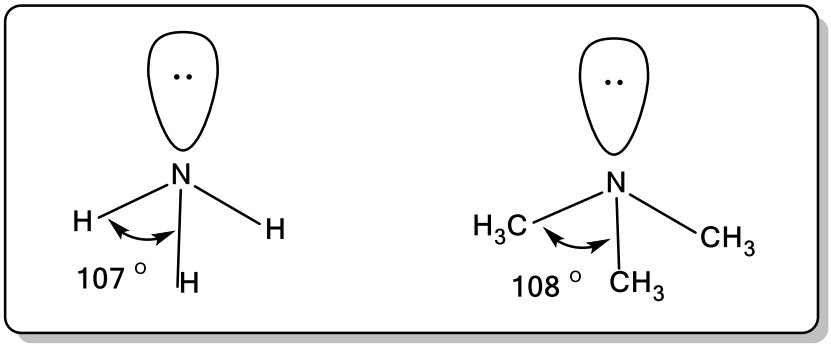
Aromatic amino compounds fall into two categories: aryl amines and arylalkyl amines. Aryl amines feature the -NH_2 group directly linked to the aromatic nucleus, such as aniline and p-toluidine. In contrast, arylalkyl amines have the -NH_2 group attached to a carbon atom within the side chain, as seen in benzylamine and α-phenylethylamine.



10.2 Structure and optical isomerism of Amines

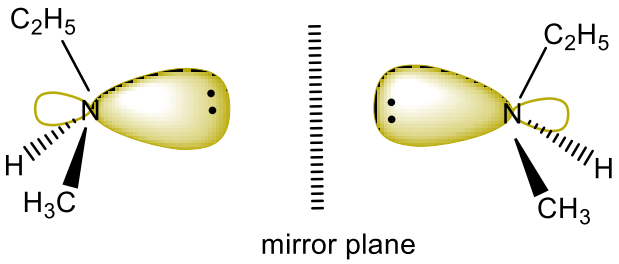
Amines, being derivatives of ammonia, share a structural similarity with their parent molecule. The functional group of amines mirrors the shape of ammonia, where nitrogen forms three bonds

and holds one lone pair of electrons. In both ammonia and aliphatic amines, nitrogen exhibits sp^3 hybridization. Consequently, the shape of ammonia is trigonal pyramidal, illustrated as

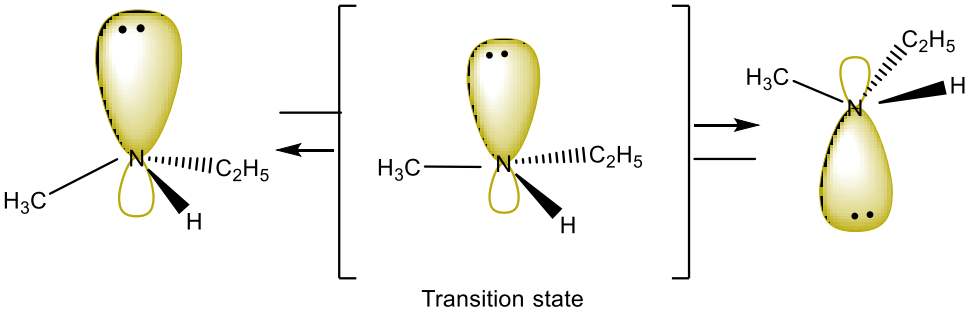


The bond angle between H-N-H in ammonia is 107º, and the bond angle in amines is assumed to be almost the same as in ammonia.

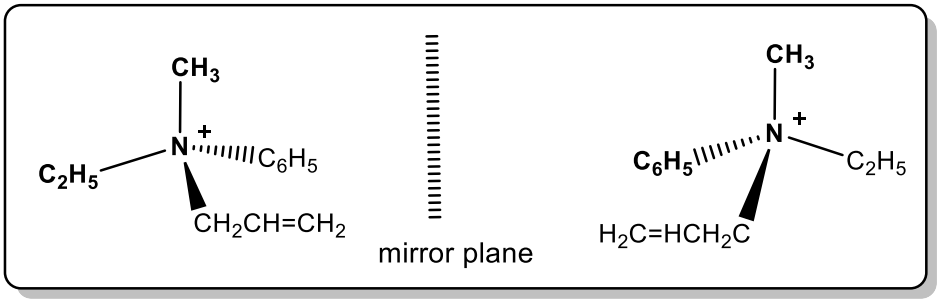
When the three substituents on nitrogen are different, nitrogen becomes chiral, allowing for the existence of enantiomers. The enantiomers of N-methylethanamine are depicted as



However, in the absence of steric hindrance, amines undergo rapid inversion at the nitrogen atom through a planar transition state, resulting in the formation of their enantiomers, as illustrated in below. Consequently, isolating the enantiomers is not possible.



Quaternary ammonium compounds lack the ability to undergo inversion, enabling the separation of their enantiomers. The enantiomers of a quaternary ammonium ion are depicted below:



10.3 Basicity of Amines

Amines are unique among neutral functional groups in that they can act as bases due to the presence of lone pair electrons on the nitrogen atom. In acid/base reactions, these lone pair electrons can attack acidic hydrogen atoms, forming a new N-H bond. This results in the formation of an ammonium salt, where the nitrogen atom now possesses four single bonds and carries a positive charge.

Amines undergo an equilibrium reaction with water, where a proton is transferred from water to the amine, generating an ammonium salt and a hydroxide ion. This process can be represented by the following general equation:

$$RNH_{2(aq)} + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

The equilibrium constant governing this reaction is known as the base ionization constant (Kb), alternatively referred to as the base dissociation constant;

$$Kb = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

pKb = -log Kb

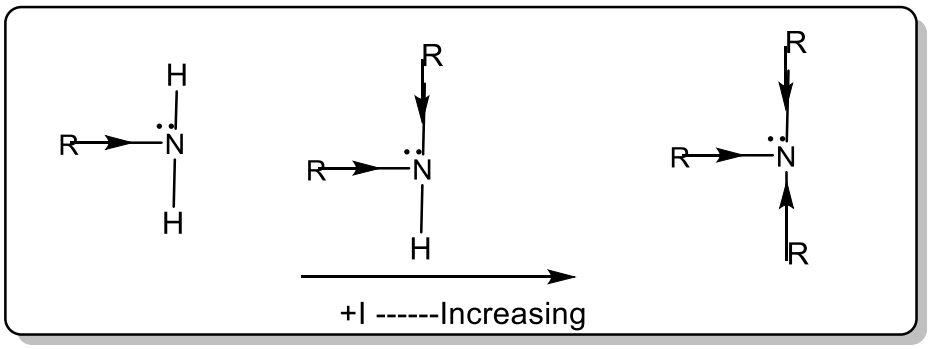
Similar to how the acidity of a carboxylic acid is determined by its **acidity constant *Ka*** the basicity of an amine can be quantified by defining a corresponding **basicity constant *Kb***. A higher value of *Kb* and a lower value of *pKb* indicate more favorable proton-transfer equilibrium and a stronger base.

The Kb and pKb values for some amines are given in the following table

Compound	Kb	pKb
NH_3 (ammonia)	**$1.8x10^{-5}$**	**4.7**
1^o Amines		
CH_2NH_2	**$4.4x10^{-4}$**	**3.35**
$C_2H_5.NH_2$	**$5.6\ x10^{-4}$**	**3.2**
$CH_3(CH_2)_2NH_2$	**$3.9x10^{-4}$**	**3.4**
2^o Amines		
$(CH_3)_2NH$	**$5.1x10^{-4}$**	**3.29**
$(C_2H_5)_2NH$	**$1.3x10^{-3}$**	**2.9**
$(C_3H_7)_2NH$	**$8.2x10^{-4}$**	**3.1**
3^o Amines		
$(CH_3)_3N$	**$5.3x10^{-5}$**	**4.3**
$(C_2H_5)_3N$	**$5.6x10^{-4}$**	**3.2**

Alkylamines exhibit greater basicity compared to ammonia due to the electron-releasing inductive effect of alkyl groups. These groups enhance the electron density around nitrogen, rendering its lone pair more readily available for interaction with acids. Additionally, the electron-releasing nature of alkyl groups stabilizes the resulting alkylammonium ion, promoting the forward shift of the equilibrium and thus reinforcing the stronger basicity of alkylamines over ammonia.

In the series of primary, secondary, and tertiary aliphatic amines, tertiary amines exhibit the highest electron-releasing effect, while primary amines demonstrate the least. Consequently, there's an expected increase in basic strength from primary to tertiary amines.



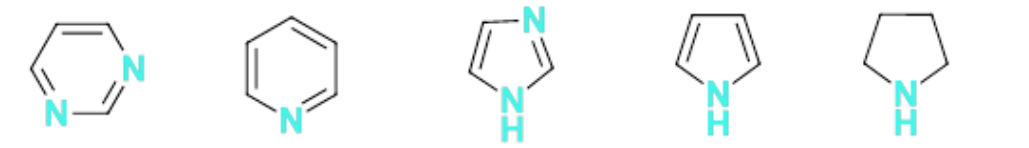
In the gas phase, the observed basicity of ethylamine, diethylamine, and triethylamine aligns with this expected order. However, in aqueous solution, the anticipated trend in basicity is disrupted, as evidenced by their respective Kb values.

$$\underset{2^{o}}{(C_2H_5)_2NH} > \underset{1^{o}}{C_2H_5.NH_2} > \underset{3^{o}}{(C_2H_5)_3.N}$$

Indeed, the basic strength in aqueous solution depends not only on the 'electron-releasing effect' but also on steric and hydration effects.

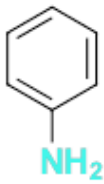
Aromatic heterocyclic amines like pyrimidine, pyridine, imidazole, and pyrrole exhibit significantly weaker basicity due to three key factors. Firstly, the nitrogen in these molecules is sp^2 hybridized, which brings it closer to the nucleus, reducing its propensity to bond with a proton compared to sp^3 hybridized nitrogens. The exceptionally low basicity of pyrrole is attributed to the extensive delocalization of the nitrogen electron pair within the aromatic ring. Imidazole, with a pKa of 6.95, is markedly more basic than pyrrole due to its sp^2 nitrogen, similar to pyridine, which enhances its basicity.

Heterocyclic amines



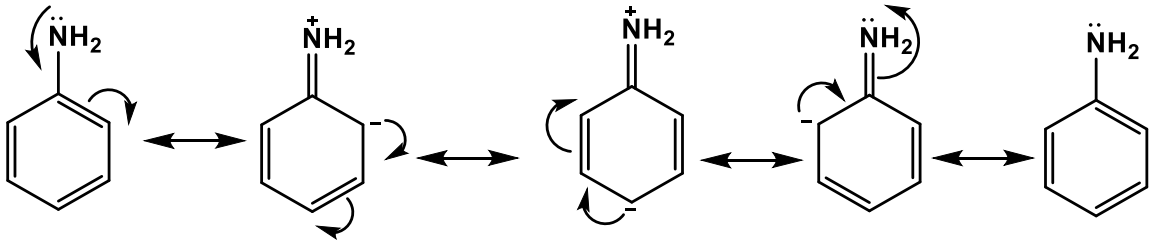
Pyrimidine (1.3) | Pyridine (5.25) | Imidazole (6.95) | Pyrrole (0.4) | Pyrrolidine (11.27)

Aryl Amines



Aniline (4.63)

In aryl amines, the larger H-N-H and H-N-C angles suggest that the nitrogen atom is more nearly planar compared to alkylamines. Additionally, in aryl amines, the lone pair of electrons is delocalized with the π electrons of the aromatic ring and due to this these are less basic than ammonia and alkyl amines. The resulting resonance structures for benzenamine are depicted below:



The resonance structures reveal the presence of double bond character in the C-N bond. Consequently, the C-N bond in benzenamine is shorter (140 pm) compared to that in aliphatic amines (147 pm).

10.4. Nomenclature of Amines

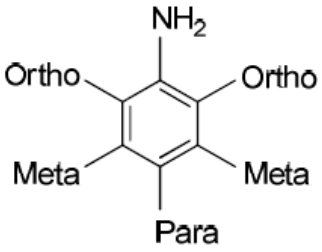
10.4.1 Aliphatic amines

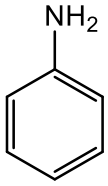
In IUPAC nomenclature, amines are typically named according to the alkyl group attached to the nitrogen atom. Primary amines are named as aminoalkanes, secondary amines as '**N-alkylaminoalkanes**', and tertiary amines as '**dialkylaminoalkanes**'.

Amines	Common name	IUPAC name
1 ° Amine		
CH_3NH_2	Methyl amine	Methanamine
$CH_3CH_2NH_2$	Ethyl amine	Ethanamine
2°Amines		
CH_3CHCH_3 with NH_2	Iso-Propyl amine	Propane-2-amine
CH_3NHCH_3	Dimethyl amine	N-Methylmethanamine
$CH_3CH_2NHCH_3$	Ethyl methyl amine	N-Methylethanamine
3° Amines		
$H_3C-N(CH_3)-CH_3$	Tri-methyl amine	N,N-Dimethylmethanamine
$H_3C-H_2C-H_2C-N(C_2H_5)-CH_3$	Ethylmethylpropylamine	N-ethyl-N-methylpropanamine

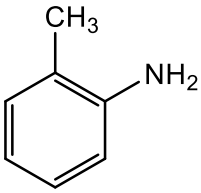
10.4.2 Aromatic Amines

The simplest aromatic amine is aminobenzene, also known as aniline. Amines containing a $-NH_2$ group typically identify the position of the amino group as position-1 of the ring. Subsequent positions are then numbered clockwise (2, 3, 4, 5, 6, etc.). Substituted positions are named as ortho (o) for the next position to the amino group, meta (m) for the third position, and para (p) for the vertically opposite position to the amino group.

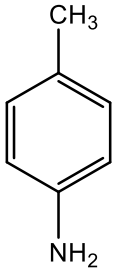




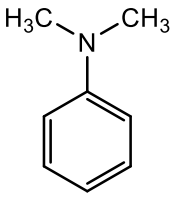
Aniline
(Benzeneamine)



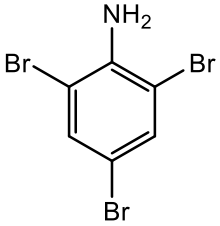
o-Toluidine
(2-Methylbenzeneamine)



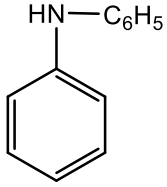
p-Toluidine
(4-methylbenzeneamine)



N,N-Dimethyl aniline
(N,N-Dimethylbenzeneamine)



2,4,6-Tribromo aniline
(2,4,6-Tribromobenzeneamine)

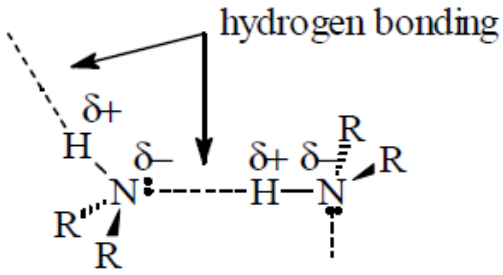


Di-phenylamine
(N-Phrnylbenzeneamine)

10.5. Physical Properties of Amines

At room temperature, lower amines exist as combustible gases. Amines within the C3-C11 range typically manifest as volatile liquids, while higher amines are solid substances. Lower amines are characterized by a distinct fishy ammoniacal odor

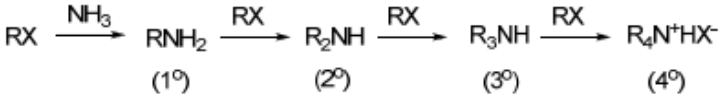
Primary & secondary amines exhibit inter-molecular hydrogen bonding. However, the N-H...H hydrogen bonds are weaker than O-H bonds due to nitrogen's lower electronegativity compared to oxygen. Consequently, the boiling points of primary amines fall between those of alcohols and alkanes with similar molecular weights. The ‘Hydrogen bonding’ factor is crucial in determining the water solubility of amines



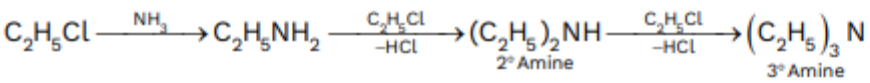
10.6 Preparation of Amines

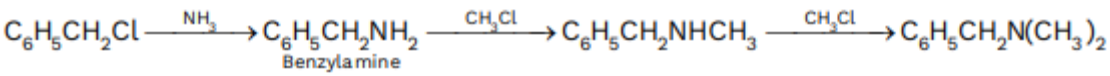
10.6.1 Direct Alkylation with alkyl halides

When alkyl halides are heated with an aqueous or alcoholic solution of ammonia in a diverse mixture of amines is produced, including primary, secondary, and tertiary amines, along with quaternary ammonium salts. The formation of these compounds occurs through a series of nucleophilic substitution reactions.Initially, the halogen atom in the alkyl halide is replaced by ammonia, resulting in the formation of a primary amine. This primary amine then acts as a nucleophile, attacking another molecule of alkyl halide to form a secondary amine. Subsequently, the secondary amine undergoes a similar reaction, acting as a nucleophile to produce a tertiary amine. Finally, the tertiary amine reacts with another molecule of alkyl halide, resulting in the formation of quaternary ammonium salts. This sequential process leads to the generation of a mixture of amines and due to this the present method has limited scope



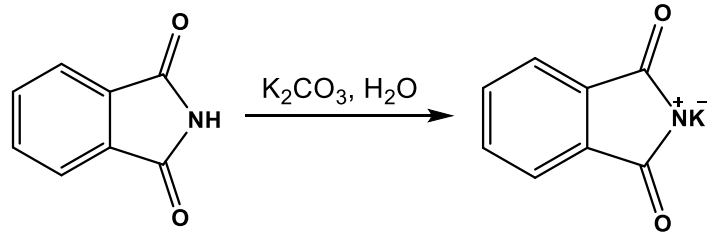
For example





10.6.2 Indirect alkylation: The Gabriel Synthesis

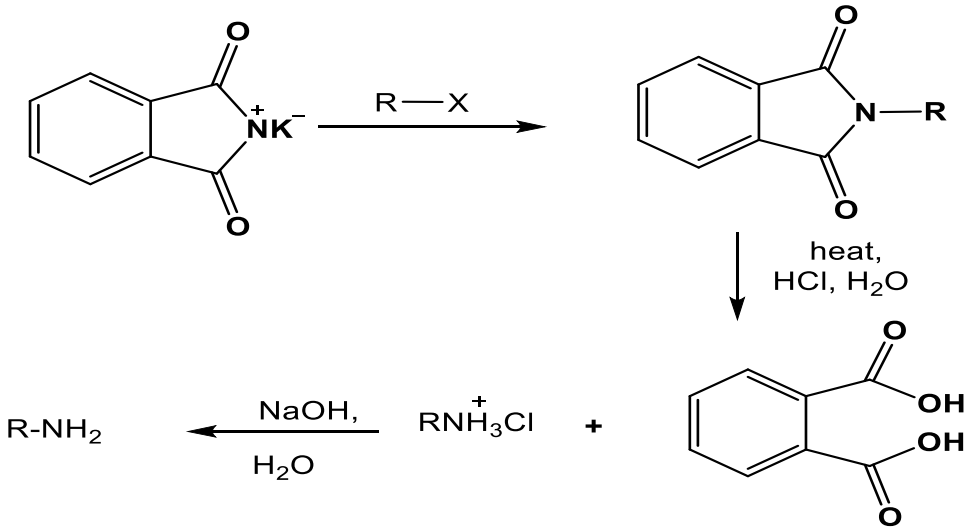
Pure primary amines can be efficiently synthesized by first protecting the nitrogen atom to allow for selective alkylation. This protection is achieved by utilizing 1,2-benzenedicarboxylic imide, where the nitrogen atom is surrounded by two adjacent carbonyl groups. The NH group in this compound is sufficiently acidic (with a pKa of 8.3) to be deprotonated using a mild base, resulting in the formation of a nitrogen anion in the form of a salt.



1,2-benzendicarboxylic imide

potassium salt with nitrogen anion

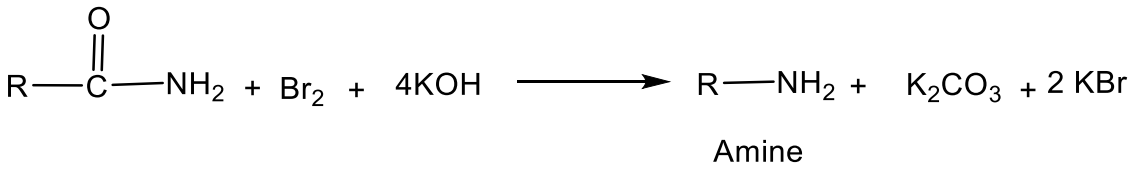
The nitrogen anion serves as a proficient nucleophile and participates in diverse nucleophilic substitution reactions. When reacted with alkyl halides, it produces N-alkyl derivatives with high yields. Subsequent acidic hydrolysis of the N-alkyl derivative yields an ammonium salt, from which the free amine can be obtained by treatment with a base. This series of reactions constitutes the Gabriel synthesis, which is utilized to prepare amines that are challenging to obtain through direct alkylation of ammonia.



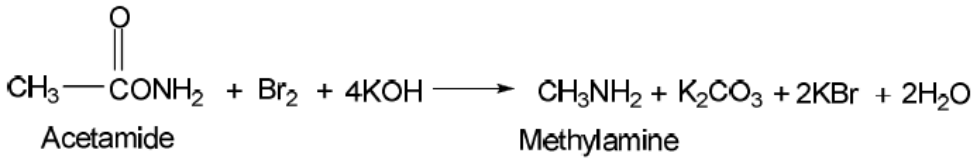
The applicability of ‘Gabriel synthesis’ is restricted to primary and un-branched secondary alkyl halides. Tertiary alkyl halides, under these conditions, tend to undergo eliminations instead of the desired substitution reactions.

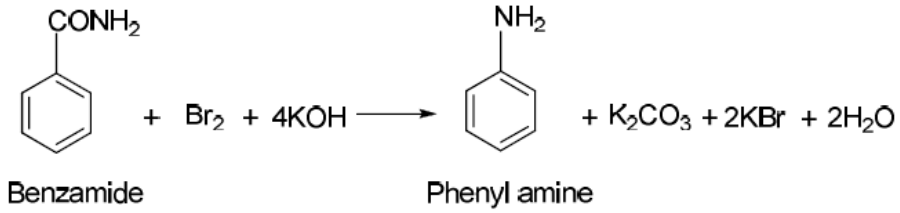
10.6.3 Hofmann's Bromamide Synthesis

The Hofmann bromination reaction is a method in organic chemistry for converting a primary amide into a primary amine. It employs bromine in either an aqueous or ethanolic solution of sodium hydroxide to accomplish this transformation.



Examples





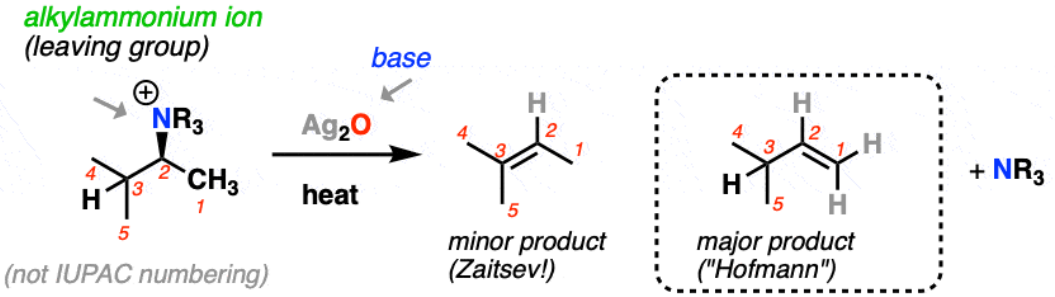
10.6.4 Hofmann Elimination (Non Zaitsev)

As we know the alkylation of amines leads to the formation of quaternary ammonium salts through successive alkylation steps. These quaternary salts are capable of undergoing bimolecular β-elimination reactions in the presence of a strong base. In this process, an alkene is generated as the trialkylamine departs as a neutral leaving group. This reaction can be depicted as follows;

Summary: The Hofmann Elimination

When the leaving group in an E2 elimination is a charged alkylammonium ion, the elimination product tends to be the **less**-substituted (*non-Zaitsev*) alkene rather than the more substituted ***(Zaitsev)*** alkene.

This type of elimination is sometimes called the "Hofmann" elimination and the less-substituted alkene is called the "Hofmann" product



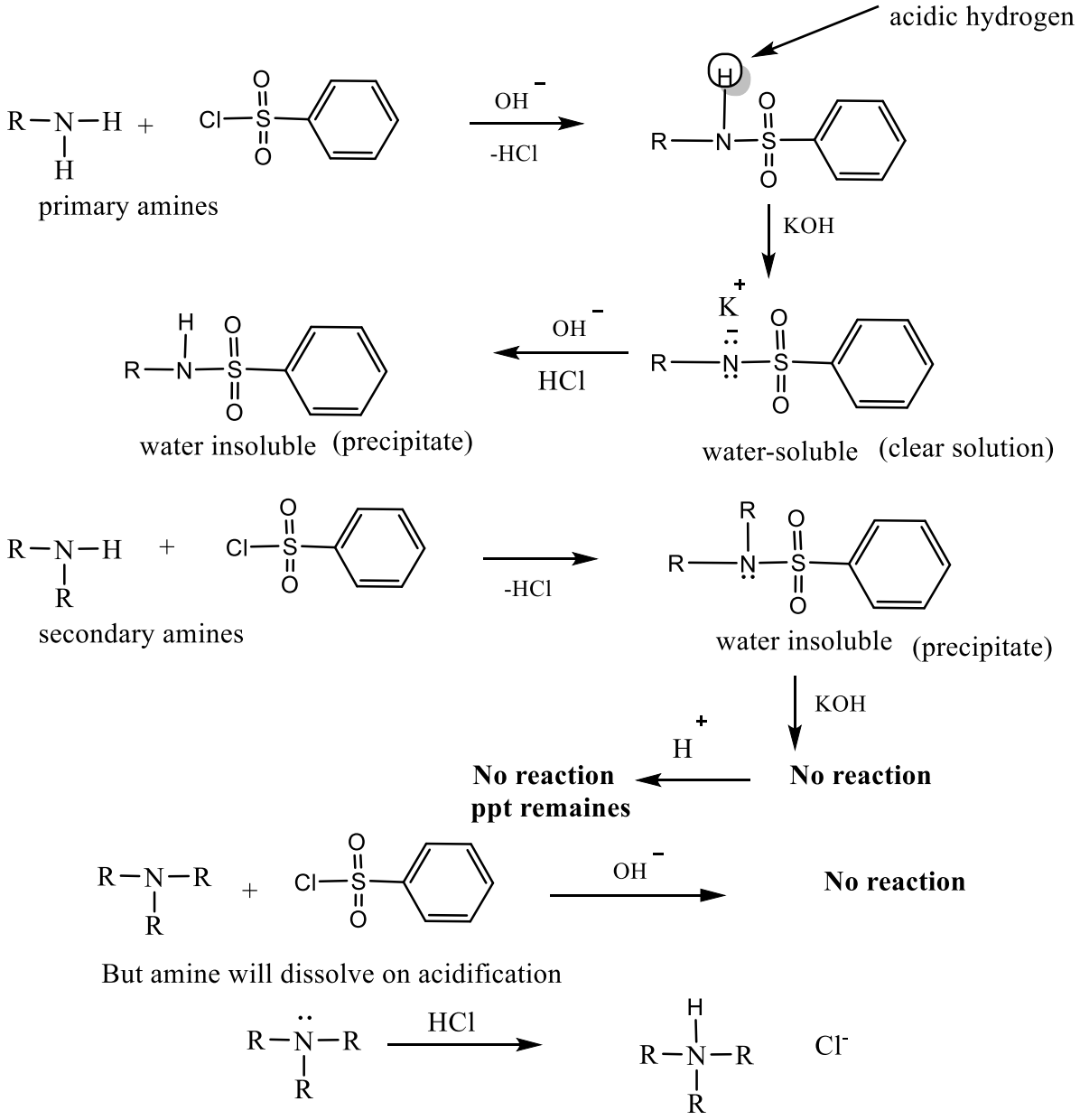
• The less-substituted alkene is favored is due to unfavorable steric interactions (*gauche interactions)* between the bulky NR_3 leaving group and neighboring alkyl groups in the E2 transition state leading to the Zaitsev product.

Wet silver oxide serves as a basis of hydroxide ions (OH^-). These hydroxide ions then remove a proton from the carbon positioned β to the nitrogen atom.This elimination reaction is known as Hofmann elimination. It's important to note that the less substituted alkene is the predominant product. Thus, this reaction exhibits regioselectivity towards the formation of the less substituted alkene.This can be understood in light of the Hofmann rule. The nitrogen atom within the (trialkylammonium) group, carrying three alkyl groups, acts as a bulky hindrance. Consequently, it obstructs the approach of the base (OH^- ion) from this direction. As a result, the base abstracts the proton from the less hindered position on the β-carbon of the molecule.

Unlike most elimination reactions, which typically follow the **Zaitsev (Saytzeff)** rule to yield the most substituted alkene, the Hofmann elimination tends to yield the less substituted alkene. The Hofmann elimination has proven valuable in elucidating the structures of numerous natural products containing amino nitrogen. Initially, the amine is subjected to exhaustive methylation using excess iodomethane, resulting in the formation of a quaternary ammonium salt. Subsequent Hofmann elimination of this salt, as described earlier, leads to the formation of an alkene. Analysis of the alkene structure obtained allows for the determination of the position of the amino group in the starting compound.

10.6.5 Hinsberg test

The Hinsberg test provides an effective means to differentiate between primary, secondary, and tertiary amines. It entails the reaction between an amine and benzene sulfonyl chloride in the presence of aqueous (KOH) potassium hydroxide.

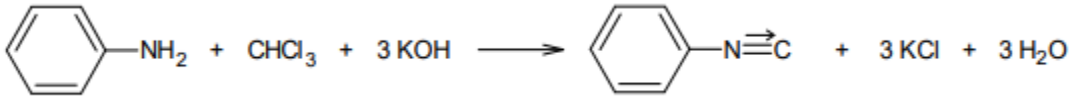


Primary and secondary amines undergo the formation of substituted sulphonamides, whereas tertiary amines do not participate in this reaction. Further differentiation can be achieved by observing the solubility of the sulphonamide derivatives. Those derived from primary amines are

soluble in potassium hydroxide, while those derived from secondary amines, lacking acidic hydrogen, are insoluble and precipitate out.

10.6.6 Carbylamine Test

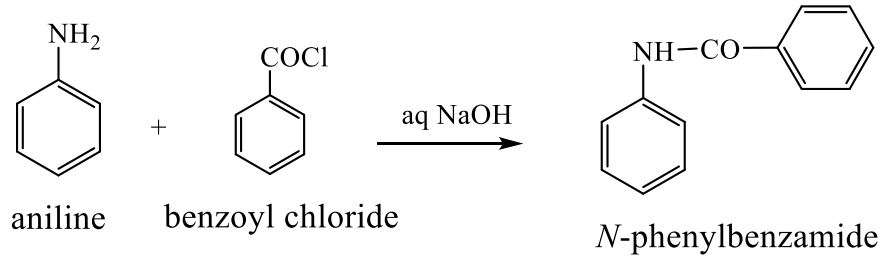
Both aliphatic and aromatic primary amines undergo a reaction with chloroform in the presence of potassium hydroxide to yield an isocyanide compound characterized by a highly unpleasant odor. This reaction is remarkably sensitive, making it suitable for detecting minute quantities of primary amines as impurities in secondary and tertiary amine samples.

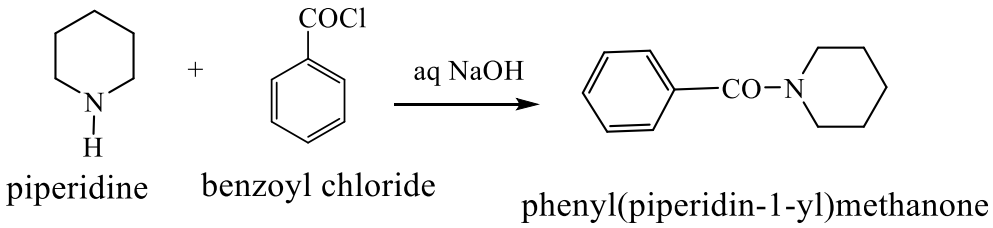


Note: Before disposing of the products down the laboratory sink, ensure to eliminate the isocyanide by heating the reaction mixture with an acid.

10.6.7 Schotten–Baumann Reaction

The Schotten-Baumann reaction is named after German chemists Carl Schotten and Eugen Baumann, who reported it in 1884 and extended it in 1886, respectively.

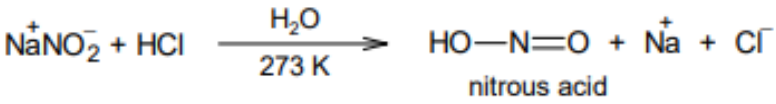




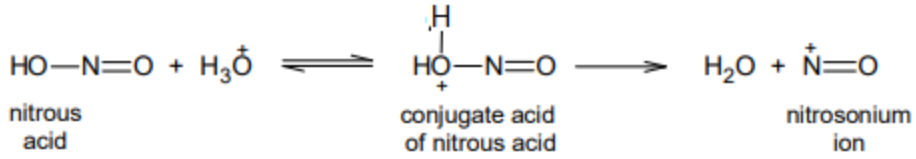
This reaction involves the benzoylation of an amine or a phenol in the presence of aqueous sodium hydroxide. For example, benzoylation of aniline with benzoyl chloride yields the corresponding amide, known as anilide**.**Tertiary amines do not gives this reaction

10.6.8 Reaction with Nitrous Acid

Nitrous acid, HNO_2, is a weak and unstable acid. Typically, it is generated in situ by reacting sodium nitrite with a strong mineral acid, commonly hydrochloric (HCl) acid, at temperatures ranging from 273 to 278 Kelvin.



Under highly acidic conditions, nitrous acid undergoes protonation, leading to the formation of the **nitrosonium ion** after subsequent water loss**.**

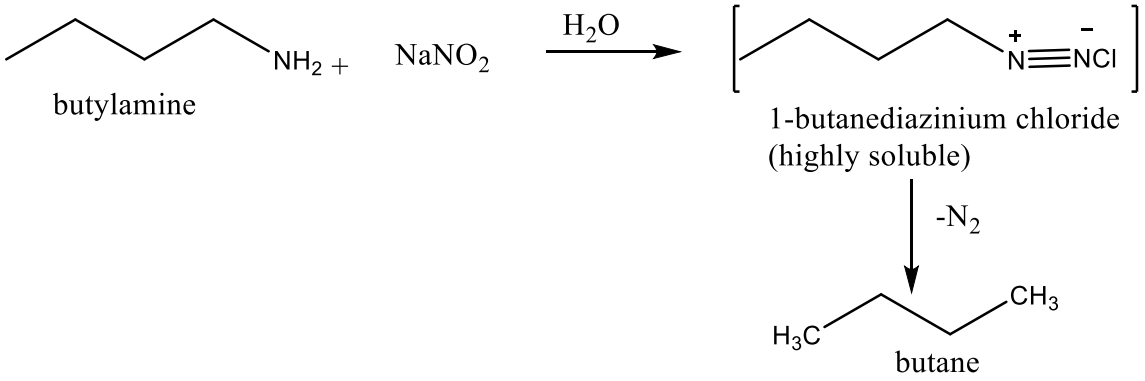


The nitrosonium ion, being electrophilic, engages in fascinating reactions with amines known as nitrosation reactions. The resulting products of nitrosation vary based on whether the amine is primary, secondary, or tertiary, and whether it is aliphatic or aromatic. Let's investigate into a detailed examination of each of these situations.

(i) Nitrosation of Primary Amines

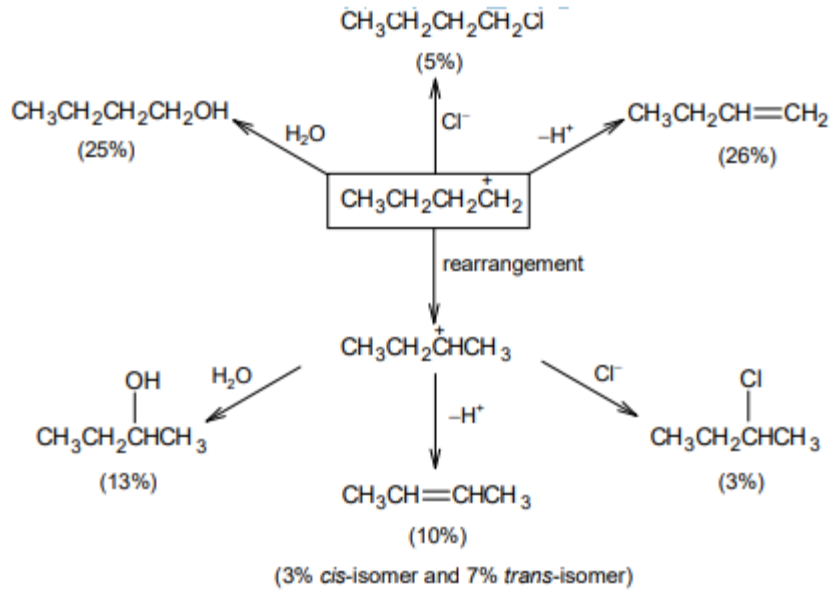
Primary amines undergo a reaction with nitrous acid to produce diazonium salts through a series of intermediate species, a process known as diazotization. When primary aliphatic amines are diazotized, they yield alkyl diazonium salts. However, alkyl diazonium salts are unstable and readily decompose, even at low temperatures, forming nitrogen and various other products through the intermediate carbocations.

Example

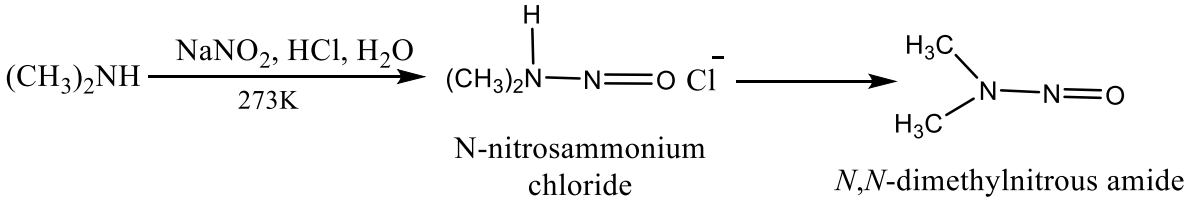


The release of nitrogen gas during diazotization provides a valuable qualitative test for aliphatic primary amines.

The carbocation generated from this process results in a complex mixture of products, as illustrated below**:**

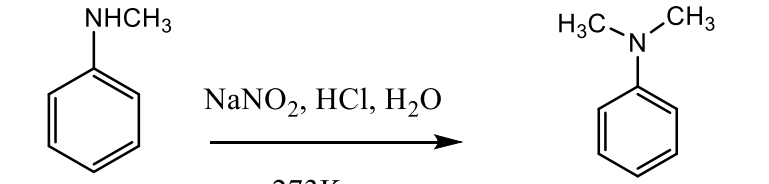


ii) Nitrosation of Secondary Amines; Both aliphatic and aromatic secondary amines undergo a reaction with nitrous acid to produce N-nitroso compounds, commonly referred to as nitrosamines. These nitrosamines typically precipitate from the reaction mixture as yellow oily liquids. Below are some examples illustrating the formation of nitrosamines



N-nitrosammonium chloride

N,*N*-dimethylnitrous amide

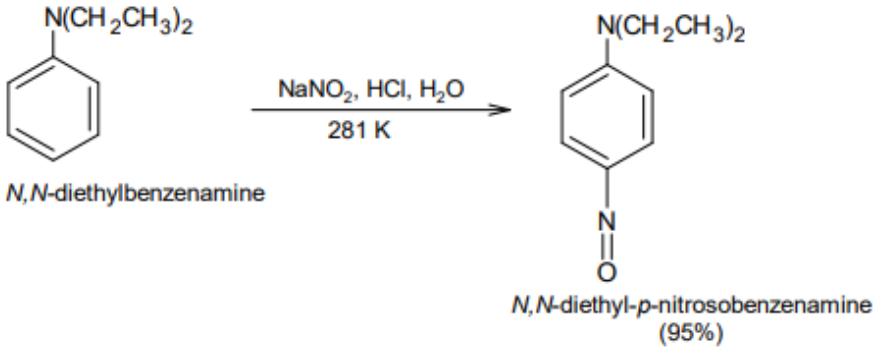


N-methylaniline

N,*N*-dimethylaniline

iii) Nitrosation of tertiary amines

Tertiary aliphatic amines undergo a reaction with nitrous acid without the release of nitrogen, resulting in the formation of complex mixtures. On the other hand, tertiary aromatic amines react with nitrous acid to produce C-nitroso aromatic compounds. Nitrosation occurs predominantly at the para position of the aromatic ring**.**



N,*N*-diethylbenzenamine

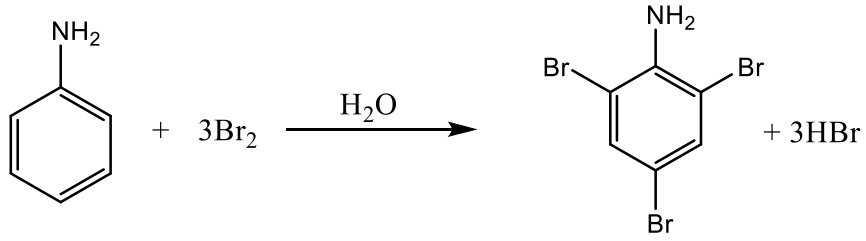
N,*N*-diethyl-*p*-nitrosobenzenamine (95%)

10.6.9 Electrophilic Substitution Reactions of Aromatic Compounds

The amino group serves to activate the aromatic ring, making it more susceptible to substitution by electrophilic reagents. Aromatic amines such as aniline undergo various electrophilic substitution reactions. Notably, the amino group exhibits ortho- and para-directing effects. In the following discussion, we will explore the intriguing electrophilic reactions of aniline.

(i) Bromination

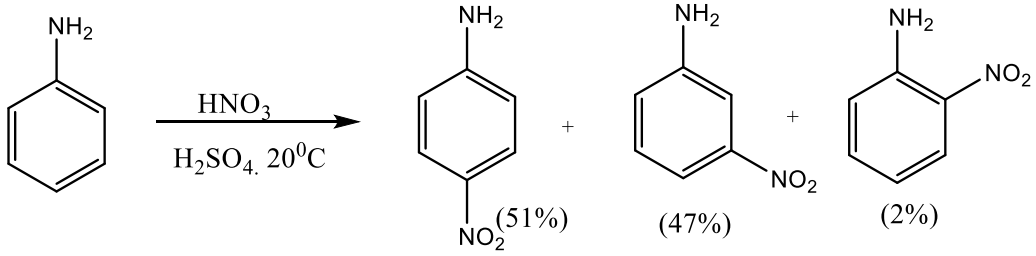
Due to their high reactivity, aromatic amines readily undergo halogenation reactions such as bromination under mild conditions, resulting in the formation of tribromoaniline, as depicted below:

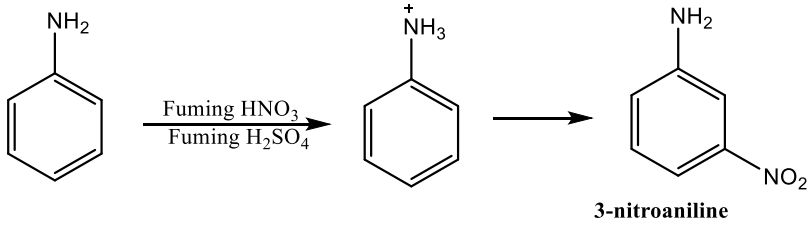


However, if only ortho- and para-substituted products are desired, the reactivity of the -NH2 group can be diminished by converting it into an acetamido group. Following this protection step, the desired electrophilic substitution reaction is conducted, followed by deprotection to yield the desired monosubstituted product.

(ii) Nitration

The nitration of aniline with nitric acid and sulfuric acid results in the conversion of the amino group to an HN_3^+ group. This positively charged group directs the electrophile NO_2^+ to the meta position, leading to the formation of a significant amount of meta-substituted product, in addition to the para-substituted product, as depicted below:





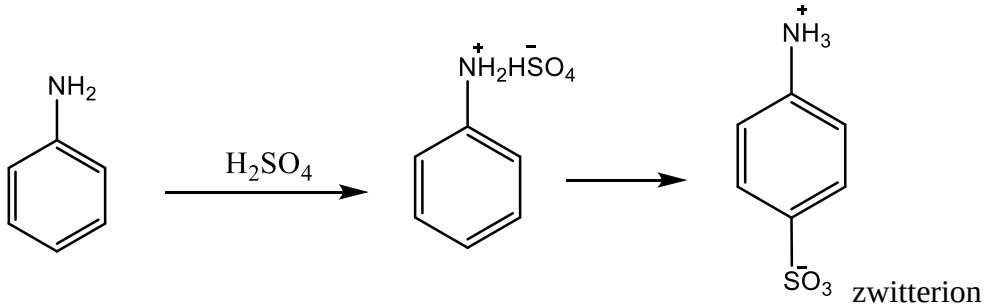
3-nitroaniline

To exclusively obtain either ortho-substituted or para-substituted product, the approach of initially protecting the $-NH_2$ group as $-NHCOCH_3$ group is employed once again. The

deprotection of the -$NHCOCH_3$ group is then performed to regenerate the -NH_2 group following electrophilic substitution.

(iii) Sulphonation

The sulphonation of aniline is accomplished by heating anilinium hydrogen sulfate, which is formed through the reaction of aniline with sulfuric acid. The primary product obtained from this reaction is sulphanilic acid, depicted below:



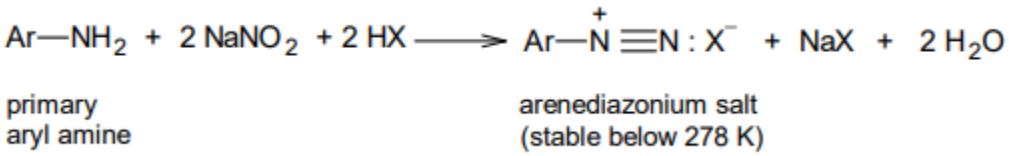
zwitterion

The sulphanilic acid obtained exists as a zwitterio

10.7 Diazonium salts

When primary amines react with nitrous acid, they produce 'Diazonium salts'. While diazonium salts derived from primary aliphatic amines are generally unstable, those originating from primary aromatic amines exhibit stability. Diazonium salts constitute a significant class of compounds with wide-ranging utility in organic synthesis. They serve as crucial intermediates, facilitating the production of diverse organic compounds. So here we discuss about the synthesis of diazonium salts prepared by reactions of aromatic primary amines.

Diazotization of primary aromatic amines results in the formation of '**Arenediazonium salts'**. Compared to alkyl diazonium salts, arenediazonium salts exhibit greater stability and can be stored at temperatures ranging from 273 K to 278 K. Arenediazonium ions participate in a wide range of reactions and serve as versatile intermediates in synthesis processes**.**

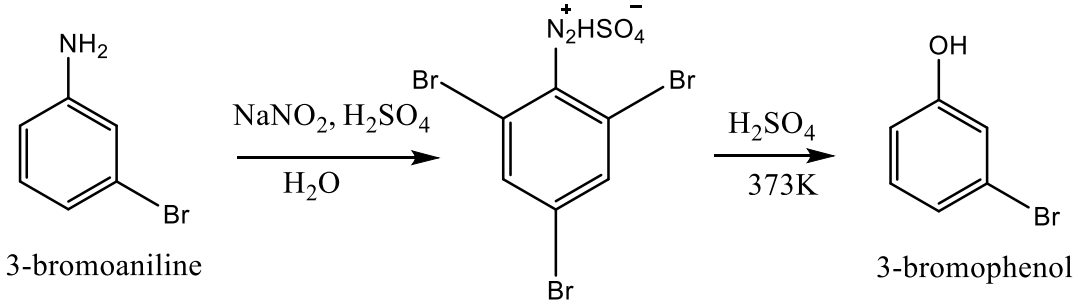


10.8. Reactions of Diazonium Salt

Arenediazonium ions are highly reactive and engage in a multitude of reactions, making them versatile intermediates for synthesizing a broad range of aromatic compounds. Here, we discussed the some important reaction by which the Arenediazonium salt can be covert to other valuable aromatic compounds

(i) Conversion to Phenol

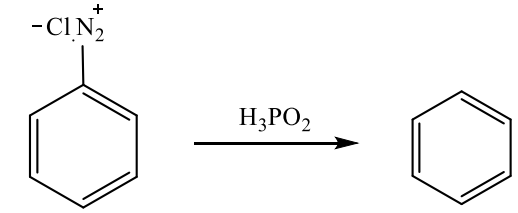
The predominant approach to synthesizing phenols typically involves heating the diazonium salt in an acidic aqueous solution.



3-bromoaniline 3-bromophenol

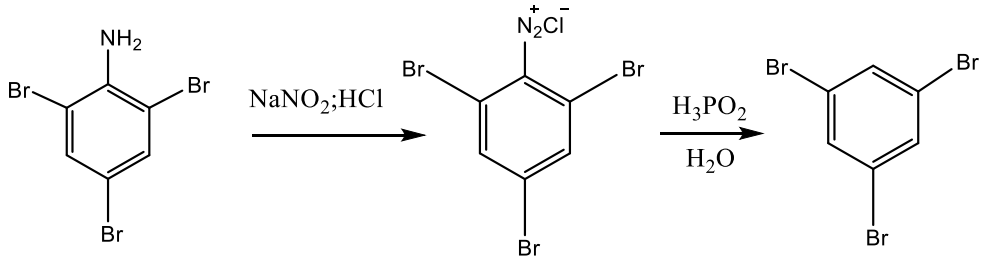
(ii) Conversion to Phenol

Treating a diazonium salt with hypophosphorous acid (H_3PO_2) replaces the diazonium group with a hydrogen atom. Such reactions are termed reductive deaminations.



Diazonium salts

This reaction finds utility in incorporating an amino group onto an aromatic ring to control the orientation of subsequent reactions. Later, the amino group can be removed by converting it into a diazonium salt, followed by treatment with H_3PO_2.



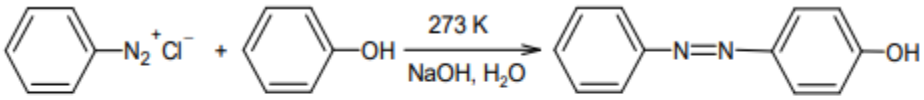
2,4,6-tribromoaniline

1,3,5-tribromobenzene

(iii) Conversion to azo dyes

The coupling reaction of a diazonium salt involves the reaction of the diazonium ion with an aromatic or heteroaromatic compound, typically in the presence of a copper catalyst. This results in the formation of an azo compound, where the diazonium group ($-N_2+$) is coupled with the aromatic ring of the other compound. Coupling reactions are widely used in organic synthesis for the preparation of azo dyes, pharmaceuticals, and other functionalized aromatic compounds.

Arenediazonium salts act as weak electrophiles and react with highly activated aromatic compounds, such as amines and phenols, to produce azo compounds.



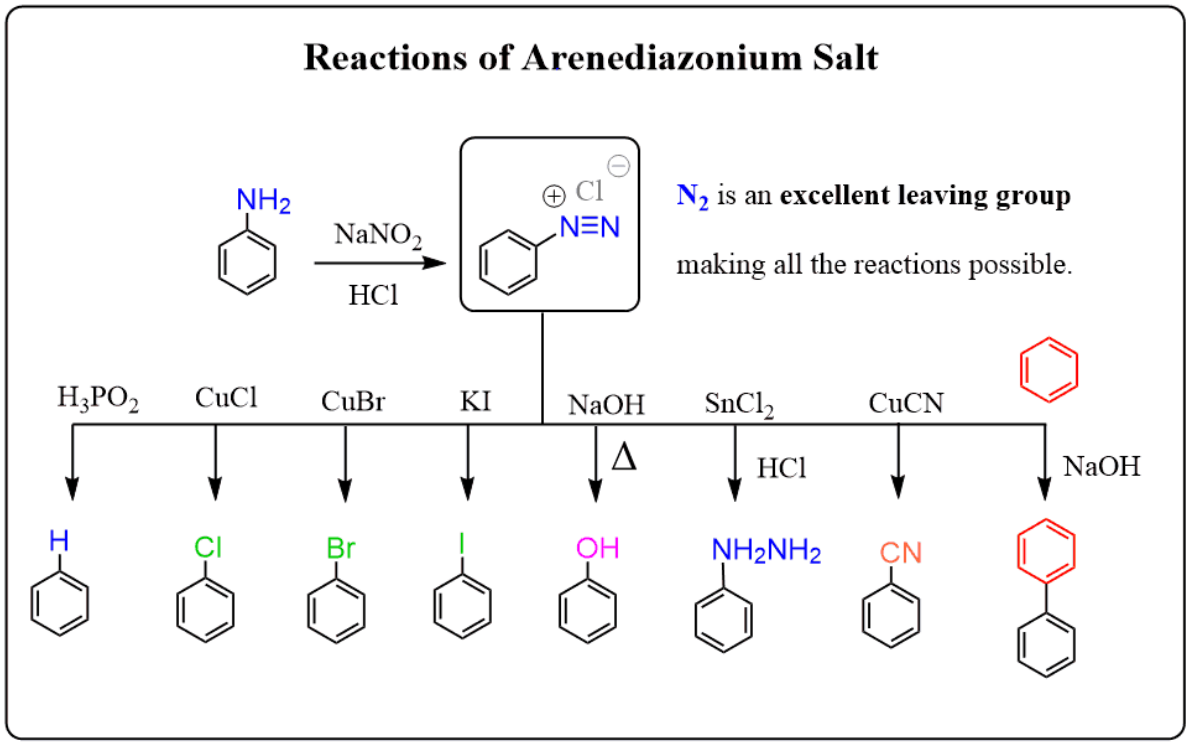
benezenediazonium chloride

benzenol (phenol)

4-hydroxyazobenzene (orange)

Coupling primarily occurs at the para position if it's available. If not, coupling occurs at the ortho position instead.

Some common reaction of **Arenediazonium salts**are summarize below



Summary

Amines, derived from ammonia through substitution of hydrogen atoms with alkyl or aryl groups, possess unique properties shaped by the lone pair of electrons on the nitrogen atom. These properties, including odor, solubility, and boiling points, vary based on the structure and classification of amines as primary, secondary, or tertiary. Their inherent basicity, allowing for proton acceptance and formation of ammonium ions, underscores their pivotal role in various chemical reactions. Synthetically, amines are synthesized through diverse methods such as nucleophilic substitution, reductive amination, Gabriel synthesis, and Hoffmann degradation. Furthermore, amines partake in a wide array of reactions, serving as nucleophiles in substitution reactions with electrophiles like alkyl halides or acyl chlorides, leading to the formation of substituted amines or amides. Transitioning to diazonium salts, these compounds serve as indispensable intermediates in organic chemistry, facilitating the synthesis of aryl halides, phenols, and azo compounds. Formed through the diazotization reaction, where primary aromatic amines are converted to diazonium salts under acidic conditions using nitrous acid, diazonium salts exhibit remarkable reactivity.

Keyword

Basicity: The ability of an amine to accept a proton, making it a base in chemical reactions.

Gabriel synthesis: A method for the preparation of primary amines from alkyl halides via the reaction with phthalimide followed by hydrolysis.

Diazotization: The conversion of primary aromatic amines to diazonium salts using nitrous acid under acidic conditions.

Hofmann elimination: A reaction in which a quaternary ammonium salt undergoes dehydrohalogenation to produce an alkene and an amine.

Coupling reaction: A reaction where a diazonium salt reacts with an aromatic compound to form an azo compound, often used in dye synthesis.

MCQ

1. Which of the following is NOT a primary amine?

A) CH_3NH_2

B) $(CH_3)_2NH$

C) $CH_3CH_2NH_2$

D) $(CH_3)_3N$ Answer: D) $(CH_3)_3N$

2. What is the general structure of a diazonium salt?

A) R-NH_2

B) R-N_2+X−

C) R-OH

D) R-NHR Answer: B) R-N_2+X−

3. Which of the following methods is commonly used to prepare amines?

A) Esterification

B) Friedel-Crafts acylation

C) Nitration

D) Gabriel synthesis Answer: D) Gabriel synthesis

4. Which of the following is a diazonium salt used in the synthesis of phenols?

A) Benzyl diazonium chloride

B) Ethyl diazonium bromide

C) Methyl diazonium sulfate

D) None of the above Answer: A) Benzyl diazonium chloride

5. Which of the following is NOT a property of amines?

A) Basicity

B) Odor

C) Acidity

D) Solubility in water Answer: C) Acidity

Short Answer Questions

1. Describe the basicity of amines and how it relates to their chemical reactivity.
2. Briefly explain how amines can be synthesized via the Gabriel synthesis.
3. What is diazotization, and what is its significance in organic chemistry?
4. Explain the mechanism of the Hofmann elimination reaction involving amines.
5. What are azo dyes, and how are they synthesized using diazonium salts

Unit -11

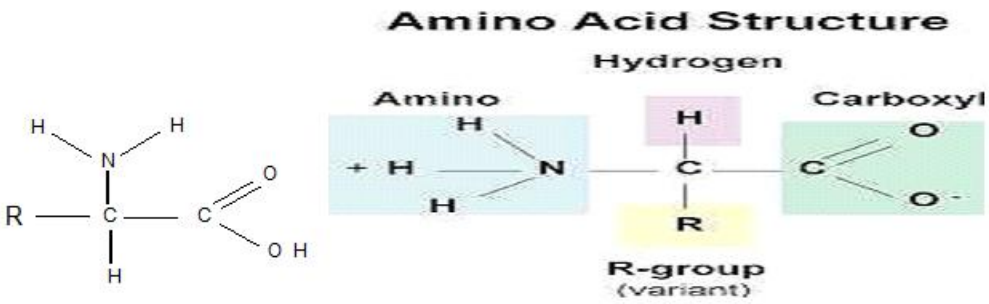
Amino Acids

Objective:

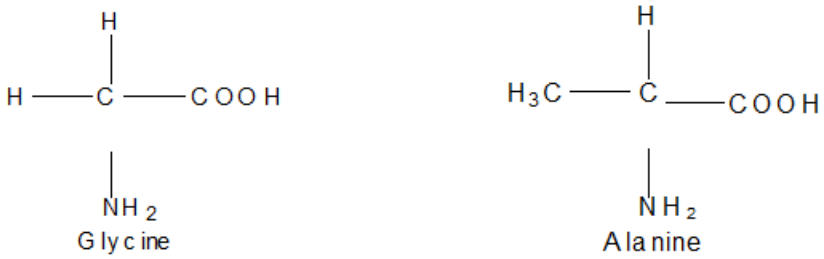
- Define vocabulary related to proteins and amino acids.
- Amino Acid Categorization
- Describe how essential and nonessential amino acids differ from one another. How an amino acid behaves around bases and acids.
- Describe the preparation methods of Amino acids
- Explain different chemical reaction of Amino acids.

11.1 Introduction: Proteins are large molecules composed of smaller building blocks called "amino acids." Organic compounds called amino acids have two groups: an amino group and a carboxylic acid group. An amine group, or the portion that contains nitrogen, is located at one end of the basic chemical backbone of all amino acids. The acid portion is at the other end. Every amino acid has the same structure. The unique structure of the chemical side chain affixed to the backbone determines how they differ from one another. Each amino acid has a unique identity and chemical makeup due to the makeup of its side chain. Proteins are made up of roughly 20 different naturally occurring amino acids, which come together to make all living tissue. Because they include nitrogen, the amino acids that make up proteins are different from fats and carbohydrates.

Because the amino group is joined to the α-carbon, the amino acids found in proteins are known as alpha (α)-amino acids. Aalpha-carbon is a carbon that is attached to any carbon in a carboxylic acid. The following formula is commonly used to represent amino acids:



Different amino acids have different values for "R." The amino group is represented by NH2, and the acid group by COOH. Glycine, where "R" stands for a hydrogen atom, is the most basic amino acid. The methyl group, or "R," in alanine is CH3.



With the exception of proline, every amino acid has –H, –NH2, and –COOH attached to the -carbon. The side chains, likewise attached to the alpha-carbon and referred to as R-groups, serve as a distinguishing factor between them. The human body requires amino acids for a variety of purposes, and they are found in large quantities in nature.

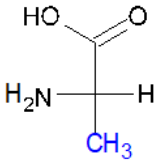
11.2 Classification of Amino acids:

All amino acids have three groups: a carboxyl group, an amino group, and an H. The only thing that separates them is their side-chain R groups. Polarity stands as the most significant property of R groupings. Therefore, the four groupings of amino acids are as follows: polar basic, polar acidic, polar neutral, and nonpolar. Each amino acid has a three-letter code that allows it to be shortened to a common name.

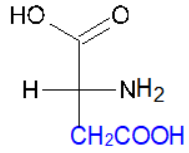
The following table lists the 20 amino acids that are frequently needed by the body to produce proteins. Since the body is unable to produce essential amino acids, eating is the only way to get them. Because the body generates non-essential amino acids, it is not necessary to get them from food.

S. No.	Essential Amino Acids	Non Essential Amino Acids
1	Histidine	Alanine
2	Isoleucine	Arginine
3	Leucine	Asparagine
4	Lysine	Aspartic Acid
5	Methionine	Cysteine
6	Phenylalanine	GlutamicAcid
7	Threonine	Glutamine
8	Tryptophan	Glycine
9	Valine	Proline
10		Serine
11		Tyrosine

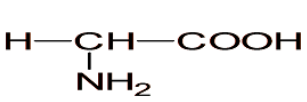
For the body to synthesize proteins, all of the essential amino acids must be present in sufficient quantities. Protein synthesis is impossible without the presence of one necessary amino acid.



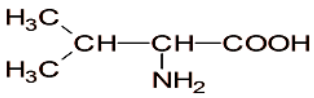
Alanine



Aspartic Acid



Glycine



Valine

11.3 Structure and Stereochemistry of Amino Acids:

An amino acid consists of an alkyl group, carboxylic acid, an amine group and a central carbon atom joined to hydrogen. With the exception of glycine, where the R represents an additional H atom, all amino acids are therefore chiral.

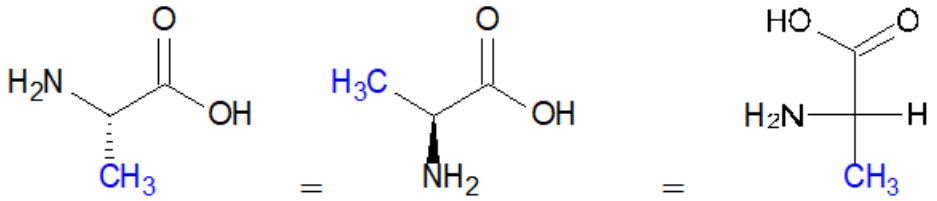
11.3.1 Optical activity:

The asymmetric α-C atom in all amino acids, excluding glycine, makes them optically active. Amino acids come in D and L forms; the L-α amino acid form is what is found naturally in proteins. Some bacteria and antibiotics include D-amino acids.

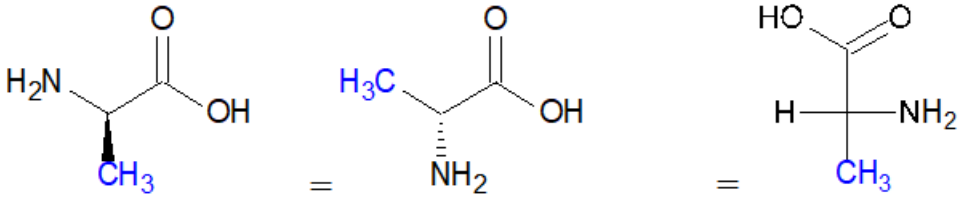
A α-carbon is attached to four distinct groups, making all α-amino acids chiral with the exception of glycine. Remember that chiral carbons must have four distinct groups attached, hence glycine is exempt because it has two hydrogen atoms connected to the α-carbon.

Amino acids can exist as D or L isomers because they are chiral compounds. The R group is always written at the bottom of Fischer projections for amino acids, while the -COOH group is always placed at the top. We have the L-isomer if the NH_2 is on the left, and the D-isomer if it is on the right. Only L isomers are present in proteins in biological systems.

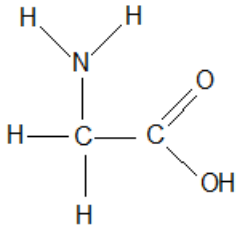
An example: L-Alanine, and D-Alanine



(S)-Ala **(L)-Ala (naturally occurring)**

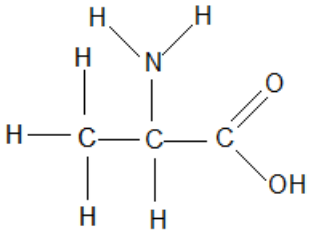


(R)-Ala **(D)-Ala**



glycine

aminoethanoic acid



alanine

2-aminopropanoic acid

11.4 Acidic and Basic Behaviour:

Amino acids have two groups: an acidic group (-COOH) and a basic group (NH2). It is the tendency of the amine group (NH2) to receive H+ and the carboxylic acid (COOH) to donate H+. A dipolar ion (two poles) known as a zwitterion is the end result of this "internal" acid-base process. Carboxylate (COO-) is the result of the carboxylic acid donating H+. Thus, carboxylic acid, the name denotes the presence of H+, or carboxylate, the absence of H+.

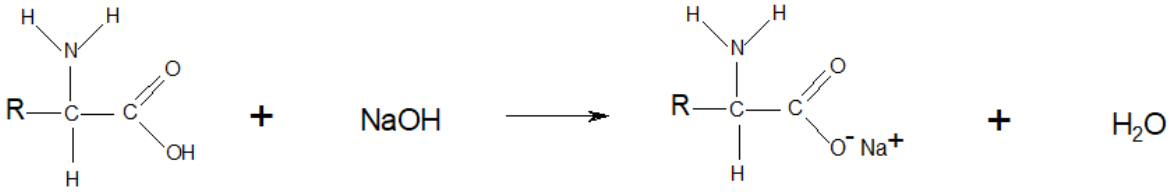
Glutamic acid (H+ on carboxylic acid) and glutamate (H+ missing) are two examples.

11.4.1 Zwitter ion: Each amino acid has two groups: an amino group and a carboxyl group. Depending on the pH of the solution in which the amino acid is dissolved, each group can exist in an acidic or basic form.

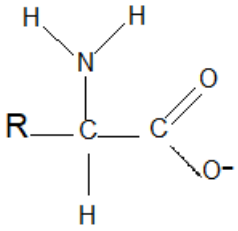
Zwitterions have two electrical charges and one neutral charge at the same time. They have opposing positive and negative charges, which cancel out to leave a zero net charge. Compounds with one negatively charged atom and one positively charged atom on a nonadjacent atom are known as zwitterion substances. Despite the word "ion" in the name, zwitterions are the neutral version of the amino acid.

Zwitterions lose H+ in basic solutions and gain H+ in acidic ones. Carboxylic acids react with bases and exhibit acidic characteristics. Amines react with acids and have basic characteristics. Thus, amino acids have both basic and acidic characteristics.

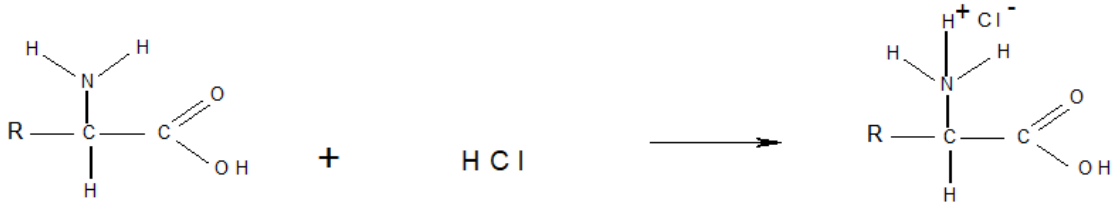
a. Reaction with Base: Strong bases, like sodium hydroxide, react with amino acids as follows:



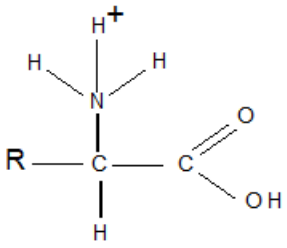
Hence, amino acids are found in anionic form at high pH values:



b. Reaction with acids: Amino acids interect with Strong acids like HCl as:



Thus, amino acids are found in cationic form at low pH:



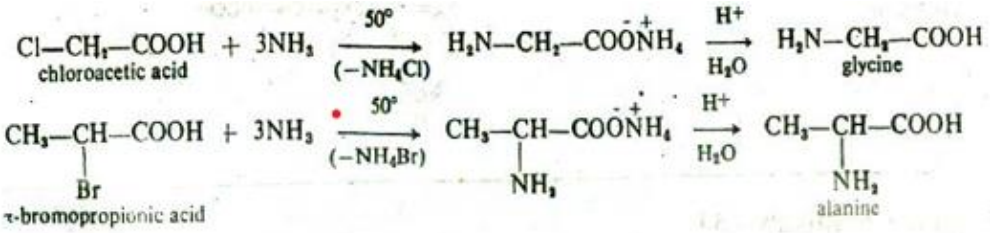
c. Reaction with itself: Amino acids can have an acid-base reaction with themselves because they include both a proton-donating and a proton-accepting group on the same molecule:

This reaction produces a double ion known as a Zwitterion. This reaction takes place in a solid state. Amino acids are consequently ionic when they are solid. This explains why they have a high melting point and are solids.

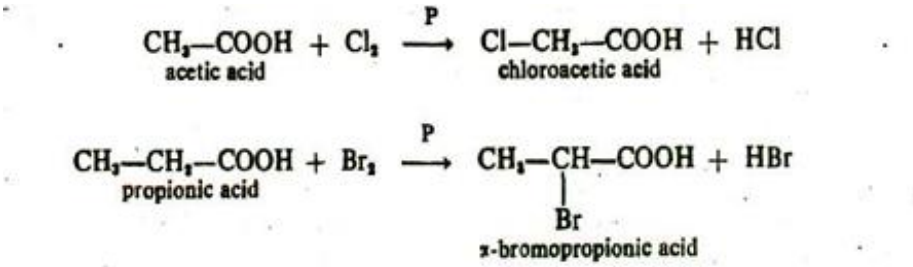
11.5 Synthesis of amino acids:

11.5.1 By Hydrolysis of Proteins: To produce a mixture of alpha-amino acids, proteins can be hydrolyzed by refluxing them with diluted hydrochloric acid. The resulting mixture can be separated via the following methods: (a) fractional crystallization; (b) Fischer's method of fractional distillation of their esters followed by hydrolysis; (c) selective precipitation as salts with phosphotungstic and picric acids; (d) Dakin's method of distribution of amino acids between n-butanol saturated with water; (e) gas chromatography, column chromatography, and (1) electrophoresis. The most commonly utilized methods are electrophoresis and paper chromatography.

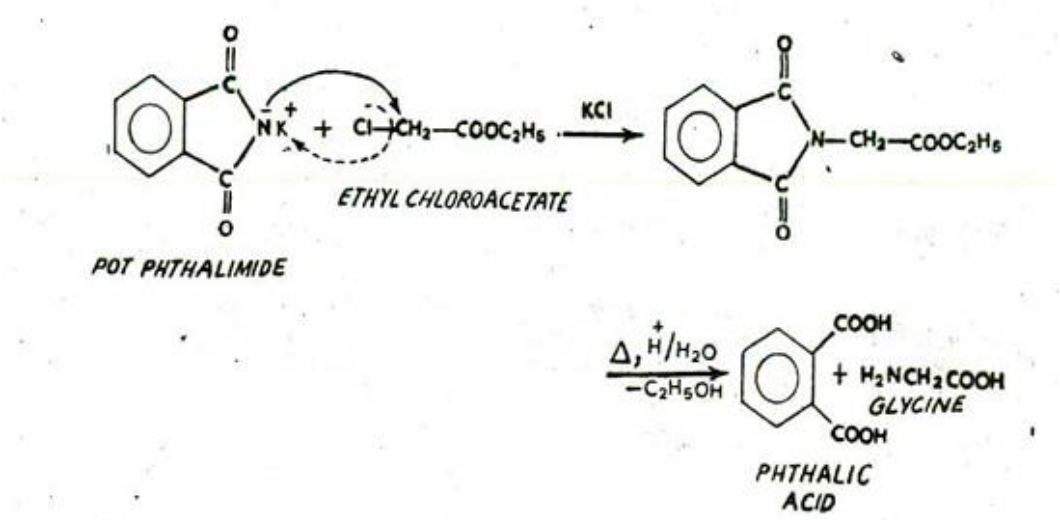
11.5.2 By Aminatlon of α-Halo Acids: An amino acid's ammonium salt is created when α-bromo or α-chloro carboxylic acids combine with an excess of liquid ammonia. Through the hydrolysis of the ammonium salt, the free amino acid is obtained.



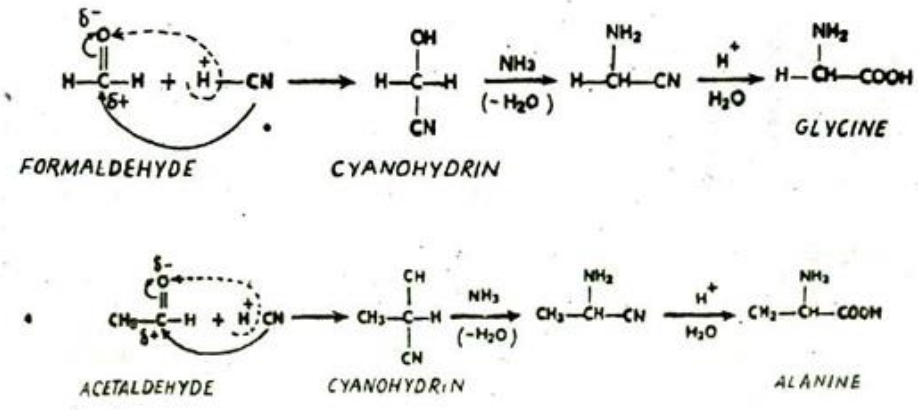
The Hell-Voihard-Zeliosky halogenation of the equivalent unsubstituted carboxylic acids can be used to prepare the required α-halo acids.



11.5.3 Gabriel synthesis: An amino acid and phthalic acid are produced when hydrolyzing an ester of a-halo acid treated with potassium phthalimide to create the equivalent substituted phthalimide.

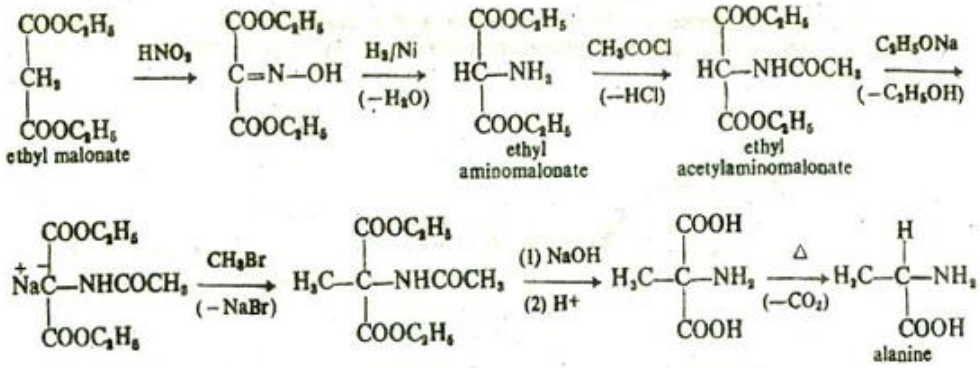


11.5.4 Strecker Synthesis: After treating an aldehyde with HCN, the matching cyanohydrin is created, which is then allowed to react with ammonia to produce an α-amino nitrite. Nitrite hydrolysis produces α-amino acid.

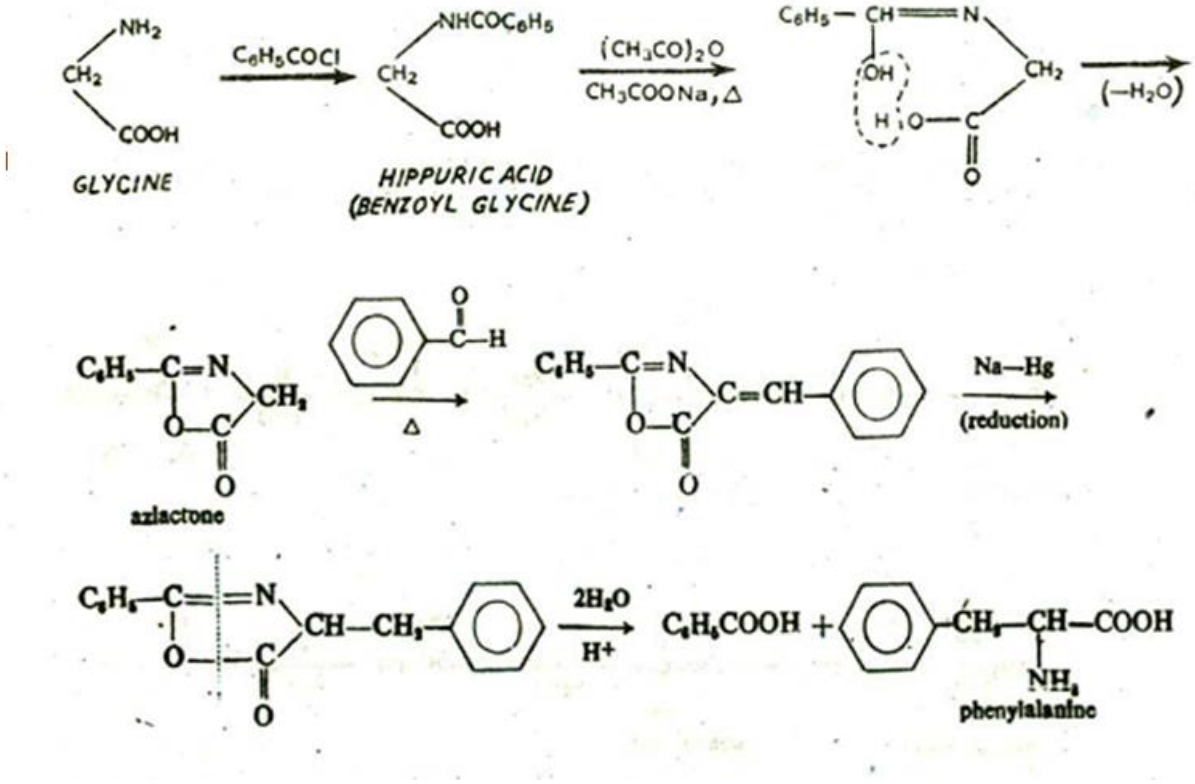


11.5.5 From methyl malonate. The conversion of ethyl malonate to ethyl acetylaminomalonate occurs in three stages. After being treated with sodium ethoxide in absolute alcohol, this produces a sodium salt that is then used to react with an alkyl halide to produce an ester that has been substituted with an alkyl halide.

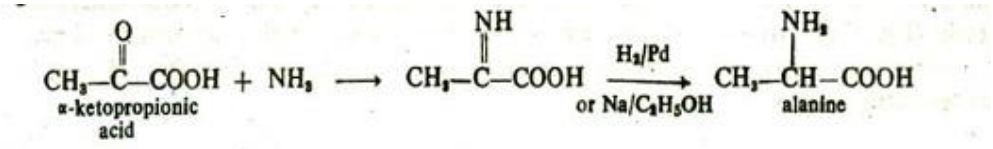
An amino acid is produced by saponification and decarboylation of this ester.



11.5.6 By Erlenmeyer Azlactonesynthesis: Process Azlactoneis produced when acetic anhydride and hippuric acid (benzoyl glycine) are combined in the presence of sodium acetate. An amino acid is produced by condensation with aldehydes, reduction, and subsequent hydrolysis.



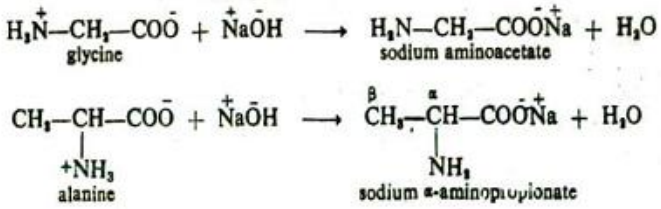
11.5.7 By using the Koop Synthesis: amino acids are produced by treating keto acids with ammonia to create the corresponding imine, which is then reduced catalytically to produce an amino acid.



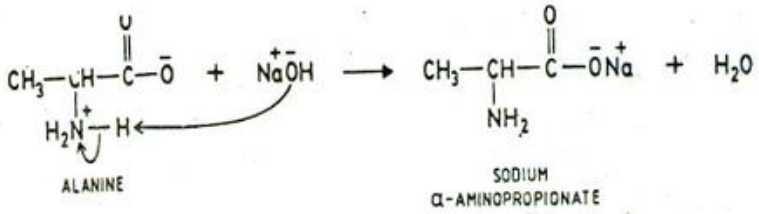
11.6 Reaction of Amino Acids:

11.6.1 Reaction of carboxyl group:

a. Reaction with base: With base amino acids form corresponding salts.

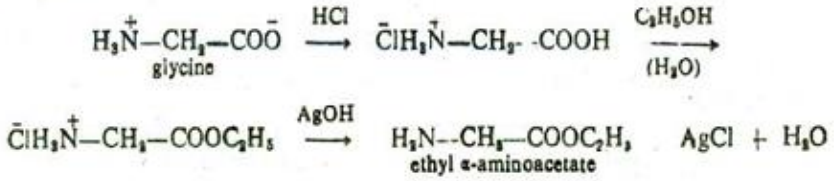


MECHANISM :

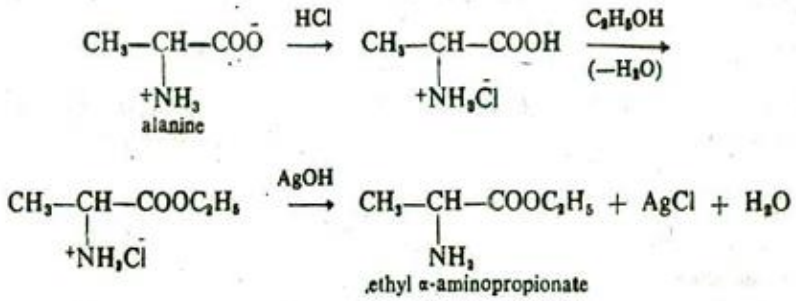


b. Esterification: By heating amino acids in the presence of anhydrous HCI, esterification can be achieved. After the ester's hydrochloride is generated, the ester may be treated with silver hydroxide to produce the free ester.

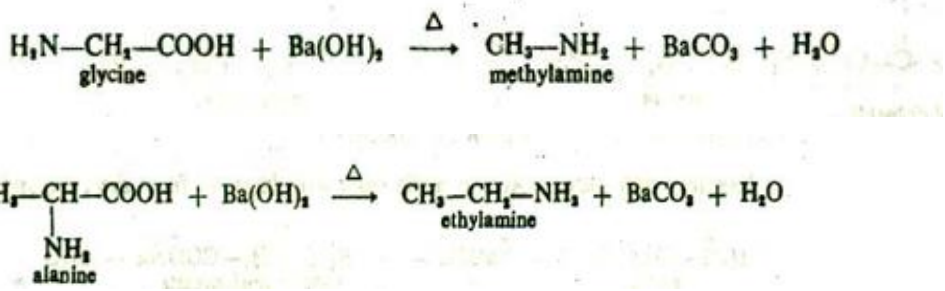
Esterification of Glycine :



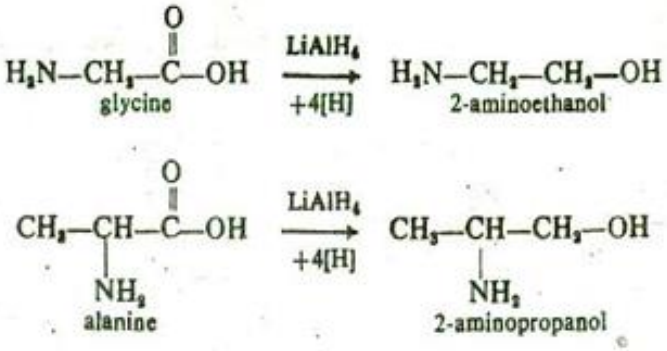
Esterification of Alanine :



c. Decarboxylation: When heated with a barium hydroxide solution, amino acids release carbon dioxide and produce primary amines.

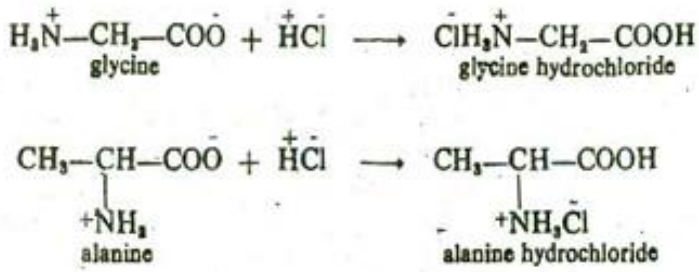


d. Reduction: Lithium aluminium hydride reduces amino acids to produce amino alcohols.

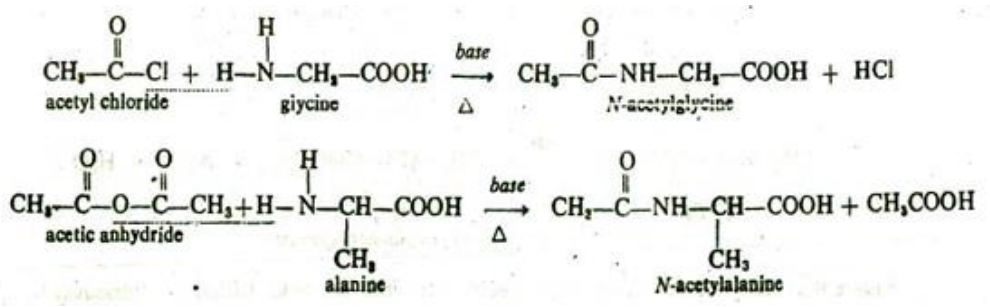


11.6.2 Reaction of Amino group:

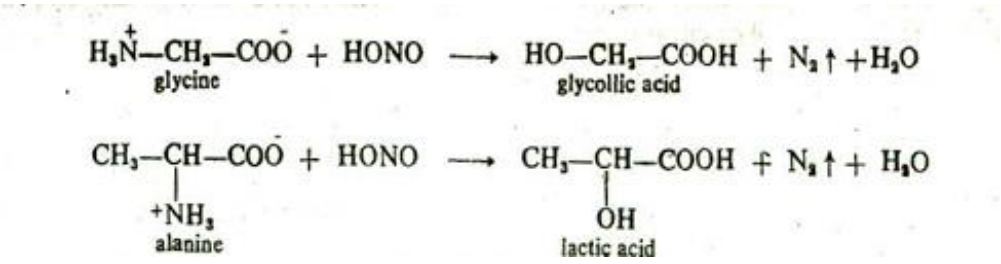
a. Reaction with strong Acids: With strong acids amino acids are converted into corresponding salts.



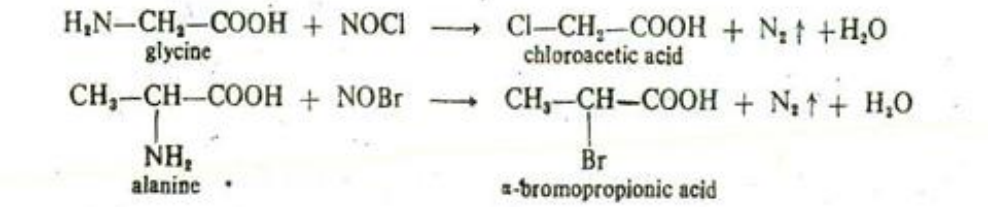
b. Acylation: N-acyl amino acids are produced when the amino group of an amino acid is acylated using either acid halides or acid anhydrides.



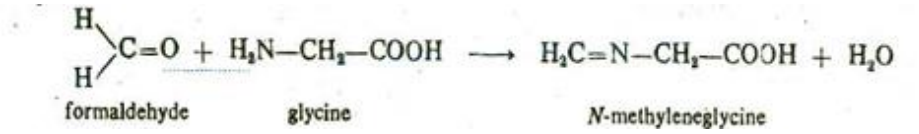
c. Reaction with Nitrous acid: Analogously to primary aliphatic amines, amino acids and nitrous acid (NaNO,+HCI) react to produce nitrogen and hydroxy acids.



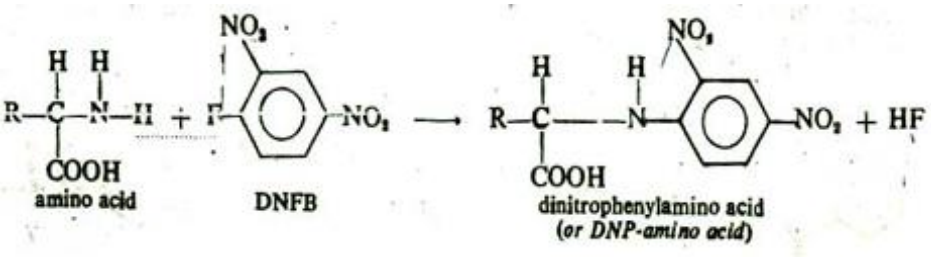
d. Reaction with Nitrosyl Halides: Nitrogen and halo acids are created when amino acids combine with nitrosyl chloride (or bromide).



e. Reaction with Formaldehyde: N-methylene amino acids are created when formaldehyde and amino acids react.

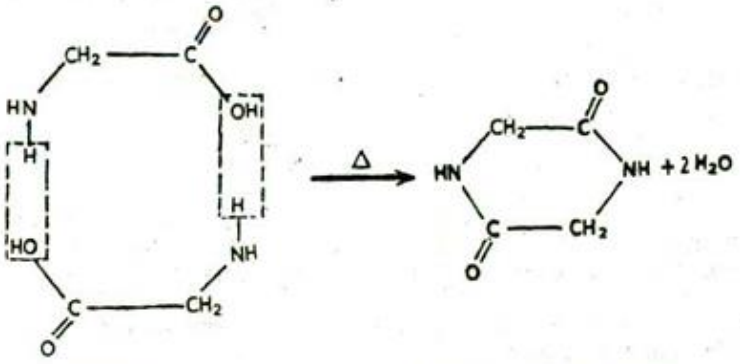


f. Reaction with 2,4-Dinitrofluorobenzene:A synonym for 2,4-Dinitrofluorobenzene is Sangar's reagent. Yellow-colored dinitrophenylamino acids, or DNP-amino acids, are the result of the reaction between amino acids and this reagent.

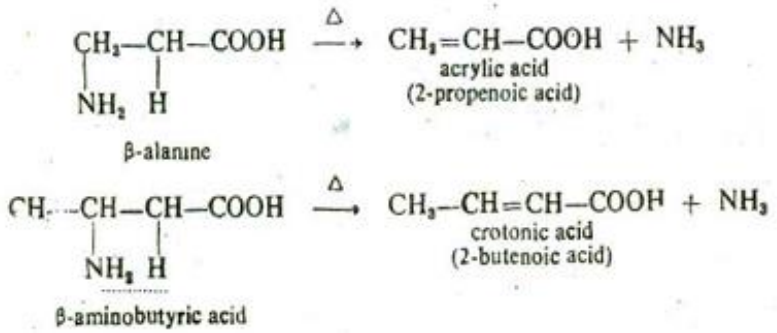


11.6.3 Reaction involve both Carboxyl and Amino Group:

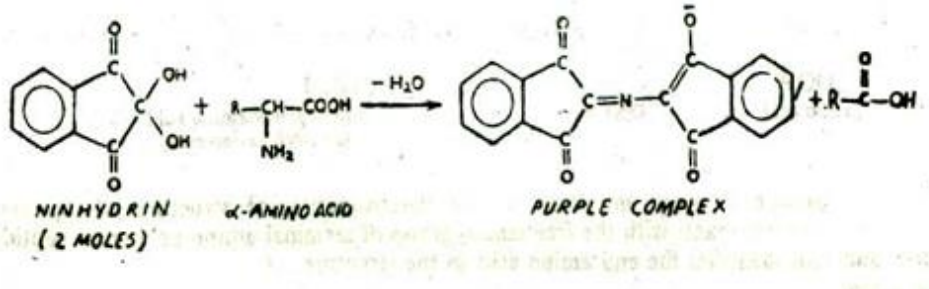
a. Heat's Effect: The amount of carbon atoms that between the carboxyl and amino groups affects how different amino acids behave when heated.When amino acids are heated to 200°C, they dehydrate, producing diketopiperazines.



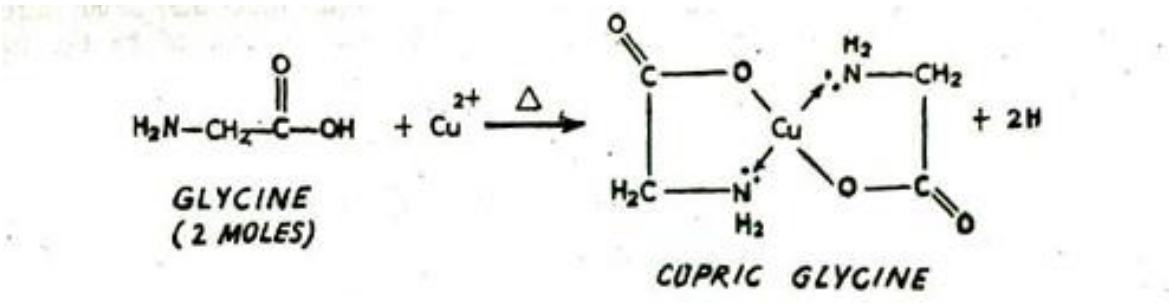
β-amino acids form α, β- unsaturated acids by lose of ammonia on heating.



b. Ninhydrin-reaction: Triketohydrindene hydrate, or ninhydrin, reacts with all α-amino acids to form the same purple complex. Tests for the presence of α-amino acids frequently use this reaction.



c. Reaction with Cupric Oxide: Deep blue complex salts are created when amino acids combine with cupric oxide in water.



Summary:

The only way that the amino acids vary is what's connected as a substituent to the The L structure is present in the majority of amino acids found in nature. The values of the amino acid's carboxyl groups and protonated amino groups are An amino acid is a zwitterion at physiological pH.Ionizable hydrogens can be found in the side chains of some amino acids. The pH at which an amino acid has no net charge is known as its isoelectric point (pI). Electrophoresis, paper chromatography, and thin-layer chromatography are methods that can be used to separate an amino acid mixture according to its polarity. Amino acids undergoes different kind of chemical reaction on the basis of place at which reaction occurs like reaction of carboxylic groups and reaction of amine groups.

Key wards:

Amino Acids: Organic substances that function as proteins' building components.

Essential amino acids: Amino acids that the body cannot produce on its own and must get from the diet are known as essential amino acids.

Non-essential amino acids: Amino acids that the body is capable of synthesizing and do not require diet are known as non-essential amino acids. Aspartic acid, glutamic acid, serine, and alanine are a few examples.

R-group side chain: An amino acid's side chain, or R group, is the portion of the molecule that varies depending on the amino acid.

MCQ:

1. The number of amino acids that are shared by all known proteins during their biosynthesis?

(A) 10

(B) 20

(C) 30

(D) 50 Answer (B)

2. All amino acids with identical protein structures

(A) have optical activity.

(B) At least one asymmetric carbon atom is present in each.

(C) (i) and (ii) together.

(D) Neither (i) nor (ii) apply. Answer (D)

3. Out of the following, which one best explains the distinction between essential and non-essential amino acids?

(A) The diet should include essential amino acids.

(B) Avoiding non-essential amino acids in the diet is advised.

(C) The body needs essential amino acids for proper operation, but it does not need non-essential amino acids.

(D) While the necessary amino acids cannot be produced by the body, non-essential amino acids may. Answer (A)

4. As amphoteric compounds, aminoacids

(A) include both basic and acidic groups.

(B) can react with either alkalis or acids to create salts.

(C) are capable of serving as buffers across a pH range.

(D) everything mentioned previously. Answer (A)

5. The isoelectric point is

(A) acidic pH For basic amino acids.

(B) dicarboxylic amino acids require an alkaline pH.

(C) neutral amino acids with a neutral pH.

(D) the pH at which there is no net charge on the amino acid. Answer (A)

Short Answer Questions:

1. Define zwitter ion.
2. What do you mean by Isoelectric point.
3. Write two methods of preparation of amino acids.
4. Write note on reaction of carboxylic group of amino acids.

Unit -12

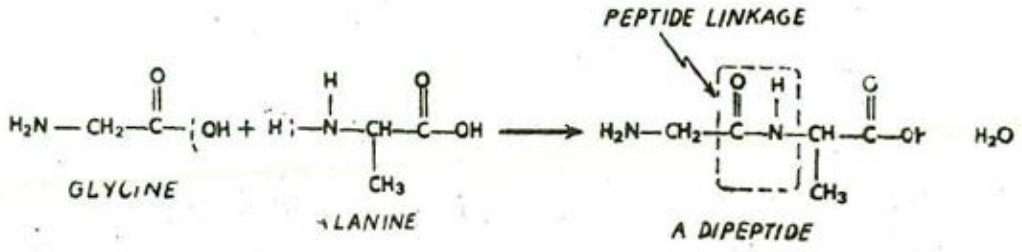
Protein and Peptides

Objective:

- Remember classification of proteins.
- Understand protein structure.
- Identify roles that proteins play.
- Explain the importance of proteins in biology.
- Understand about the Peptide bond and Peptide synthesis.

Peptides

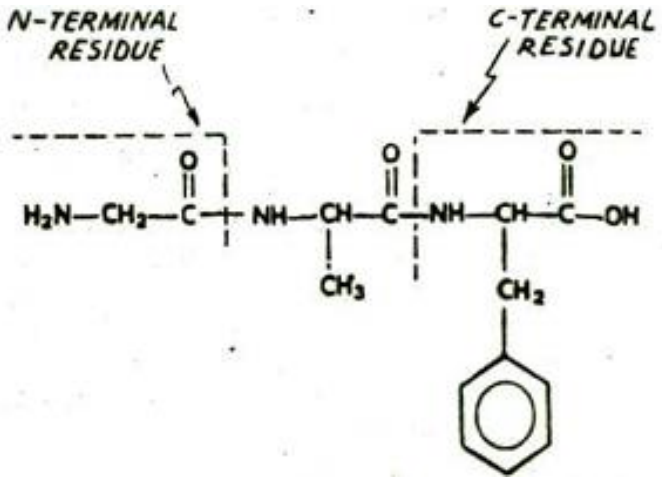
12.1 Introduction: Peptide bonds, which are created between the amino groups of one amino acid and the carboxyl groups of another, hold the numerous α-amino acids that make up proteins together. Dipeptides are created when two amino acids combine in this manner.



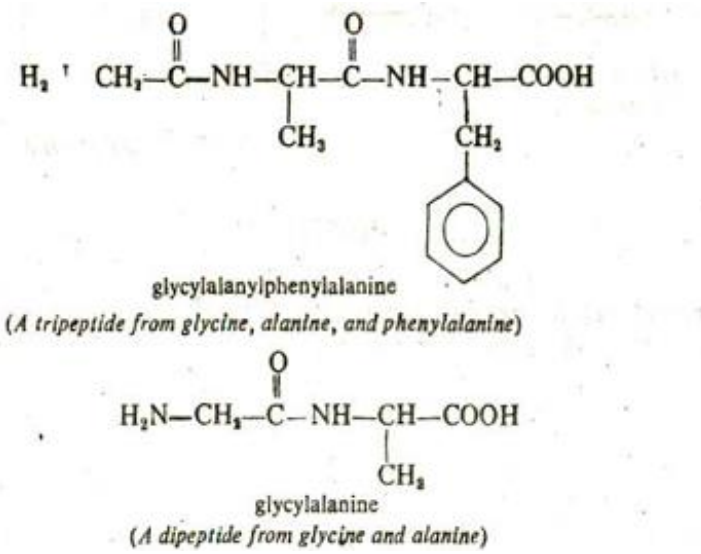
A tri-peptide is created when three amino acids are combined. A tetra-peptideis created when four amino acids are combined. This type of combination of numerous amino acids is known as a polypeptide. The difference between polypeptides and proteins is not readily apparent, but proteins are defined as polypeptides with at least 100 amino acids.

12.2 N-Terminal And C-Terminals Amino Acid Residues:

An amino acid is referred to as the N-terminal residue of a peptide when it has a free amino group. Throughout the polypeptide chain, it is always written on the left. C-terminal residue is the phrase used to describe the amino acid that has a free carboxyl group. Every time, the polypeptide chain is written with it on the right side.



12.3 Nomenclature of Peptides: The amino acids that make up a peptide are listed in the order that they appear, beginning with the N-terminal amino acid. With the exception of the C-terminal amino acid, all amino acids have the suffix "-yl" instead of the usual "-ine" suffix.

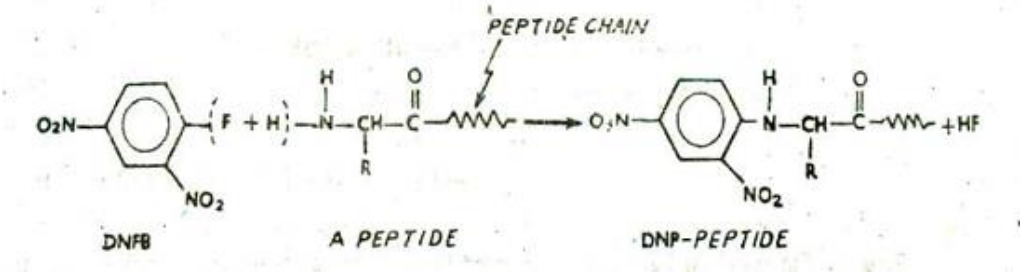


These kinds of peptide names are not frequently utilized. The common three-letter abbreviations are utilized instead. As an illustration, Gly-Ala-Phe can stand for glycylalanylphenylalanine.

12.4 Determination of Peptide Structure:

We often start by fully hydrolyzing a peptide (or protein) in order to ascertain its structure. To break all of the peptide bonds, the peptide is refluxed with diluted hydrochloric acid. The kind and quantity of amino acids included in the peptide are revealed by an analysis of the resultant

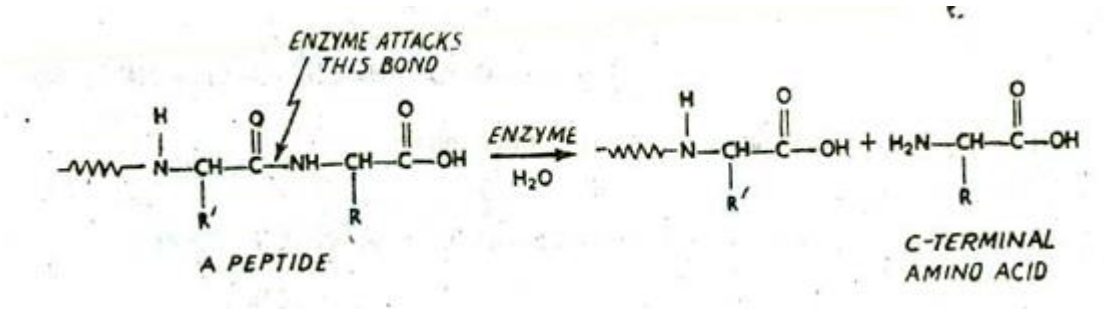
solution. Nevertheless, full hydrolysis provides no information regarding the peptide's amino acid sequence.



12.4.1 End-Group Analysis: The Sanger's approach can be used to identify the N-terminal amino acid of the peptides. Prior to the peptide being hydrolyzed, 2, 4-dinitrofluorobenzene (DNFB) reacts with the free amino group of the N-terminal residue.

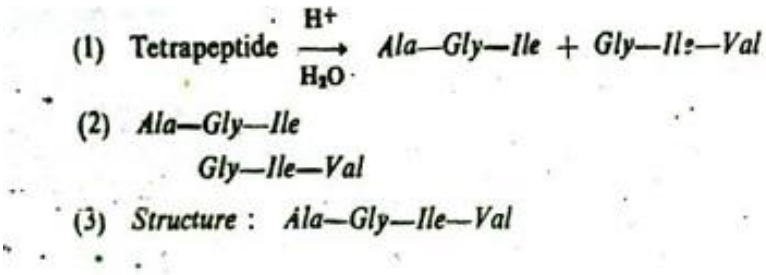
It is simple to separate and identify the N-terminal amino acid's dinitrophenyl (DNP) derivative since it is colored.

The enzyme carboxypepeidase is capable of the identification of the C-terminal amino acid. The C-terminal amino acid, which can be separated and isotified, is cleaved specifically by this enzyme.



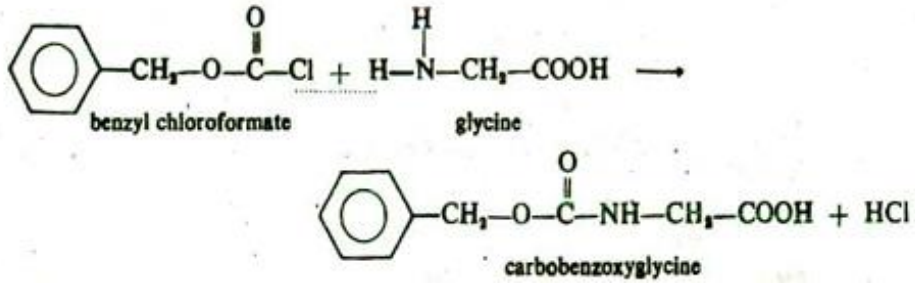
Peptide partial hydrolysis yields data that can be used to determine the internal amino acid sequence. Higher peptides such as di-, tri-, tetra-, and tri-are produced when the peptide undergoes partial hydrolysis. The N-terminal, C-terminal, and central amino acids of each tripeptide are identified when the tripeptide fragments are separated from one another. The structure of the original peptide can be inferred once all of the tripeptides' structures are known. The information can then be put together like pieces of a puzzle.

Let's use the scenario of every unknown tetrapeptide as an example. It comprises valine, isoleucine, and alanine, according to thorough hydrolysis, separation, and analysis. We now perform an end-group analysis on the unidentified peptide. The DNP-derivative of alanine is obtained by hydrolyzing it after DNFB treatment. Alanine must therefore be the amino acid at the N-terminus. Valine is obtained through carboxypeptidase treatment. We obtain two distinct tripeptides from the partial hydrolysis of the unidentified tetrapeptide. Subsequently, these tripeptides undergo comprehensive hydrolysis and end-group examination. We can ascertain the original tetrapeptide's amino acid sequence by overlaying the parts.

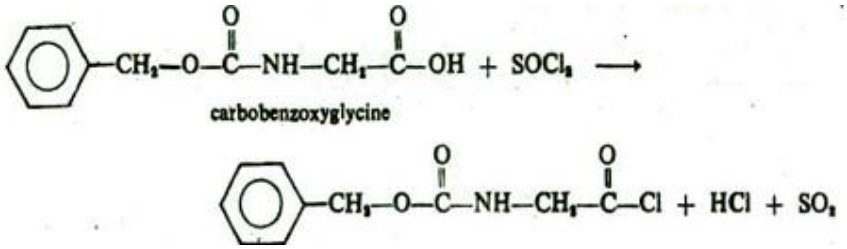


12.5 Synthesis of Peptides: The following procedures can be used to obtain particular peptides. We use glycylalanine, or Gly—Ala, as an illustration.

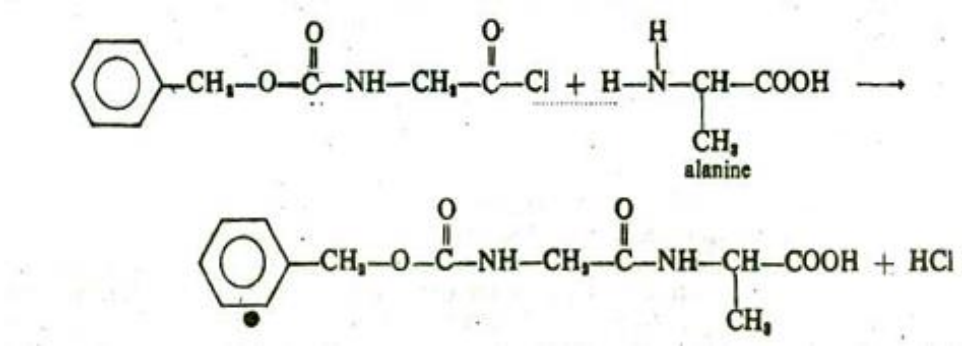
Step 1: Glycine's amino group is shielded by the treatment of benzyl chloro-formate.



Step 2: After being treated with thionyl chloride, the protected glycine is changed into the equivalent acid chloride.



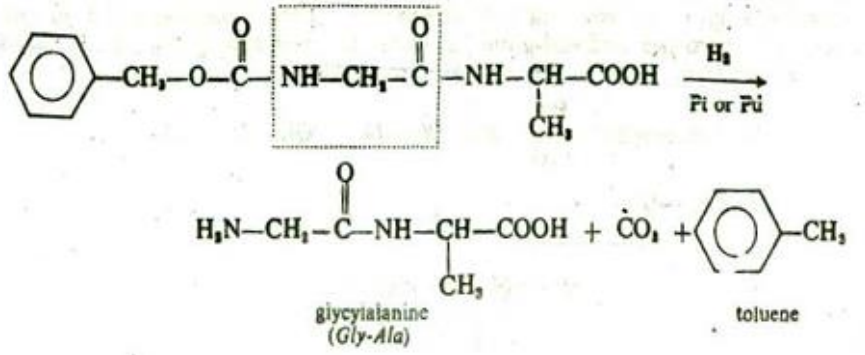
Step 3: Alanine and the acid chloride are condensed together.



Two reactions will happen if the reaction is carried out directly with glycine acid chloride and the amino group of glycinc is not protected as in Step (I).

In this stage, glycine acid chloride will react with alanine and the amino group of another glycine acid chloride molecule.

Step 4: Glycine's protective group is eliminated through reduction.



In order to synthesize higher peptides, the carboxyl group of each new peptide is reacted with $SOCl_2$ and a new amino acid, leaving the protecting group and the amino group alone. Small proteins like ribonuclease, which has 124 amino acid units, have been successfully synthesized despite the arduous nature of polypeptide synthesis.

Proteins

12.6 Introduction: The Greek term proteios, which means "a protein" first, is where we get the word "protein." The term conveys these substances' significance. Amino acid residues joined by peptide bonds to make proteins. An vital part of all living organisms, the resulting polymer is known as a protein.

Naturally occurring polyamides, proteins are created when many amino acid molecules condense under precisely regulated circumstances. Proteins are polymers of amino acid monomers that exist naturally and are connected by peptide bonds. The polymerization of amino acids into proteins is a chemical process that involves dehydration. They are heat labile, colloidal in nature, non-dialysable, and have a large molecular weight (greater than 5000).

Amino acid monomers, which make up proteins, are organic polymers found in nature. The carbon atom that makes up an amino acid (NH_2) and a carboxylic acid group (COOH) are two functional groups that are connected to this atom. In addition, an additional organic group called a "R" group and a hydrogen atom are joined to the core carbon atom. The identification of the amino acid is determined by the identity of the R group.

Proteins are essential for many biological systems, including oxygen transport, skin and hair structure, muscular function, enzyme function as biological catalysts, hormone regulation, and the list goes on and on. The monomeric unit of proteins, amino acids, are huge complex polymers that make up proteins. Peptide bonds, an amide linkage, are used to join amino acids together. We start our examination of proteins by reviewing the amino acids that are frequently present in proteins. According to estimates, proteins make up roughly 18% of the human body. Proteins are composed of the elements carbon (C), hydrogen (H), and oxygen (O), but they also contain nitrogen (N), just like carbohydrates and lipids.

Protein characteristics are determined by the arrangement of its amino acids. Sheath keratin, insulin, hemoglobin, antibodies, and enzymes are a few examples of proteins.

12.7 Classification: There are two protein classification schemes. They can be categorized as simple proteins or conjugated proteins based on their composition using one technique. They are categorized using their physiological functions in the second way.

12.7.1 Classification According to Composition:

A. Simple Proteins: Simple proteins are those that, when hydrolyzed, only produce a-amino acids. They are further separated based on whether or not they agglomerate when heated and on how soluble they are in different solvents.

- **a. Albumins:** Heat causes the water-soluble proteins known as albumins to coagulate. They can be found in both plants and mammals. Serum albumin and egg albumin are two examples.

b. Globulins: Globulins are soluble in diluted salt solutions that coagulate when heated, but insoluble in water. Both plants and animals contain them. Vegetable and serumglobulinare two examples.

c. Scleroproteins (Albuminoids): In water and the majority of other solvents, sclerosproteins are insoluble. Only animals contain them. Keratin, found in fingernails and hair, is one example.

d. Glutenin: In dilute acids and alkalis, which coagulate when heated, glutenins are soluble but insoluble in water. For instance, wheat contains glutenin.

e. Histones: When diluted ammonium hydroxide is added, histones become soluble in water but insoluble when heated. Animals carry them. Hemoglobin is one example of globin.

f. Prolamines: Heat does not cause prolamines to coagulate; they are soluble in 70% ethanol but insoluble in water. Corn zein and wheat gliadin are two examples.

g. Protamines: Heat cannot cause protamines to coagulate; they are soluble in water and diluted ammonium hydroxide. Salmon and sturgeon are two examples of foods that contain salmine.

B. Conjugated Proteins: Conjugated proteins hydrolyze to produce both a-amino acids and a nonprotein substance. The prosthetic group is the term for the nonprotein substance. Depending on the type of prosthetic group, conjugated proteins are further separated into multiple classes.

a. Glycoproteins: The prosthetic group of glycoproteins is a derivative of carbohydrates. One of the glycoproteins found in saliva is called mucin.

b. Phosphoprotiens: A-amino acids connected to phosphoric acid are found in phosphoproteins, which are proteins. One member of this class is casein, which is present in milk.

c. Chromoprotiens: A basic protein and a prosthetic group containing pigmentation are joined to form chromoproteins. Instances of chromoproteins include cytochromes and hemoglobin.

d. Nucleoproteins: In the nucleus of plant and animal cells, complex molecules known as nucleoproteins are widely distributed. Nucleic acids operate as prosthetic groups. The ccii

nuclei found in yeast, chromosomes, glandular tissues, and other materials are examples of nucleoproteins. Nuclein and nucleohistons are more examples.

e. Lipoproteins: Protein molecules with phospholipids and cholesterol esters linked to them make up lipoproteins. Membranes of cells contain them and they are present in brain and nerve tissue.

12.7.2 Classification According to Functions:

The following groups are included in the functional classification of proteins:

a. Structural Proteins: These are fibrous proteins, like collogen, which makes up the skin, cartilage, and bone that make about half of the total protein in humans.

b. Contractile Protein: Muscles include proteins called contractiles. Two examples are actin and myosin.

c. Harmones: Numerous proteins serve as harmones, or conduits for information between various organ systems. One typical example of a protein harmone is insulin.

d. Enzymes: Members of this particular protein category act as catalysts, giving chemical reactions in living things specificity and control. Examples of the class include trypsin and pepsin.

e. Antibodies: Antibodies are made to drive out invading species from the body when they release foreign proteins or antigens during an invasion. Antibodies include things like gamma globulins, which are found in blood.

f. Blood Proteins: Hemoglobin, fibrinogen, and albumins are the three main types of proteins found in blood. Respectively, their presence supports blood coagulation, oxygen transport, and osmotic pressure maintenance.

12.8 Protein Structure:

The arrangement of the amino acids that make up a certain chain distinguishes proteins from one another. Additionally, they vary in the manner in which the protein chain—also known as a peptide chain—is connected, coiled, or twisted. Multiple degrees of structure are used to characterize protein molecules. Four headings can be used to explain it.

12.8.1 Primary Structure: The amino acid sequence within a poly-peptide chain is referred to as the key structure. The nature and function of proteins will alter if this sequence is altered. Proteins are classified according to their primary structure, which is their amino acid sequence. It differs from one protein to another based on the job that each one must do.

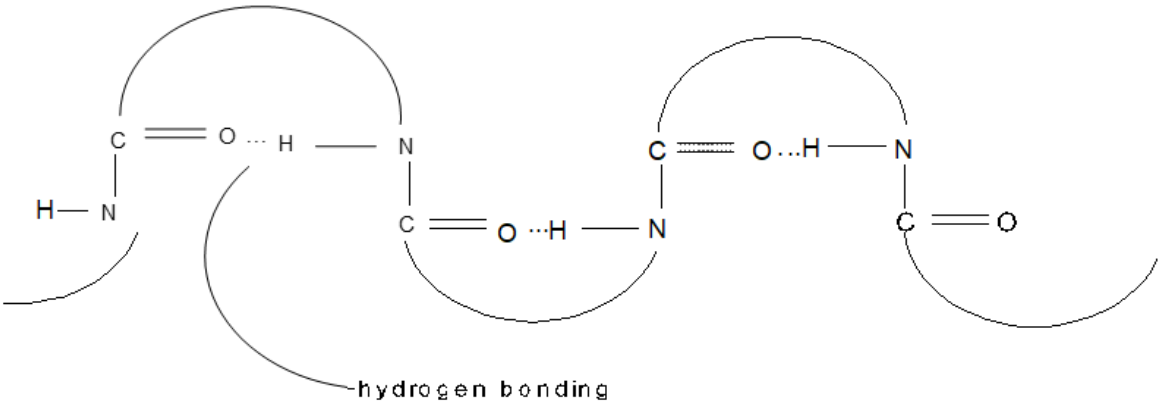
For example, the amino acid codes for each of these three-letter symbols are gly, ala, leu, iso, and gln.

A protein can include thousands of amino acids, each of which is organized in a certain order.

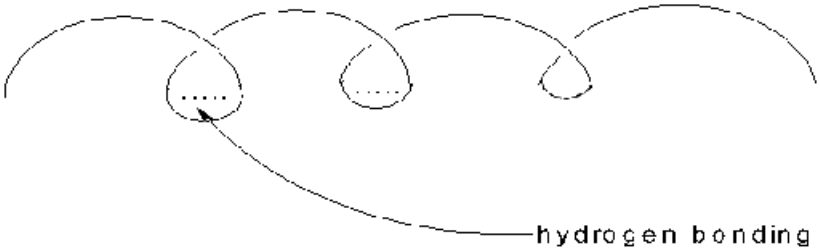
-C-C-N- is the chemical building block of all chains. We also refer to this backbone as a peptide chain. A compound is referred to be a dipeptide when two amino acids combine in a chain. Polypeptides are groups of several amino acids together in a chain. The backbone and polar groups of proteins are both bound by water molecules. An amino acid loses -OH from -COOH and another amino acid loses -H from -NH2 to form a peptide bond in a condensation reaction that forms polypeptides and proteins. Dipeptides are changed into polypeptides, which are then transformed into proteins through the repetition of this process (polymerization). The diagram makes use of the strand formula for an amino acid, which has changeable group R. The opposite process, known as enzyme-catalyzed hydrolysis, breaks down proteins into polypeptides and amino acids.

12.8.2 Secondary structure: A long polypeptide chain can exist in a shape known as secondary structure. This explains how the backbone chain segments of a protein or peptide are structured. The consistent folding of a lengthy polypeptide chain produced this structure. The hydrogen bonding between the H atom of the -NH group and the oxygen atom of the CO group of an amide that is either the same polypeptide chain or a different one is what causes this folding. A polypeptide chain will typically fold into an α- or β-sheet, or another repeating geometric shape, to save energy. There are two distinct types of chains.

The hydrogen atoms on one peptide link can create a hydrogen bond with the nitrogen or oxygen atoms on another peptide link, causing the structure to coil up, which is why protein molecules are not straight.



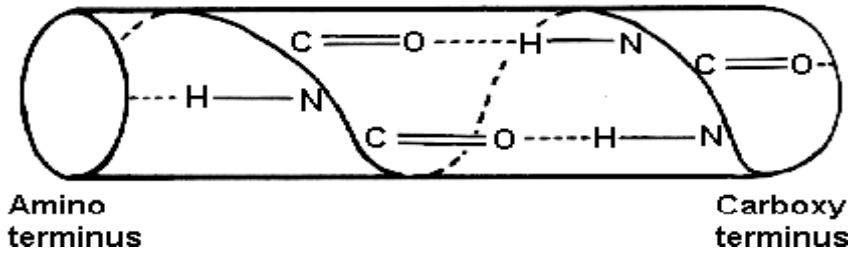
This coiling produces a helical helix that is the protein's secondary structure:

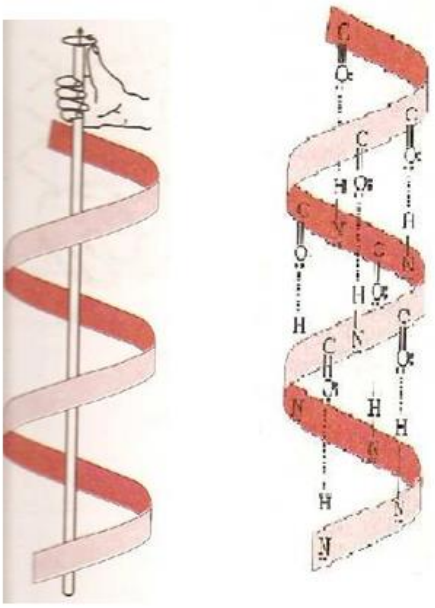


α-helix structure: a structure formed by the polypeptide chain twisting into a right-handed screw (helix). Each amino acid residue's -NH group is hydrogen bonded to the CO of a neighboring helix in this instance. The α-helix is said to have a pitch of 5.4 Å because the structure repeats itself every 5.4 Å along the helix axis. α-helices consist of 3.6 residues of amino acids every turn; so, a helix including 36 amino acids would have 10 turns. The increase in the α-helix per residue is 1.5 Å, so that the distance between residues along the helix axis is 5.4/3.6 or 1.5 Å.

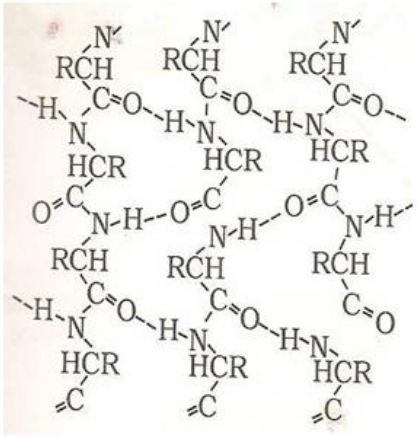
A peptide bond located four residues distant (from Oi to Ni+4) is hydrogen-bonded to every main chain C=O and N-H group. This results in a steady and consistent layout. The helix axis and the peptide planes are approximately parallel, and the 'dipoles' within the helix are aligned, meaning that all C=O groups point in the same direction while all N-H groups point in the opposite direction. Generally directed towards the amino-terminal end of the helix, side chains extend outward from the helix axis.

Toilet roll representation of the main chain hydrogen bonding in an alpha-helix.





α–helix structure



β- pleated structure

Numerous alpha helices make up a human hair strand. A protofibrilis created by weaving three alpha helices together, as the diagram below illustrates. A microfibrilis formed by the bonding and coiling of eleven protofibrils. An irregular bundle known as a macrofibrilis created when hundreds of these microfibrils are bundled together. To create a full strand of hair, these are then combined with both living and dead cells. A fibrous protein present in silk is called fibrin. Due to hydrogen bonding, the polypeptide chains in its pleated sheet structure are arranged in a parallel fashion.

β-pleated structure: The protein structure known as the β-pleated structure is characterized by polypeptide chains that are nearly stretched to their maximum length, arranged side by side, and secured together by hydrogen bonds. Hydrogen bonds between the main chain's C=O and N-H

groups bind two or more polypeptide chains that run next one another in a regular fashion to form a β-sheet. That means that every hydrogen bond in an α-sheet connects various polypeptide segments.

In comparison, the α-helix has a single secondary structural element involved in all hydrogen bonding. Neighboring residues in an α-strand have R-groups (side chains) pointing in different directions? Adjacent residues are spaced 3.5 Å apart axially. The β-strand has a pitch of 7 Å since there are two residues in each repeat unit. Comparing this to the α-helix, neighboring residues are only separated by 1.5 Å along their axial length. The β-conformation polypeptides are obviously much longer than the α-helical conformation polypeptides.

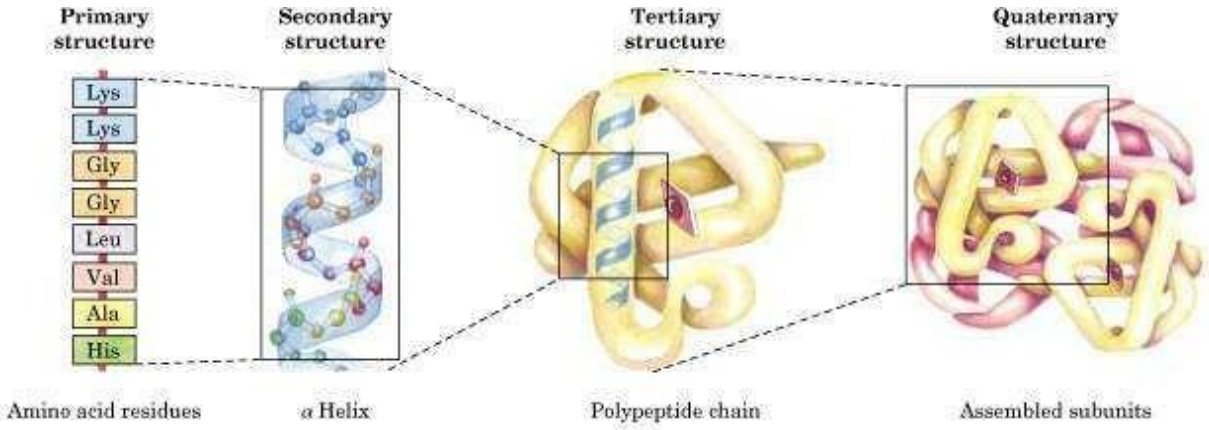
12.8.3 Tertiary structure: A protein's tertiary structure is the three-dimensional configuration of all of its atoms. In order to maximize their stability, proteins fold spontaneously in solution. Free energy is released each time there is a stabilizing interaction between two atoms. The protein becomes more stable with the release of more free energy. Thus, a protein folds to maximize the amount of interactions that stabilize it. It speaks about the overall folding of the polypeptide chain, or the subsequent folding of 20 structures. Structures in 2^o and 3^o are stabilized by Hydrogen Bonding, Disulphide linkage, vanderwalls's force and electrostatic force.

The process of folding a polypeptide chain to bring the various secondary structure components together in a certain configuration is referred to as tertiary structure. The domain is the unit of tertiary structure, just as helices and sheets are units of secondary structure. Tertiary structure in multi-domain proteins refers to the configuration of the chains inside each domain as well as the arrangement of the domains in relation to one another.

12.8.3 Quaternary structure: This describes how two or more polypeptide chains, or subunits, are arranged spatially in relation to one another. Units of tertiary structure aggregate to produce homo- or hetero-multimers at the quaternary structure level of form. Oligomers are proteins that contain several peptide chains. Subunits are the individual chains.

A monomer is a protein that has one subunit; a dimer is a protein that has two subunits; a trimer is a protein that has three subunits; and a tetramer is a protein that has four subunits. One example of a tetramer is hemoglobin. There are two of each class and two distinct subunit types. The same hydrophobic interactions, hydrogen bonds, and electrostatic attractions that keep

individual protein chains in a specific three-dimensional shape also hold the subunits together. It is discovered that this occurs very frequently, particularly with enzymes.



12.9 Functions of proteins:

12.9.1 Transport functions:

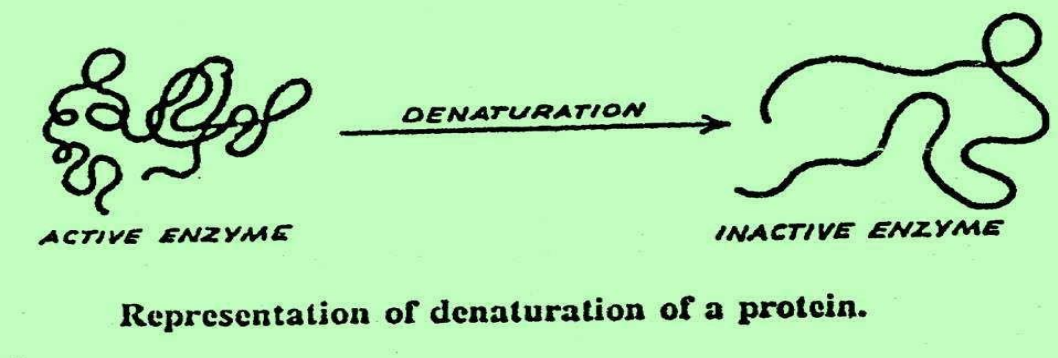
- Transmit molecules or ions between cells or across membranes. For example, bile pigment, free fatty acids, and calcium are all carried by albumin.
- Air is carried by hemoglobin.
- Enzymes (proteins) have a catalytic function in chemical processes.
- Certain hormones made of proteins, including insulin, are responsible for regulating metabolism.
- The myosin and actin-produced contraction of muscle.
- Protection: Immunoglobulins fend off bacterial and viral invasion.
- Hemorrhage is prevented by blood clotting factors.
- The digestive and respiratory systems are shielded by mucin.
- Liquid equilibrium
- Acid-base equilibrium
- The immune system
- The Enzymes
- Red blood cells, skin cells, and intestinal cells were replaced.
- Collagen is foundin teeth, skin, and tendon

- Fluids: albumin maintains the proper equilibrium between intracellular and extracellular fluid as
- well as blood vessels, or else swelling
- Can act as buffers and raise or lower pH.
- Immune system: antibodies and mucus destroy infections
- Lactose intolerance and enzymes
- Hormones: insulin, etc.

12.9.2 Static functions in structural terms

The structural elements of the cell membrane, cytoplasm, organelles, and nuclei are proteins. Mechanical support: the structure of blood vessels, ligaments, and tendons is made up of collagen and elastin. In the structure of the skin, hair, and nails, keratin is crucial. Ossein enters the skeletal system.

12.10 Protein Denaturation: Many intramolecular attractions contribute to a globular protein's tertiary structure, which can be upset by environmental changes and result in denatured protein. Denaturation is the process of breaking down a protein's highly ordered tertiary structure. Rupture of non-covalent bonds (hydrogen bonds, hydrophobic bonds, and electrostatic bonds) results in a change in the secondary, tertiary, and quaternary structure of proteins.Any force that shatters the bonds that keep the protein in its three-dimensional form will cause the protein to denature, or unfold. Proteins are easily denatured due to the weakness of these linkages. A random coil is the completely arbitrary structure of a denatured protein. Protein structure is disrupted in all orders except fundamental structure upon denaturation.



Representation of denaturation of a protein.

The albumins unfold and coagulate when heated, significantly reducing their solubility. Denatured enzymes also stop being catalytically active.

12.10.1 Denaturation can occur for a variety of reasons, some of which include the following:

a. Physical agents:

- Over 70ºC in temperature. The attractive forces may be disrupted by heating because it increases molecular mobility.
- The alteration that takes place in an egg white when it is cooked or whipped is a well-known example. X-rays; • Ultraviolet radiation; • Vibrant shaking; • Stirring; • Repeated freezing and thawing.

b. Chemical agents:

- Ionic bonds are broken by heavy metal salts like Mg 2+ and Pb 2+.
- Extreme pH levels of strong acids and bases. Because the pH affects many of the side chains' charges, changing it denatures proteins. This breaks hydrogen bonds and electrostatic attractions.
- Reagents that are sulfur-containing, such as mercaptoethanol, which reduces S-S bonds.
- Reagents with alkaloids, such as phosphotungestic acid and picric acid
- Alcohol
- A few chemicals, such urea and guanidine hydrochloride, denature proteins by creating stronger hydrogen bonds with the protein groups than the groups themselves make. Proteins are denatured by detergents like sodium dodecyl sulfate because they attach themselves to the nonpolar regions of the protein and interfere with the hydrophobic interactions that normally occur. Proteins are also denatured by organic solvents because they interfere with hydrophobic interactions.

12.11 Denaturation effects:

12.11.1 Physical changes:

- Reduced solubility (caused by internal non-polar groups being exposed) and a slower rate

of diffusion across membranes.

- A rise in protein viscosity as a result of chains unfolding and molecular size expansion.

12.11.2 Chemical alterations:

- Breaking of non-covalent bonds, which could also include disulfide bonds.
- Exposure to some of the internal groups found in protein molecules, such as SH.

12.11.3 Biological Changes:

- Decrease in the biological activity of hormone-producing proteins and enzymes.
- Modifications in the antigenic characteristics of proteins.
- Peptide chains unfold to make denatured proteins easily digestible.

Summary:

As polymers of amino acids joined by peptide (amide) bonds, peptides and proteins are formed. The number of amino acid residues in a polypeptide is often greater than that of a dipeptide, which has two, tripeptides, oligopeptides, and five total. Remaining amino acids range from 40 to 4000 in proteins. Peptide bonds are the amide bonds that join the residues of amino acids. The double bond nature of a peptide bond is around 40%. The free carboxyl group, or C-terminal amino acid, is written on the right of a protein or peptide, and the free amino group, or N-terminal amino acid, is written on the left. The arrangement of all the disulfide bridges and the order in which the amino acids are ordered make up a protein's fundamental structure. A protein's secondary structure explains how specific regions of its backbone fold. A protein folds to optimize the quantity of hydrophobic (interactions between nonpolar groups) and covalent (bonds between opposite charges), hydrogen, and other stabilizing interactions. Different types of secondary structures include coil conformations, α and β-helices, and more. A protein's three-dimensional configuration containing every atom is called its tertiary structure. "Oligomers" are proteins that contain several peptide chains. Subunits are the terms for the individual chains. An enzyme's subunit arrangements in relation to one another in space are described by its quaternary structure.

Key wards:

Peptide Bond: A peptide is created when the carboxyl group of one amino acid and the amino group of another form a chemical connection.

Primary Structure: The arrangement of amino acid residues connected by peptide bonds determines the linear sequence of amino acids in a protein chain.

Secondary Structure: The localized folded structures that arise in a protein chain and are usually maintained by amino acid hydrogen bonds.

Tertiary Structure: The three-dimensional configuration that arises from the interactions between side chains of amino acids within a protein molecule.

Quaternary structure: Quaternary structure refers to the arrangement of multiple polypeptide chains or protein subunits within a complex.

MCQ:

1. Proteins are-

(A) Macromolecules whose name implies first or first.

(B) Account for at least 50% of the cell's dry weight.

(C) In live tissue, there are hundreds of distinct molecules.

(D) Everything mentioned previously Answer (D)

2. Complex proteins could consist of

(A) Liposomal and glycoproteins

(B) Nucleoproteins and hemeproteins.

(C) Metalloproteases and phospholipids.

(D) Everything mentioned previously. Answer (D)

3. High biological significance of protein

(A) Certain necessary amino acids can be found in proteins

(B) Originate solely from animal sources.

(B) Are difficult to break down and metabolize.

(D) Are required in the diet, particularly for younger people. Answer (D)

4. The formation of a peptide bond

(A) happens when the α-amino group of one amino acid and the α-carboxyl group of another amino acid undergo a condensation reaction.

(B) A non-carboxyl group's reaction can result in the formation.

(C) both (a) and (b)

(D) without (a) or (b). Answer C)

Short question:

1. Recognize the differences between fibrous and globular proteins. How can you explain amino acids' amphoteric behavior?
2. How does denaturation affect the way proteins are structured?
3. When an egg is boiled, where does the water inside go?
4. Explain the following in terms of proteins.
   (i) Peptide bonding (ii) Primary configuration (iii) Denaturing
5. What kinds of secondary protein structures are commonly found?

Unit - 13

Carbohydrates

Part-1; Monosaccharides

Objectives;

- Understand the molecular structure and functional groups of monosaccharides like glucose and fructose.
- Explore the various isomeric forms and their significance in biological processes.
- Investigate the reactions and chemical properties of carbohydrates, including oxidation and reduction reactions.
- Identify the alpha and beta anomers in cyclic monosaccharides like glucose, distinguishing them based on the orientation of the hydroxyl group at the anomeric carbon.

13.1 Introduction:

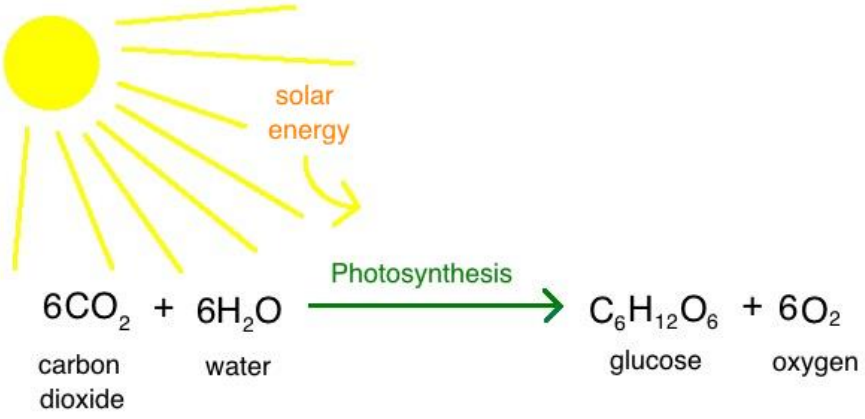
Carbohydrates are essential macronutrients found in a wide array of foods and beverages. They serve as the primary basis of energy for living organisms, giving fuel for numerous metabolic processes within the body. Structurally, carbohydrates are organic compounds composed of carbon (C), hydrogen (H), and oxygen atoms (O), typically in the *ratio* of 1:2:1.

These molecules come in various forms, including simple sugars like glucose, fructose, and galactose, as well as complex carbohydrates such as starches, glycogen, and dietary fiber. Simple sugars are easily digestible and rapidly converted into energy, while complex carbohydrates take longer to break down, offering a sustained release of energy over time.

Beyond their role as energy providers, carbohydrates also play crucial roles in biological processes such as cell signaling, immune function, and protein synthesis. Additionally, dietary fiber, a type of complex carbohydrate, aids in digestion, promotes satiety, and helps maintain bowel regularity.

Carbohydrates in green plants are synthesized through photosynthesis, a biochemical process. Here, simple compounds like carbon dioxide (CO2) and water (H2O) are converted into glucose ($C_6H_{12}O_6$), facilitated by the green pigment chlorophyll found in plant leaves. The energy

essential for this transformation is sourced from sunlight, absorbed by chlorophyll during photosynthesis.



Chemically the carbohydrates, a category of naturally occurring compounds, comprise carbonyl compounds (either aldehydes or ketones) alongside multiple hydroxyl groups. This group can also encompass derivatives that yield these compounds upon hydrolysis. Widely distributed across nature, carbohydrates are commonly known as "saccharides." Those carbohydrates soluble in water and possessing a sweet taste are termed "sugars."

13.2 Structure of carbohydrates

Carbohydrates were once defined by the formula $Cn(H_2O)m$, including common sugars like glucose, fructose, and sucrose. Today, the definition extends to polyhydroxy aldehydes or ketones, their derivatives, and polymers. The study of carbohydrates formed a distinct field within organic chemistry due to their solubility in water and challenges in crystallization, requiring unique skills compared to other natural products like terpenes or alkaloids.

The term "monosaccharide" denotes derivatives of carbohydrate with a single chain of carbon, while "disaccharide" and "trisaccharide" describe molecules comprising three or two ‘monosaccharide’ units linked by acetal or ketal bonds. "Oligosaccharide" and "polysaccharide" refer to larger assemblies with "a few" and various monosaccharide units, correspondingly, with the distinction often set at around 10 units.

By the mid-19th century, European chemists, particularly in Germany, had identified several relatively pure carbohydrates, including sucrose, cellulose, starch, glucose, fructose, mannose, and lactose. Emil Fischer created phenyl-hydrazine in 1878 as part of his thesis research at the University of Munich. He later found, in 1884, that carbohydrates yielded crystalline

phenylosazone when treated with two phenyl-hydrazines alongside the aldehyde group and the adjacent carbon.

Carbohydrates are carbon-based macromolecules composed of hydrogen, carbon, and oxygen generally following the formula '**$Cx(H_2O)y$**'. They are often referred to as hydrates of carbon, as they contain hydrogen and oxygen in a ratio similar to that of water. While many carbohydrates adhere to the $Cx(H_2O)y$ formula, exceptions exist, such as 2-deoxyribose ($C_5H_{10}O_4$). Nonetheless, the majority of carbohydrates align with this formula.

13.3 General Properties of Carbohydrates: Here we summarize the some common properties of Carbohydrates as

1. **Chemical Composition**: Carbohydrates are built by of carbon, hydrogen, and oxygen atoms, usually in the ratio of 1:2:1. Their molecular formula is often represented as $(CH_2O)n$, where "n" represents the number of carbon atoms.
2. **Solubility**: Many carbohydrates are soluble in water due to the presence of hydroxyl groups (-OH) in their structure. However, solubility may vary depending on the size and structure of the carbohydrate molecule.
3. **Sweetness**: Sugars, a type of carbohydrate, often exhibit a sweet taste. The degree of sweetness can vary depending on the specific sugar molecule.
4. **Crystalline vs. Amorphous**: Some carbohydrates, particularly sugars, can form crystalline solids with well-defined structures. Others, such as starch and cellulose, are amorphous and lack a regular crystalline arrangement.
5. **Hygroscopicity**: Carbohydrates have the ability to absorb water molecules from the surrounding environment, making them hygroscopic. This property can affect their texture and stability in various applications.
6. **Reducing or Non-Reducing**: Certain carbohydrates, such as glucose and fructose, have a reducing property due to the presence of an aldehyde or ketone functional group. Others, like sucrose, do not exhibit reducing behavior.
7. **Polymerization**: Carbohydrates can undergo polymerization to form larger molecules known as oligosaccharides or polysaccharides. This process involves linking multiple monosaccharide units through glycosidic bonds.

8. **Energy Source**: Carbohydrates serve as a prime source of energy for living organisms. Upon digestion, they are disintegrating into simple sugars like Glucose, which can be readily utilized by cells for energy production.
9. **Structural Function**: Certain carbohydrates, such as cellulose and chitin, serve structural roles in plants and animals, providing rigidity and support to cell walls and exoskeletons, respectively.
1. **Biological Functions**: Carbohydrates play diverse roles in biological processes, including cell signaling, immune response, and cell-cell recognition. They also serve as precursors for the synthesis of other biomolecules like nucleic acids and lipids.

13.4. Classification of Carbohydrate

Carbohydrates can be broadly classified into two categories:

(i) **Sugar;** Crystalline constituents that are water soluble and sweet. Examples include glucose, fructose, and cane sugar.

(ii) **Non-sugars**; Are tast-eless, water insoluble and typically exist in an amorphous form. Examples include starch, cellulose, and other complex carbohydrates.

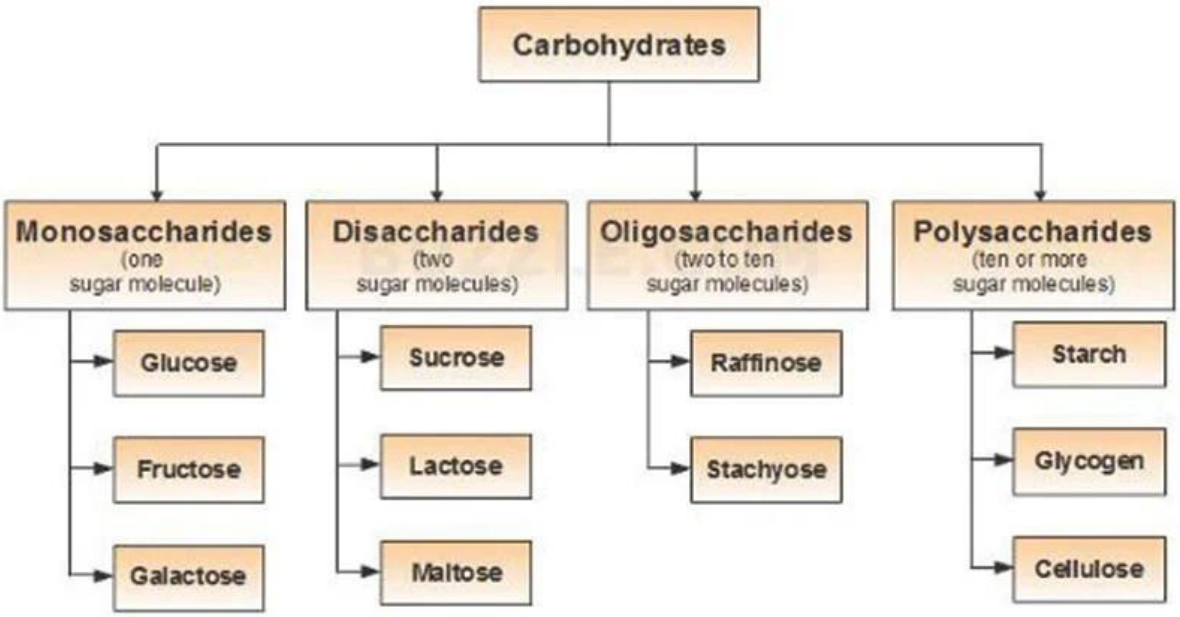
Carbohydrates are now typically categorized into following primary groups for systematic classification.

Mono-saccharides: Built by one sugar molecule. Galactose, fructose, and glucose are a few examples.

Di-saccharides: Consists of a glycosidic bond tying two monosaccharide molecules together. Glucose + fructose, lactose + galactose, and maltose + glucose are examples of common disaccharides.

Oligo-saccharides: Carbohydrates containing a small number (usually 3-10) of monosaccharide units linked together. Common food sources for them include lentils, beans, and several vegetables.

Polysaccharides: Polysaccharides are complex carbohydrates composed of long chains of monosaccharide units linked by glycosidic bonds. They serve as energy storage molecules (starch in plants, glycogen in animals) and structural components (cellulose in plants, chitin in fungi and animals).



13.5 Nomenclature of carbohydrates

Carbohydrates comprise 'Hydroxy and Aldehydic or Ketonic' groups and named by'**IUPAC system'** of nomenclature.

Compound	Common name	IUPAC name
$CH_2OHCHOHCHO$	Glyceraldehyde	2, 3-dihydroxy propanol
$CH_2OHCOCH_2OH$	Dihydroxyacetone	1,3-dihydroxy propanone
$CH_2OH(CHOH)_4CHO$	Glucose	2,3,4,5,6-pentahydroxyhexanal
$CH_2OH(CHOH)_3COCH_2OH$	Fructose	1,3,4,5,6-pentahydroxyhexan-2-one

13.6 Glucose

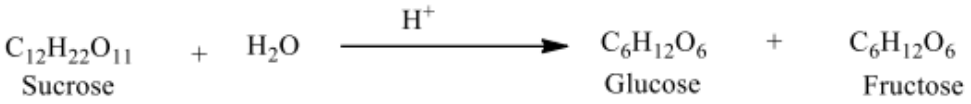
Glucose is a monosaccharide, often referred to as a simple sugar, and is one of the most important carbohydrates in biology. It is the main energy source for all living things and is essential to many metabolic functions.Glucose is the most prevalent monosaccharide and is commonly referred to as Dextrose because its natural occurrence primarily involves the optically dextrorotatory isomer.

Glucose belongs to the aldohexose group of carbohydrates, characterized by having six carbon atoms and an aldehyde functional group (-CHO).Its molecular formula is $C_6H_{12}O_6$.Glucose exists

in as linear and in cyclic forms when in solution. It produces a six-membered ring structure called a pyranose ring when it is in a cyclic state.

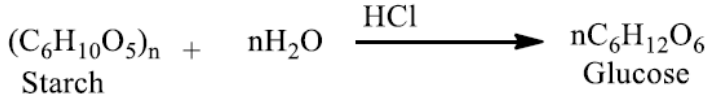
13.6.1 Preparation of Glucose

(i) From Sugar: From sucrose (cane sugar), glucose can be prepared through hydrolysis, a process that breaks down the disaccharide sucrose into its constituent monosaccharides, glucose, and fructose.



(ii) From Starch:

Glucose is commercially produced by hydrolyzing starch through a process involving boiling with dilute sulfuric acid at high temperatures under pressure.



In this method, an aqueous solution of starch extracted from corn is treated with dilute sulfuric acid to acidify it. The mixture is then subjected to high-pressure steam heating in an autoclave. Once hydrolysis is achieved, the resulting liquid is neutralized to a pH of 4-5 using sodium carbonate. The solution obtained is then concentrated under reduced pressure to yield glucose crystals.

13.6.2 Physical properties of Glucose

- **Appearance**: Glucose characteristically looks as a white and odorless crystalline solid in its pure form. It is also available as a colorless powder or liquid
- **Taste and Odor**: Glucose has a sweet taste, though not as sweet as sucrose. It is odorless in its pure form.

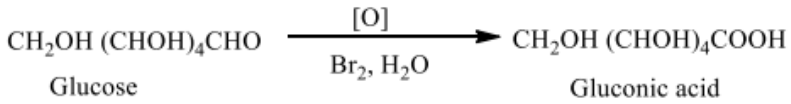
- **Solubility**: Glucose is highly soluble in water, forming a clear, colorless solution. It is also soluble in ethanol and insoluble in non-polar solvents
- **Melting Point**: Glucose has the melting point of is approximately 146-150°C (295-302°F). However, it may decompose before melting at higher temperatures.
- **Optical Activity**: Glucose exhibits optical activity due to its asymmetric carbon atom. In its natural form, it rotates plane-polarized light to the right (dextrorotatory), hence the name "D-glucose".
- **Crystalline Structure**: Glucose can form various crystalline structures, including monohydrate and anhydrous forms, depending on temperature and pressure conditions during crystallization.
- **Specific Gravity**: The specific gravity of glucose depends on its concentration and temperature, typically ranging between 1.50 to 1.55 g/cm³ for aqueous solutions.

These physical properties contribute to the diverse uses of glucose in various industries, including food, pharmaceuticals, and biotechnology.

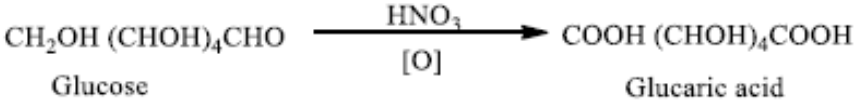
13.6.3 Chemical Reactions of Glucose

(A) Reactions with –CHO group

(i) Oxidation: In the presence bromine water glucose oxidize to gluconic acid in the case only –CHO is reacted.

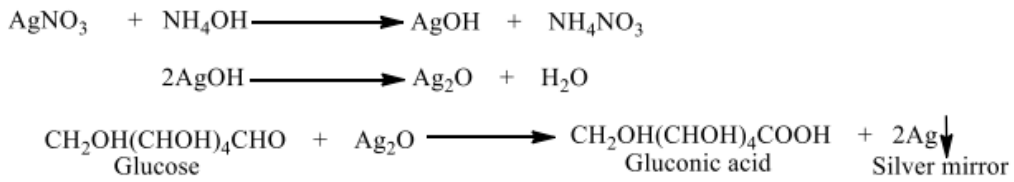


- In the presence of Nitric acid both terminal –CHO and –CH_2OH get oxidized to glucaric acid.

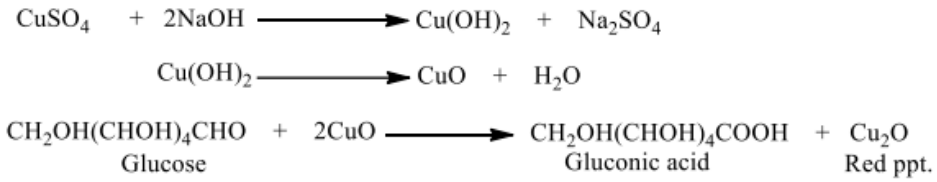


- In the presence of Tollen's reagent and Fehling reagents the glucose oxidized to Gluconic acid.

Tollen's reagent

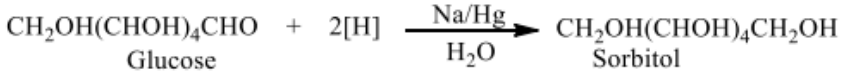


Fehling reagent

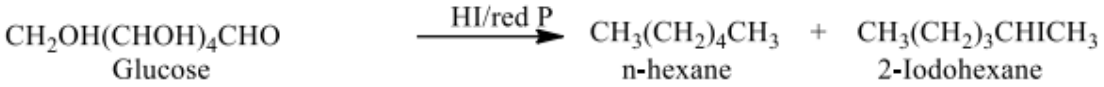


(ii) Reduction reaction of glucose

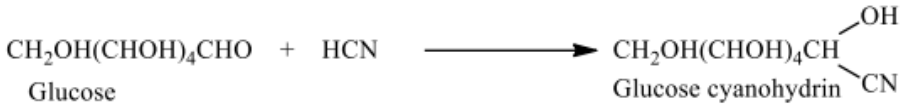
- With the sodium amalgam glucose reduced to Sorbitol.



- With Red P and HI glucose reduced to mixture of n-Hexane and 2-idohexane.



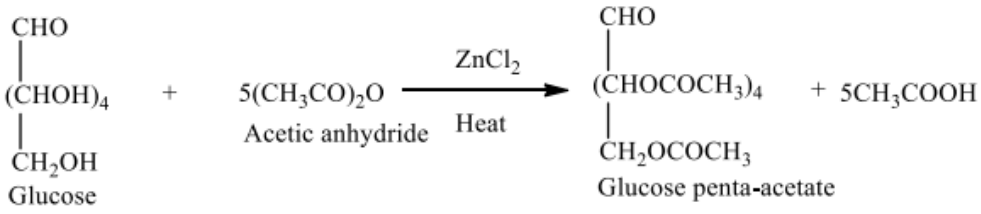
With HCN aldehydic group of glucose gave the cyanohydrins.



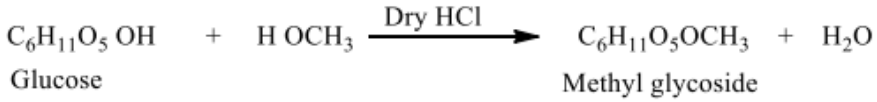
- Reaction with NH_2OH oximes of glucose obtained.

(B) Reactions of hydroxyl group

- Glucose leads to the formation of penta acetate after reaction with acitic anhydrides or acetyl chlorides.

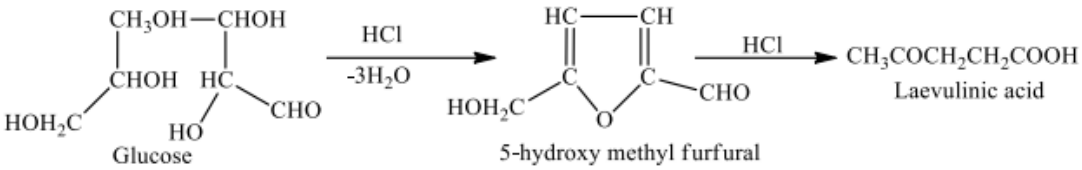


- Glucose haves the methyl glucoside after reaction with dry HCl

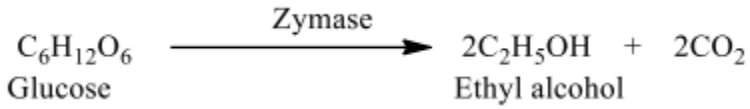


(C) Other Miscellaneous reactions

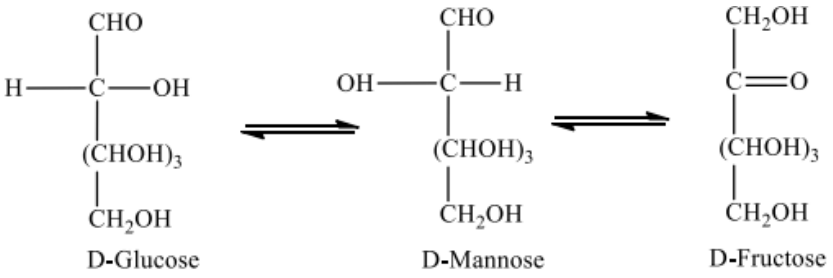
- When the glucose was heated with Conc. HCl 5-hydroxy methyl furfural is obtained which further covert to laevilinic acid.



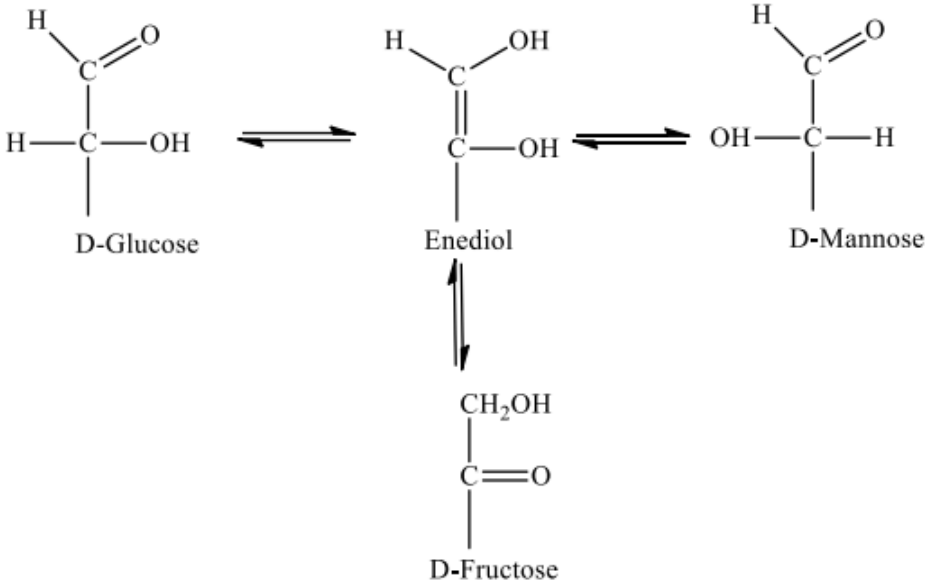
- The Glucose undergoes fermentation in ethylalcohol in presence of enzyme Zymase. This reaction is used in preparation of wines and alcohols.



- In presence of dilute alkali glucose rearrange to mixture of D-glucose, D-fructose and D-Mannose. This is the equilibrium can shown by any of these three hexoses.



This explains why D-fructose, despite containing a ketonic C=O group, exhibits the ability to reduce ‘Fehling's solution or Tollens' reagent’. The rearrangement of monosaccharides in weakly alkaline solutions is known as the ‘Lobry de Bruyn-Van Ekenstein rearrangement’.

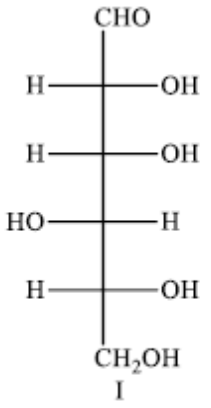


13.6.4 Glucose structure

- Based on molecular weight and element determination the molecular formula of Glucose find $C_6H_{12}O_6$.
- It gave the n-hexane after reaction HI and red P the n hexane so indicate the straight chain of six cabons.
- The formation of a pentaacetate when treated with acetic anhydride shows the presence of five hydroxyl groups in the molecule.

- Glucose reveals the presence of a carbonyl group by reacting with hydrogen cyanide to generate cyanohydrins and with hydroxylamine to form an oxime. In addition, it produces a phenyl-hydrazonewhen exposed to phenyl-hydrazine.
- Glucose under mild oxidation conditions with bromine water or sodium hypobromide yields gluconic acid, a monocarboxylic acid with the same number of carbon atoms as glucose (six), suggesting the presence of an aldehyde group.
- Catalytic reduction of glucose yields sorbitol, a hexahydric alcohol, which forms hexaacetate when treated with acetic anhydride. This confirms the presence of an aldehyde group and five hydroxyl groups in glucose.
- Oxidation of '**gluconic acid'** with nitric acid produces glucaric acid, a di-carboxylic acid with the identical number of carbon atoms as glucose, indicating the existence of a primary alcoholic group besides the aldehyde group in glucose.

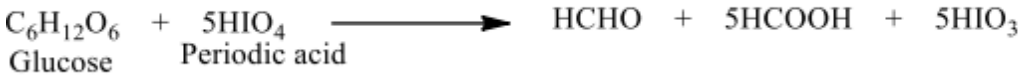
  Based on the reactions described above, Fischer proposed an open-chain structure for glucose, depicted as follows...



I

D-(+)-Glucose

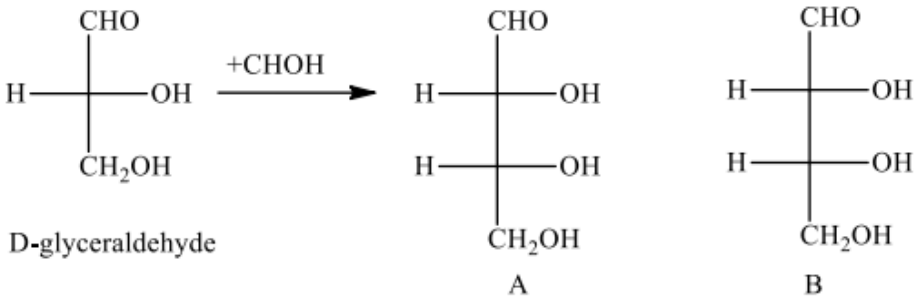
The proposed structure of glucose is further supported by its cleavage reaction with periodic acid. One mole of glucose reacts with five moles of periodic acid, yielding five moles of '**Formic acid** and one mole of **Formaldehyde**'.



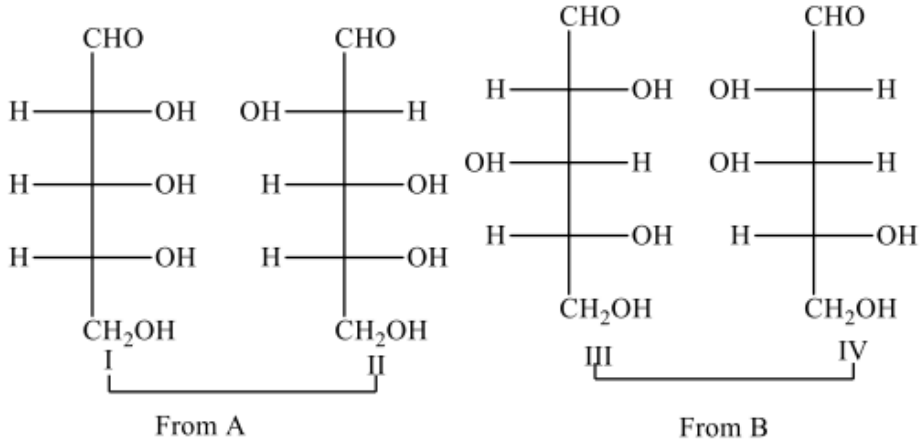
13.6.5 Configuration of D-Glucose

Emil Fischer established the configuration of D-glucose through reasoning analogous to the following arguments...

- To construct four probable ‘D-pentoses’, we begin with the configuration of ‘D-glyceraldehyde’ as the reference. Two potential ‘D-aldotetroses’ (labeled A and B) can be created by appending a -CHO group just below the -CHO group of glyceraldehyde, followed by positioning an OH group to the right and then to the left.



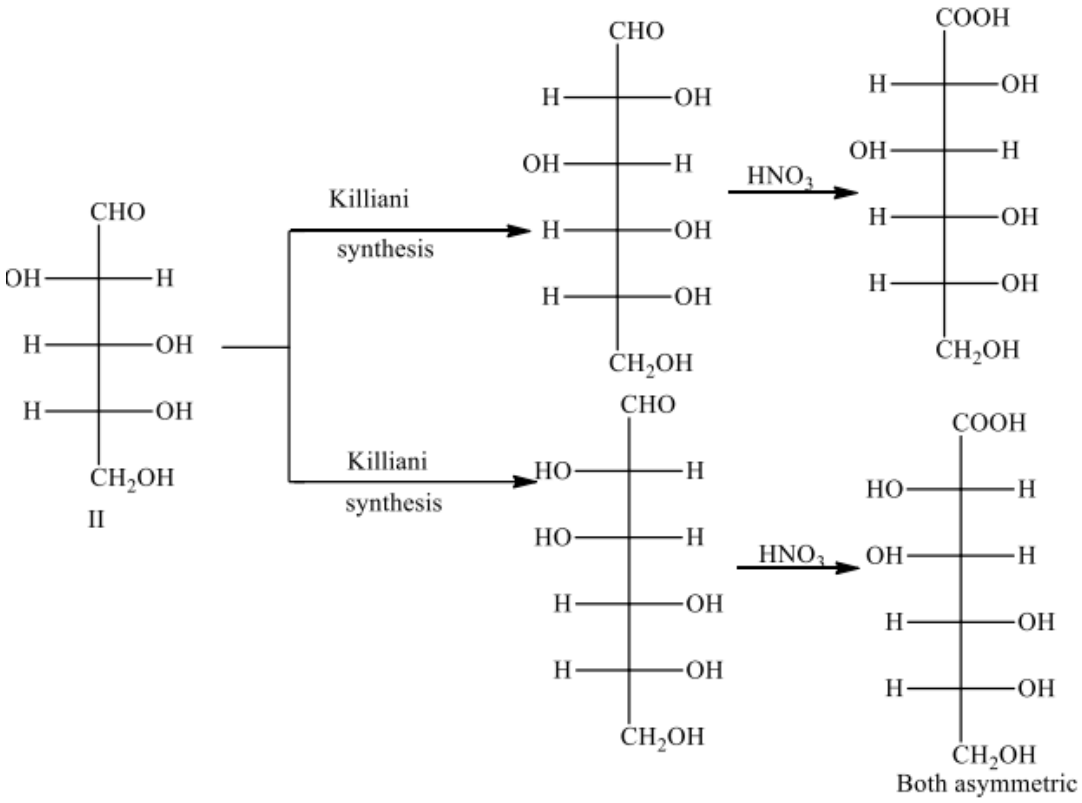
Similar way, each of the two ‘D-tetroses (A &B) yields two ‘D-aldopentoses’. Therefore, a total of four possible ‘D-aldopentoses ‘are obtained:



- D-Arabinose can have either configuration II or IV. Upon oxidation with nitric acid, the terminal CHO and CH_2OH groups of D-arabinose are oxidized, resulting in the formation of two optically active dicarboxylic acids. Configurations II and IV can produce two optically active di-acids, whereas configurations I and III can only yield meso acids,

which possess a plane of symmetry. Hence, ‘D-arabinose’ is determined to be either configuration II or IV.

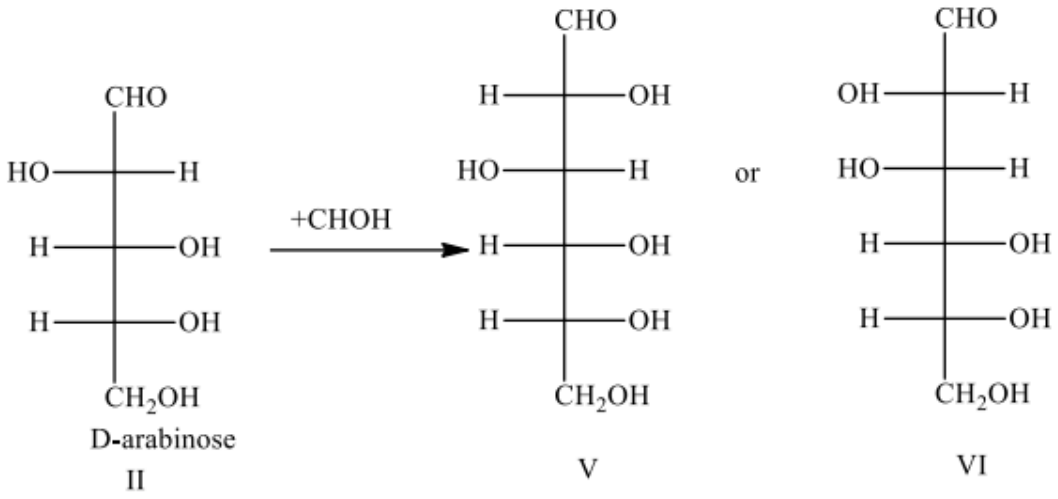
- Confirmation of configuration II for D-arabinose is achieved through the ‘Killiani-Fischer synthesis’, which produces two epimeric aldohexoses, D-glucose and D-mannose. Upon oxidation with nitric acid, these aldohexoses yield two optically active di-carboxylic acids. The theoretical feasibility of this reaction indicates that D-arabinose must possess configuration II, not IV.



Following a similar line of reasoning, it becomes apparent that if ‘D-arabinose’ possessed configuration IV, the two dicarboxylic acids derived from it would consist of one meso and one asymmetric form. Thus, it is established that D-arabinose must have configuration II.

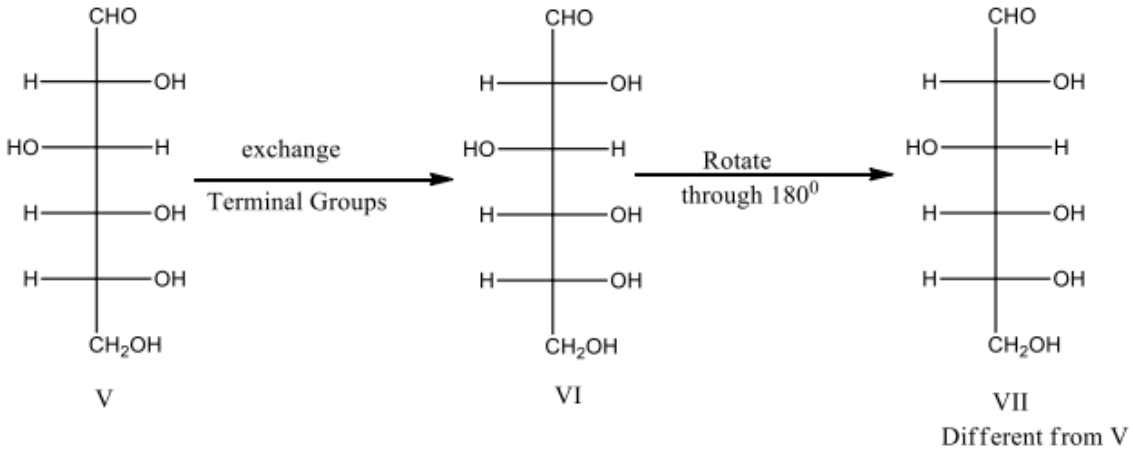
- The Ruff degradation of D-glucose and D-mannose results in the production of D-arabinose in each instance. During the **Ruff degradation**, the -CHOH group positioned below the -CHO group is removed. Therefore, the configuration of the two aldohexoses,

D-glucose and D-mannose, can be inferred by incorporating a new CHOH group below the -CHO group in the structure of D-arabinose's form II.



Therefore configuration of D-glucose is V or VI.

- D-Glucose &L-Glucose yield identical di-carboxylic acids. This implies that the two sugars differ solely in the arrangement of their terminal groups (-CHO and -CH_2OH). Hence, exchanging the terminal groups in D-glucose should theoretically result in a different aldohexose (L-glucose). Let's now consider configuration formulas V and VI (one of which corresponds to D-glucose) from this perspective.



Rotating formula VII through 180 degrees in the plane of the paper results in an aldohexose VII, distinct from V. However, performing a like procedure with formula VI does not yield a dissimilar sugar.

The above arguments indicate that D-glucose possesses the configuration depicted by form V.

13.6. 6 Cyclic structure of D-Glucose

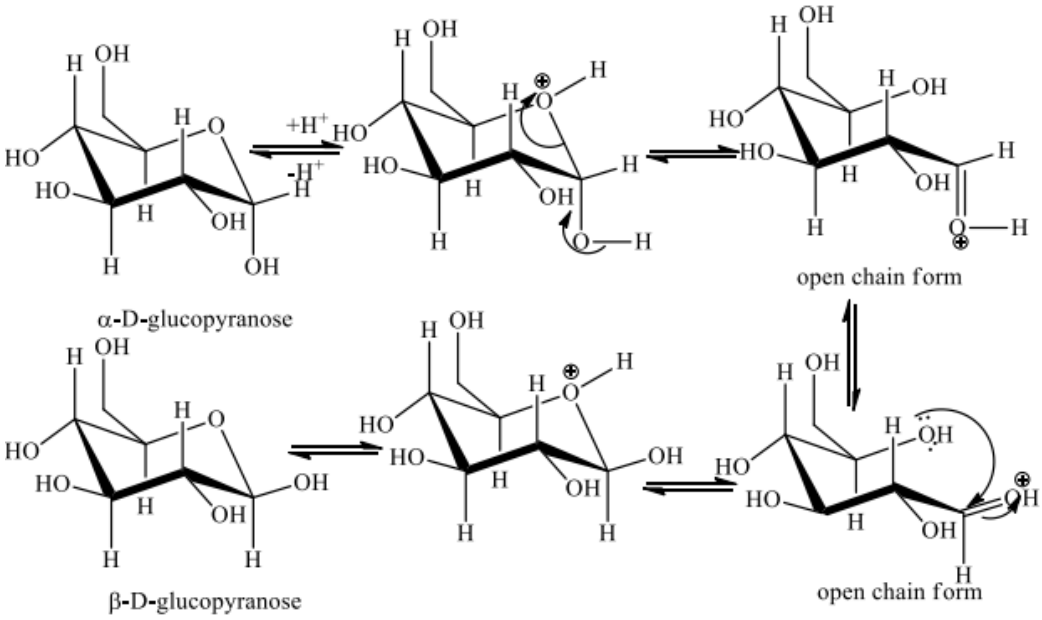
Despite possessing an -CHO group, glucose does not undergo certain representative reactions of aldehydes:

(a) Glucose not forms an addition product with sodium bisulfite.

(b) Glucose does not react with ammonia.

(c) Glucose does not yield positive results in Schiff's test and the 2,4-dinitrophenylhydrazine test, unlike various other aldehydes.

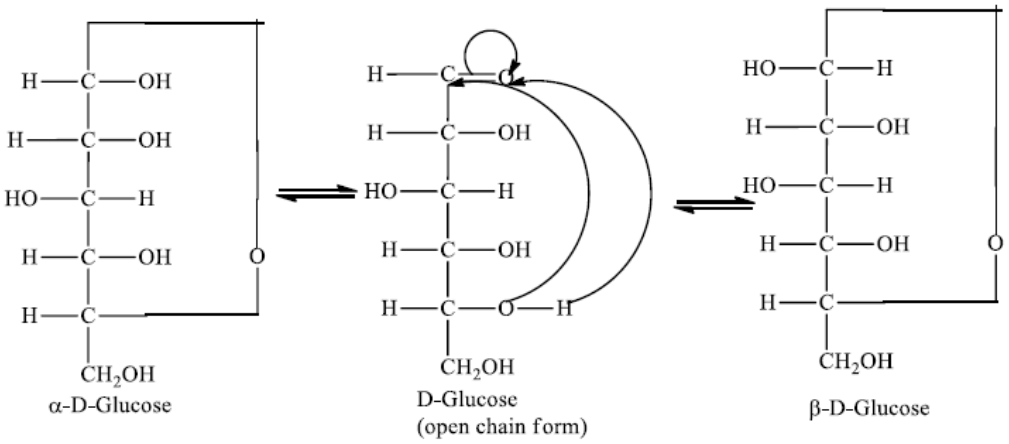
- Glucose after reaction with hydroxylamine forms an oxime, whereas glucose penta-acetate not reacted with the hydroxylamine. This suggests that the -CHO group is not exist in glucose penta-acetate.
- D-glucose exists in two stereoisomeric forms, namely α-D-glucose and β-D-glucose, which exhibit distinct crystalline structures, melting points, and optical rotations. Crystallization of glucose from a concentrated solution at 303 K yields the α-form with a melting point of 419 K and [α]D= +111°, whereas the β-form is obtained from a hot saturated solution at a temperature above 371 K, with a melting point of 423 K and [α]D= +19.2°.
- Mutarotation occurs when either α-D-glucose or β-D-glucose is dissolved in water. Over time, both forms interconvert, resulting in an equilibrium mixture containing approximately 36% α-D-glucose and 64% β-D-glucose. During **mutarotation,** the glucose ring is opened to reveal its free carbonyl form. This process starts as the opposite of hemiacetal (or hemiketal) production. The hydroxyl group at C-5 can approach the carbonyl carbon from the opposite face by rotating 180º degrees around the link to the carbonyl group. The other anomer is then produced by hemacetal production. A combination of bases and acids can accelerate ‘mutarotation’.



Mutarotation Mechanism under acidic conditions

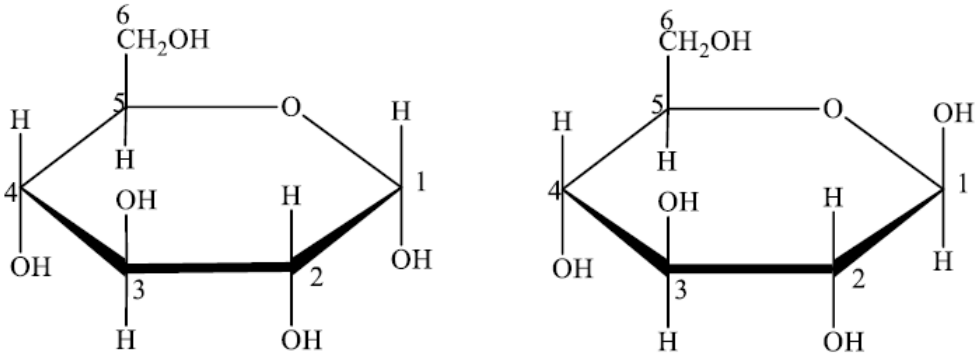
13.6.7 Anomers of glucose

Glucose undergoes cyclization to form a hemiacetal between the -CHO group and the -OH group on the C-5 atom. Consequently, the C-1 carbon becomes asymmetric (chiral), resulting in the formation of two isomers differing in the orientation of H and -OH groups around the C-1 atom. These isomers are known as '**α-D-glucose** and **β-D-glucose'**. The α-D-glucose isomer has the right side -OH group on the while the β-D-glucose isomer has the left side -OH group. These pairs of optical isomers, differing only in configuration around the C1 atom, are termed '**anomers'**. They are not mirror images of each other and thus are not enantiomers. The C-1 carbon is referred to as the anomeric carbon or glycosidic carbon.



Fisher projection formula

The Haworth projection formulae or pyranose structures of D-glucose depict the cyclic form of glucose, specifically the six-membered ring known as a pyranose ring. In these representations, carbon atoms are depicted as corners of a polygon, with oxygen atoms forming bridges between certain carbons. The orientations of substituents (such as -OH groups) are indicated by the direction of their bonds in relation to the ring.For D-glucose, the most stable pyranose form is the α-D-glucopyranose and β-D-glucopyranose. In the Haworth projection, α-D-glucopyranose is depicted with the -OH group on the anomeric carbon (C1) oriented below the ring, while in β-D-glucopyranose, the -OH group on the anomeric carbon is oriented above the ring.



α-D-Glucose
or
α-D-Glucopyranose

β–D-Glucose
or
β-D-Glucopyranose

13.7. Fructose

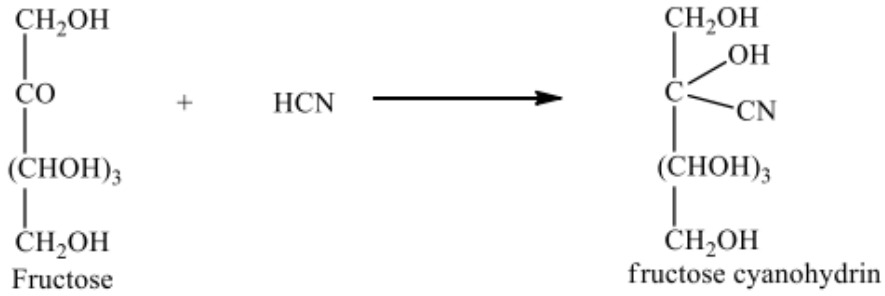
Fructose, also known as fruit sugar, is a simple sugar or monosaccharide that, along with glucose, plays a fundamental role in human nutrition as a source of energy. It is naturally occurring in many fruits, vegetables, and honey, contributing to their sweetness. Chemically, fructose has the same molecular formula as glucose ($C_6H_{12}O_6$), but its structure differs, making it a distinct monosaccharide.

13.7.1 Physical State: Fructose is commonly found as a white, crystalline solid in its pure form. However, in nature, it is often encountered as a syrupy liquid when dissolved in water, such as in fruit juices and honey.

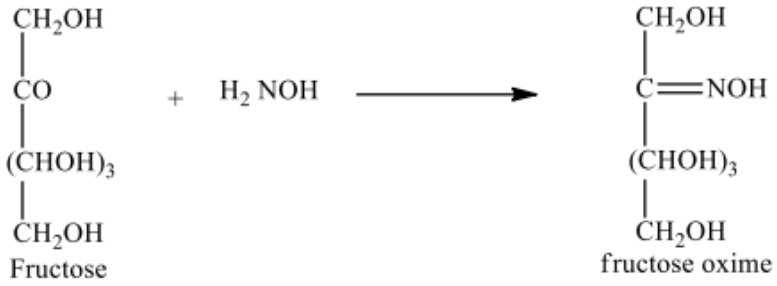
- **Solubility**: Fructose is highly soluble in water due to its hydrophilic (water-attracting) hydroxyl (-OH) groups. This high solubility contributes to its sweet taste and makes it suitable for use as a sweetening agent in various food and beverage products.
- **Sweetness**: Fructose is sweetest naturally occurring sugars, about 1.2 to 1.8 times sweeter than table sugar (sucrose). This high sweetness potency allows for the use of smaller quantities of fructose to achieve the same level of sweetness as sucrose, making it a popular sweetener in the food industry.
- **Melting Point**: The melting point of fructose depends on its crystalline form and purity. Pure fructose typically melts at around 103-105°C (217-221°F). However, impurities and hydration may affect its melting point.
- **Hygroscopicity**: Fructose has hygroscopic properties, meaning it readily absorbs moisture from the atmosphere. This hygroscopic nature can lead to clumping or caking of fructose crystals when exposed to humid environments.
- **Optical Activity**: Fructose is optically active, meaning it rotates the plane of polarized light. Pure fructose has a specific rotation of approximately +92.4° when measured in a polarimeter using sodium D-line light at a wavelength of 589 nanometers.

13.7.2 Some representative chemical properties of Fructose

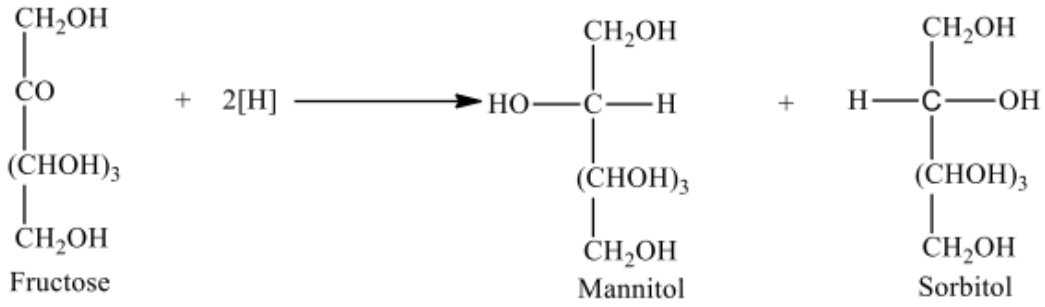
(i) Reaction with HCN



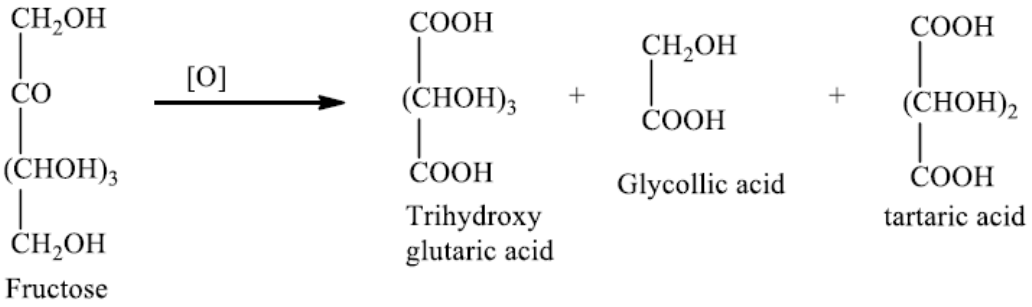
(ii) Reaction with NH_2OH (Hydroxyl amine hydrochloride)



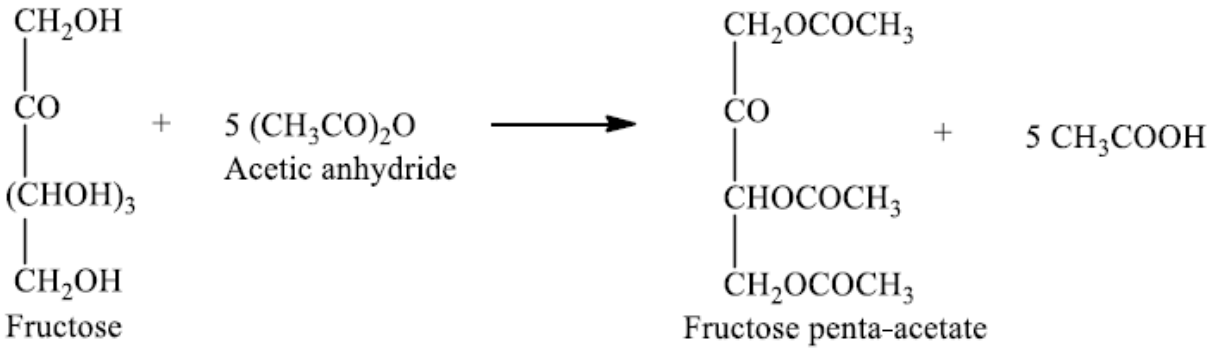
(iii) Reduction



(iv) Oxidation



(v) Acetylation



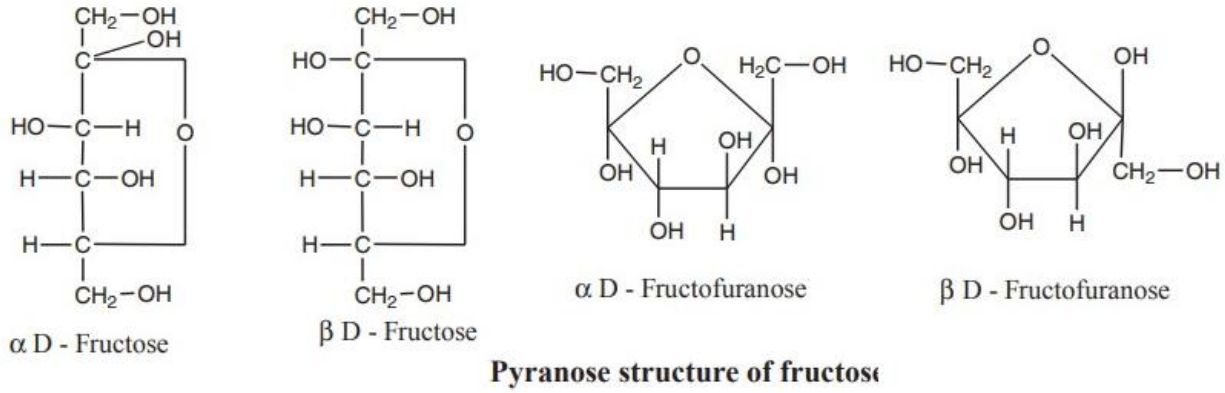
13.7.3Structure of Fructose

- Elemental analysis and molecular weight determination of fructose confirm its molecular formula as $C_6H_{12}O_6$.
- Fructose undergoes reduction to yield sorbitol, which upon further reduction with HI and red phosphorus produces a mixture of n-hexane and 2-iodohexane. This reaction suggests that the six carbon atoms in fructose are arranged in a straight chain.
- Fructose reacts with hydroxylamine, HCN, and phenylhydrazine, indicating the presence of a carbonyl group (either -CHO or C=O) in the fructose molecule.
- Treatment of fructose with bromine water does not elicit a reaction, indicating the absence of an aldehyde group (-CHO).
- Oxidation of fructose with nitric acid yields glycollic acid and tartaric acids, both of which contain fewer carbon atoms than fructose. This observation suggests the presence of a ketonic group at position 2 in the fructose molecule, where the molecule undergoes cleavage during oxidation.

(i) Fischer Projection: In Fischer projection, fructose is depicted as a linear chain of six carbon atoms, with the carbonyl group (C=O) at carbon two. The carbon atoms are numbered from one to six, starting with the carbon adjacent to the carbonyl group. Hydroxyl (-OH) groups are attached to each carbon atom except for the carbonyl carbon. The stereochemistry around each carbon atom can be indicated using wedges (pointing toward the viewer) and dashes (pointing away from the viewer) to represent the spatial arrangement of substituent groups.

(ii) Cyclic Structure of D-Fructose

Fructose exhibits the phenomenon of mutarotation, indicating its ability to exist in two forms: α-fructose and β-fructose. These forms are cyclic in structure and interconvert through the open-chain structure. These pyranose and cyclic structures of '**α-D-fructose and β-D-fructose'** are depicted below**:**



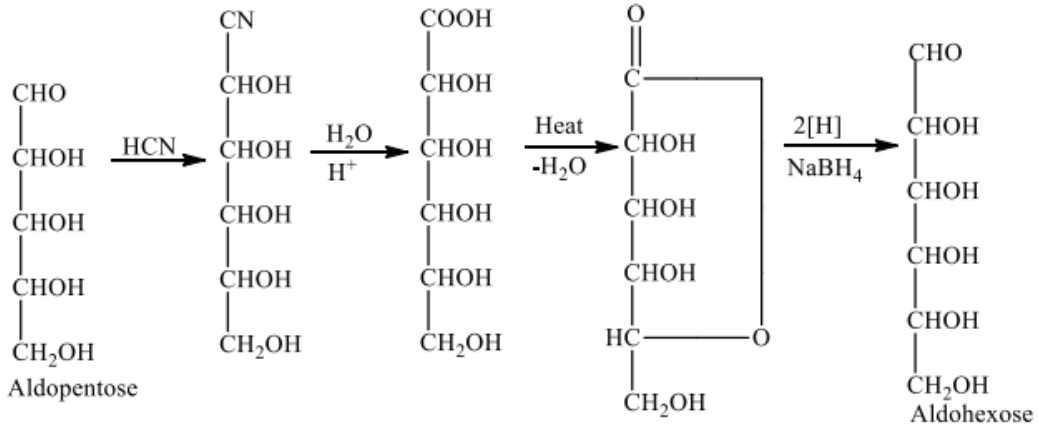
Pyranose structure of fructose

13.8 Chain Ascending and descending of Monosaccharide's

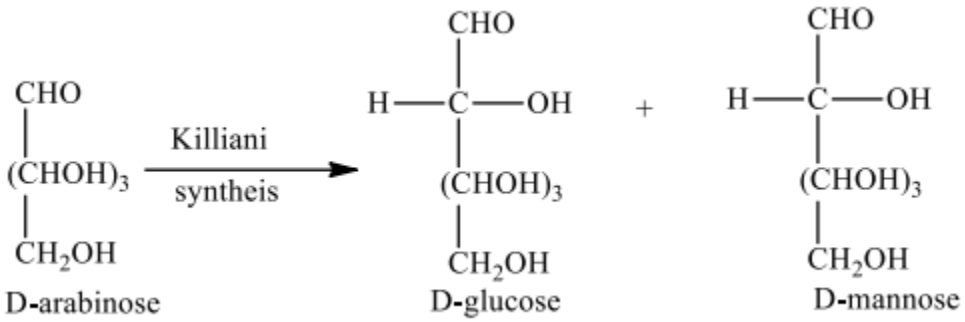
13.8.1 Ascending of Chain

The Killiani-Fisher synthesis extends aldose chains by one carbon atom through the following steps:

- Cyanohydrin formation.
- Hydrolysis of cyanide (-CN) to carboxylic acid (-COOH), yielding aldonic acid.
- Transformation of aldonic acid to lactone *via* heating.
- Lactone reduction using sodium NBH to obtain a upper aldose.



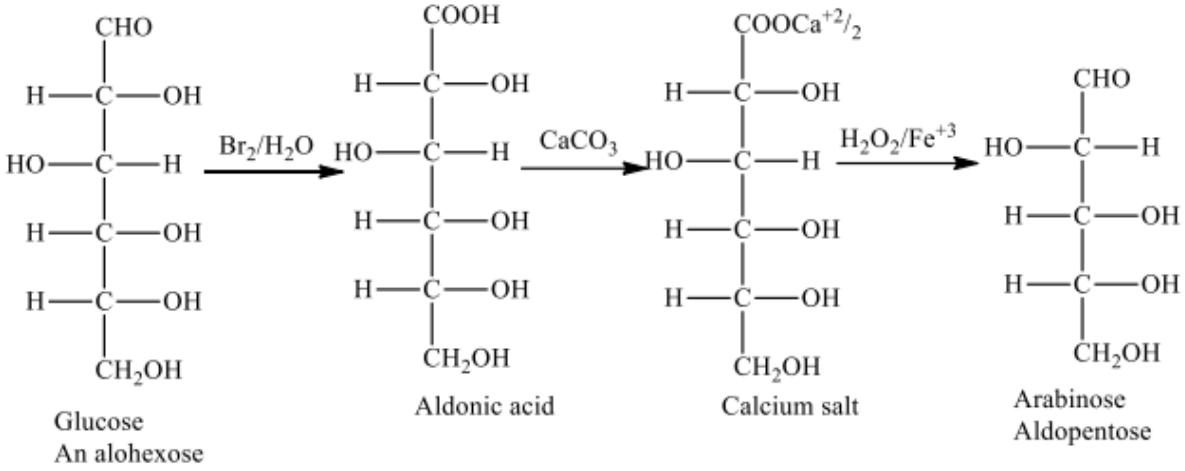
Using the Killiani-Fisher synthesis on D-arabinose yields two aldohexoses: D-glucose and D-mannose. These isomers only vary in their configuration at C-2.



13.8.2 Descending of chain

(i) (Ruff degradation)

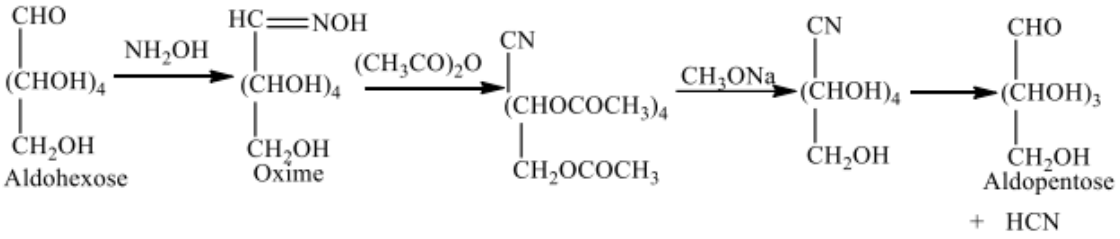
The Ruff degradation is a chemical reaction used to convert aldoses (sugars with an aldehyde group) into shorter-chain aldoses. It involves the oxidation of the primary alcohol group at the end of the sugar chain to a carboxylic acid group, followed by cleavage of the carbon chain to produce a shorter sugar molecule.



(ii) **Wohl's degradation** In Wohl's degradation, the aldose undergoes several steps:

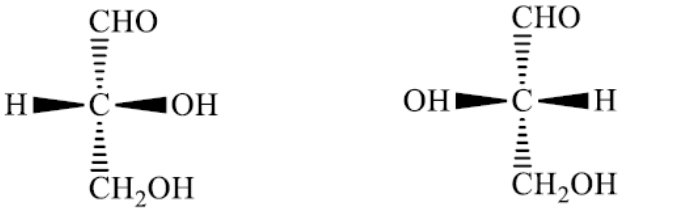
- The aldose is transformed into its oxime by treatment with hydroxylamine.
- The oxime is then treated with acetic-anhydride, leading to dehydration and the formation of a nitrile.

- Next, the nitrile is treated by sodium methoxide.
- The resulting cyanohydrin begins degradation to yield a lower aldose.



13.9. Configuration of Monosaccharide's

In the early stages of organic stereochemistry development, determining the absolute configurations of compounds was challenging. Chemists focused primarily on establishing relative configurations. In 1885, Emil Fischer addressed this challenge by selecting glyceraldehyde (CHO-CHOH-CH_2OH) as a standard compound and arbitrarily fixing its relative configurations. Glyceraldehyde exists in two enantiomeric forms, depicted as:



D(+)-Glyceraldehyde (I)

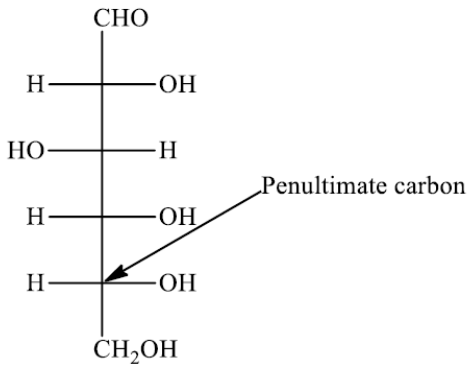
L(-)-Glyceraldehyde (II)

Compound-I was observed to be dextrorotatory, while compound-II was found to be laevorotatory. The distinguishing factor between the configurations of the two compounds lies in the arrangement within their Fisher projection formulas: in compound I, the -H group is positioned on the left-hand side, and the -OH group is situated on the right-hand side. Conversely, in compound II, this arrangement is reversed.

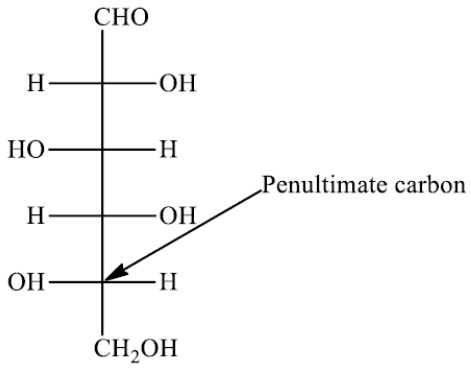
To assign configurations to other compounds, chemists related their configurations to that of **D- or L-glyceraldehyde.**

n 1951, Bijvoet utilized x-ray crystallography to confirm that the arbitrarily assigned configurations of glyceraldehydes indeed corresponded to their precise absolute configurations. Consequently, if the configurations of glyceraldehydes were accurate, then the derived relative configurations of other compounds necessity also represent their correct absolute configurations.

Thus, **D-** and **L-Glyceraldehydes** became pivotal reference molecules for all mono-saccharides. A mono-saccharide whose penultimate carbon (the chiral carbon farthest from the utmost oxidizing end, i.e., -CHO) matches the configuration of D-glyceraldehyde adopts the L-configuration. Similarly, a monosaccharide whose penultimate carbon matches the configuration of '**L-glyceraldehyde'** assumes the **L-configuration**. This principle can be exemplified using the below examples:



D-configuration
(because the configuration at penultimate carbon is the same as that of D-Glyceraldehyde



L-configuration
(because the configuration at penultimate carbon is the same as that of L-Glyceraldehyde

Summary

The study of carbohydrates, particularly monosaccharides like glucose and fructose, involves an in-depth analysis of their physical and chemical properties, shedding light on their fundamental roles in biology and chemistry. Glucose, a six-carbon aldohexose, embodies distinct physical traits. It exists as a crystalline solid, contributing to its role as a common component in various foods such as fruits, vegetables, and honey. Glucose exhibits a sweet taste and is highly soluble in water, facilitating its transportation in biological systems. Chemically, glucose features

multiple functional groups, including an aldehyde group and several hydroxyl (-OH) groups, rendering it reactive in numerous chemical reactions. These reactions include oxidation, reduction, glycosidic bond formation, and mutarotation, illustrating its versatility in biological processes.

Fructose, also known as fruit sugar, is a ketohexose sharing the same chemical formula ($C_6H_{12}O_6$) as glucose. It possesses unique physical properties, notably its heightened sweetness compared to glucose, making it a prevalent natural sweetener in fruits, honey, and certain vegetables. Fructose, like glucose, is soluble in water and exhibits stability under standard conditions. Its ketone functional group distinguishes it from glucose chemically, influencing its reactivity in chemical transformations. Fructose can partake in reactions such as oxidation, reduction, and glycosidic bond formation, albeit with differences attributable to its ketone structure.

Keywords

Monosaccharide: The simplest form of carbohydrates, consisting of a single sugar unit and cannot be hydrolyzed into simpler sugars.

Glucose: A monosaccharide with six carbon atoms that serves as a primary source of energy for living organisms.

Fructose: A monosaccharide regularly found in honey and fruits, sweeter than glucose.

D-glucose: The most common form of glucose found in nature, also known as dextrose.

Anomer: Isomers of monosaccharides that differ only in the configuration about the hemiacetal or hemiketal carbon atom.

Monomer: A molecule that can undergo polymerization to form a polymer.

MCQ

1.Which monosaccharide is commonly referred to as blood sugar?

(A) Glucose (B) Fructose (C) Galactose (D) Sucrose **Answer: (A)**

2. Which functional group does glucose contain?

a) Ketone b) Ester c) Aldehyde d) Carboxyl **Answer: c)**

3. Which monosaccharide possesses a ketone functional group?

a) Glucose b) Fructose c) Galactose d) Ribose **Answer: b)**

4. In which category of carbohydrates do glucose and fructose belong?

a) Disaccharides b) Polysaccharides

c) Monosaccharides d) Oligosaccharides **Answer: c)**

5. Which monosaccharide exhibits a higher sweetness level?

a) Glucose b) Galactose c) Ribose d) Fructose **Answer: d)**

Short Answer Questions

1. Explain the structural difference between glucose and fructose.
2. How does the presence of an aldehyde group in glucose impact its reactivity in chemical reactions?
3. What are anommers
4. Discuss the cyclic structure of D glucose.
5. Discuss the methods for inceasing the carbons in glucose

Unit - 14

Carbohydrates (Disaccharides and Polysaccharides)

Objectives

- Understand the structure and formation of disaccharides, including sucrose, lactose, and maltose.
- Explore the glycosidic bond formation between monosaccharide units in disaccharides and the role of enzymes in these processes.
- Analyze the chemical properties of disaccharides, such as their solubility, sweetness, and susceptibility to hydrolysis.
- Study the structure, function, and diversity of polysaccharides such as starch and cellulose,
- Understand the structural differences between alpha and beta linkages in polysaccharides and their impact on physical properties.

14.1 Introduction of Disaccharides

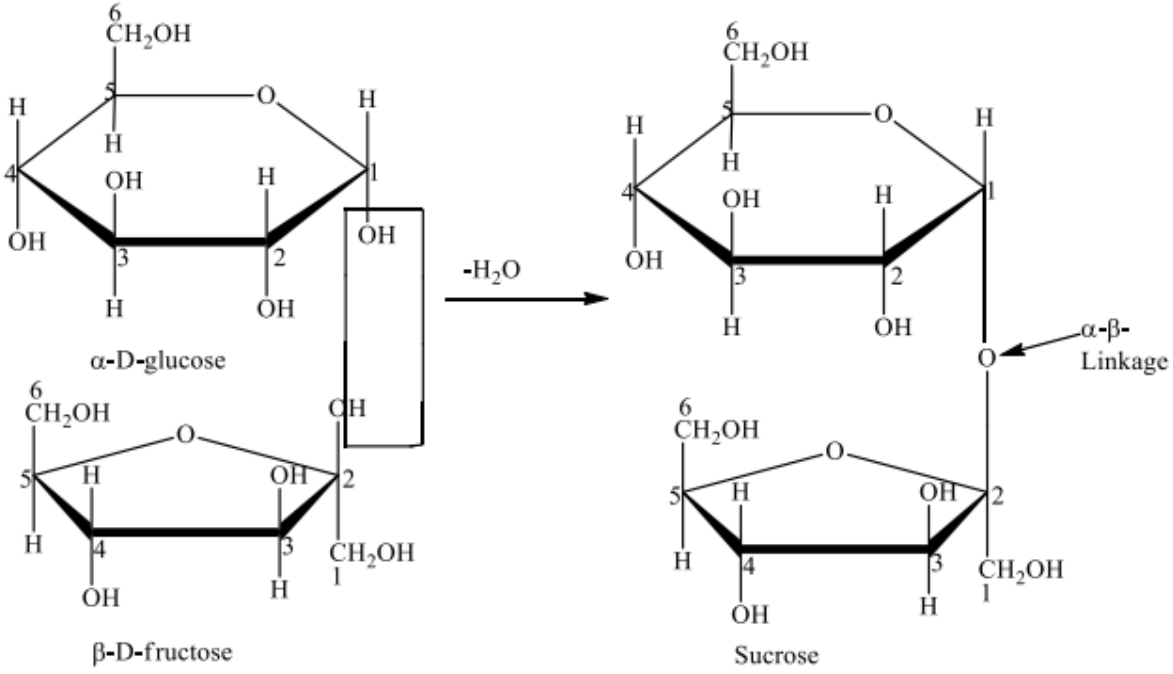
Disaccharides are a type of carbohydrate composed of two monosaccharide units joined mutually by a glycosidic bond. Monosaccharides are simple sugars like fructose, glucose and galactose. When two monosaccharides undergo a condensation reaction, a water molecule is removed, and the remaining molecules form a glycosidic bond, creating a disaccharide.

Some common examples of disaccharides include:

1. **Sucrose:** This is the common table sugar, composed of glucose and fructose units joined together. It's found naturally in many plants, especially sugar cane and sugar beets.
2. **Lactose:** Present in milk and dairy products, lactose consists of one glucose molecule linked to one galactose molecule.
3. **Maltose:** It is formed by the linking of two glucose molecules and is commonly found in germinating grains, malted barley, and some starchy foods.

14.2 Sucrose; Sucrose, commonly known as cane sugar, is one of the most widely used disaccharides in the world. It's a natural sugar found in many plants, with sugarcane and sugar beets being the primary commercial sources. Sucrose plays a significant role in human nutrition

and food industry due to its sweetness, solubility, and versatility in food applications.Chemically, sucrose is a disaccharide composed of one molecule of glucose and one molecule of fructose linked together by a glycosidic bond. Its molecular formula is $C_{12}H_{22}O_{11}$. The glucose and fructose units are joined together by a specific type of glycosidic bond called an α-1,2-glycosidic linkage. This bond is formed through a condensation reaction between the hydroxyl groups of the two monosaccharides, resulting in the elimination of a water molecule.



14.2.1 Significance in Chemical Reactions: Due to its structure lacking a free hemiacetal or hemiketal group, sucrose exhibits several distinctive chemical properties:

- **Does not form an osazone:** Sucrose does not react with phenylhydrazine to form an osazone because osazone formation requires a free hemiacetal or hemiketal group, which is absent in sucrose.
- **Does not reduce Tollen's reagent or Fehling's solution:** Sucrose is classified as a non-reducing sugar because it does not contain a free aldehyde or ketone group. Therefore, it does not undergo oxidation reactions with Tollen's reagent or Fehling's solution.
- **Does not exhibit mutarotation:** Mutarotation is the process where the specific rotation of an optically active compound changes over time when dissolved in water due to the

establishment of an equilibrium between its anomeric forms. Since sucrose lacks a hemiacetal group, it cannot undergo mutarotation.

14.2.2The manufacture of sucrose;

Commonly known as table sugar, involves several steps from harvesting the raw material to refining the final product. Here's an overview of the typical process:

- **Cultivation and Harvesting:** Sucrose is primarily extracted from two sources: sugarcane and sugar beets. These crops are cultivated in suitable climates and harvested once they reach maturity. Sugarcane is typically harvested by cutting the stalks close to the ground, while sugar beets are uprooted from the soil.
- **Extraction of Juice:** After harvesting, the sugarcane stalks are crushed to extract the juice. Similarly, sugar beets are sliced and subjected to a diffusion process to extract the sugar-rich juice. The extracted juice contains a mixture of water, sucrose, and other compounds.
- **Clarification:** The extracted juice undergoes a clarification process to remove impurities such as plant debris, proteins, and minerals. This is often achieved by adding lime (calcium hydroxide) to the juice, which helps to precipitate impurities. The clarified juice is then filtered to remove the precipitates.
- **Concentration:** The clarified juice is concentrated by boiling it in multiple stages in evaporators. This process removes excess water from the juice and increases the concentration of sucrose. The resulting thick syrup is known as raw juice or raw sugar.
- **Crystallization:** The concentrated syrup is seeded with sugar crystals to initiate crystallization. As the syrup cools, sucrose molecules form crystals. The size and quality of the sugar crystals are controlled through the process parameters such as temperature, agitation, and seeding.
- **Separation:** Once crystallization is complete, the sugar crystals are separated from the remaining liquid, known as molasses. This separation is typically achieved using centrifuges, where the sugar crystals are spun off from the molasses.
- **Washing and Drying:** The separated sugar crystals are washed with water to remove any remaining impurities or residual molasses. After washing, the sugar crystals are dried to reduce moisture content and ensure stability during storage and transportation.

- **Refining:** The dried sugar crystals undergo further refining to produce the final refined white sugar. This refining process involves multiple purification steps, including filtration, decolorization with activated carbon, and crystallization under controlled conditions to produce uniform, fine-grained sugar.
- **Packaging:** The refined sugar is packaged into various sizes and formats for distribution and sale. It may be packaged in bags, boxes, or other containers suitable for consumer or industrial use.

14.2.3 Properties of sucrose

Cane sugar, also known as sucrose, possesses several important properties that contribute to its versatility and widespread use in various applications. Here are some key properties of cane sugar:

- **Sweetness:** Cane sugar is known for its sweet taste, making it a popular choice as a sweetener in food and beverages. It is approximately 200 times sweeter than an equal amount of sour or bitter substance, which makes it highly effective in enhancing the flavor of foods.
- **Solubility:** Cane sugar is highly soluble in water, which means it dissolves readily to form a clear, sweet solution. This property makes it easy to incorporate into beverages, syrups, and various culinary preparations.
- **Hygroscopicity:** Cane sugar has hygroscopic properties, meaning it can absorb moisture from the surrounding environment. This property affects its texture and shelf life, as sugar can become clumpy or sticky when exposed to high humidity. Anti-caking agents are often added to commercial sugar products to prevent clumping.
- **Crystalline Structure:** Sucrose naturally forms crystals, which can vary in size depending on the processing method and conditions. The crystalline structure of sugar contributes to its texture in foods like candies and frostings, where fine or coarse sugar crystals are desired for specific applications.
- **Browning and Caramelization:** When heated, cane sugar undergoes caramelization, a chemical reaction that gives rise to its characteristic golden brown color and rich flavor. This property is utilized in the preparation of caramel sauces, candies, and baked goods, where the browning of sugar enhances both taste and appearance.

- **Preservation:** Cane sugar has preservative properties due to its ability to lower water activity in food products. By reducing water availability, sugar helps inhibit microbial growth and prolong the shelf life of jams, jellies, and fruit preserves.
- **Fermentability:** Cane sugar serves as a fermentable substrate for yeast and other microorganisms, making it a crucial ingredient in the production of alcoholic beverages such as wine, beer, and spirits. During fermentation, yeast converts the sucrose in sugar-containing liquids into alcohol and carbon dioxide.
- **Stability:** Cane sugar is chemically stable under normal conditions, meaning it does not readily undergo degradation or react with other substances. This stability contributes to the long-term storage and preservation of sugar-containing products.
- **Non-reducing Sugar:** Sucrose is classified as a non-reducing sugar because it does not contain a free aldehyde or ketone group, which are necessary for reducing sugars to undergo certain chemical reactions such as oxidation with Tollen's reagent or Fehling's solution.

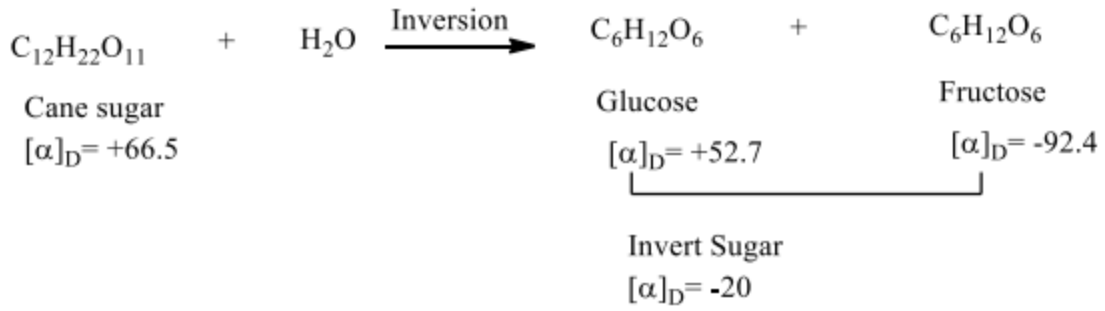
Overall, the unique properties of cane sugar make it an indispensable ingredient in the food and beverage industry, where it contributes to flavor, texture, shelf life, and other essential characteristics of a wide range of products

14.2.3 Hydrolysis of sucrose

Hydrolysis or inversion of sucrose refers to the chemical reaction in which sucrose, a disaccharide composed of glucose and fructose, is broken down into its constituent monosaccharides, glucose, and fructose. This process occurs in the presence of water and a catalyst, typically an acid or enzyme.

Mechanism of Hydrolysis:

- **Acid-Catalyzed Hydrolysis:** In the presence of an acid catalyst, such as hydrochloric acid or sulfuric acid, the glycosidic bond between glucose and fructose in sucrose is cleaved. The acid catalyst provides a proton, which protonates the glycosidic oxygen atom, making it more susceptible to nucleophilic attack by water.



- **Enzymatic Hydrolysis**: In biological systems, the hydrolysis of sucrose is catalyzed by the enzyme sucrase, also known as invertase. Sucrase acts as a biocatalyst, accelerating the hydrolysis of sucrose into glucose and fructose.

$C_{12}H_{22}O_{11}$ (sucrose) + $H_2O \rightarrow C_6H_{12}O_6$ (glucose) + $C_6H_{12}O_6$ (fructose)

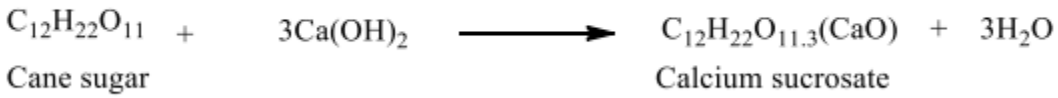
Enzymatic hydrolysis occurs naturally in the human digestive system and is also utilized in industrial processes such as the production of invert sugar.

Sucrose, a naturally occurring disaccharide, exhibits dextrorotatory optical activity, meaning it rotates polarized light to the right. When sucrose undergoes hydrolysis, it breaks down into its constituent monosaccharides: glucose and fructose. Interestingly, while glucose remains dextrorotatory, fructose is laevorotatory, meaning it rotates polarized light to the left. As a result, the resulting mixture of glucose and fructose becomes laevorotatory overall, despite glucose's dextrorotatory nature.This inversion of optical activity, from dextrorotatory to laevorotatory, is termed "inversion," hence the name "invert sugar" for the resulting mixture. The enzyme responsible for catalyzing this inversion process is called invertase.

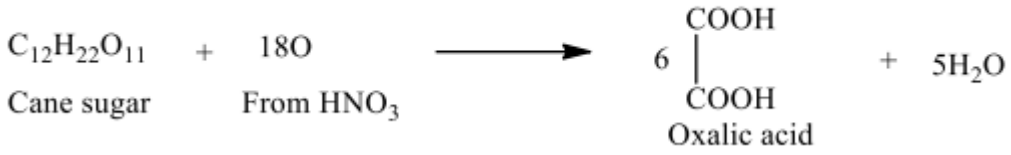
- **Sucrosates Formation**

When sucrose solution reacts with calcium, barium, or strontium hydroxides, the hydroxide ions (OH^-) from the metal hydroxides react with the hydroxyl groups (-OH) of sucrose. This reaction results in the formation of saccharate complexes, where the metal cations are coordinated with the sugar molecules.

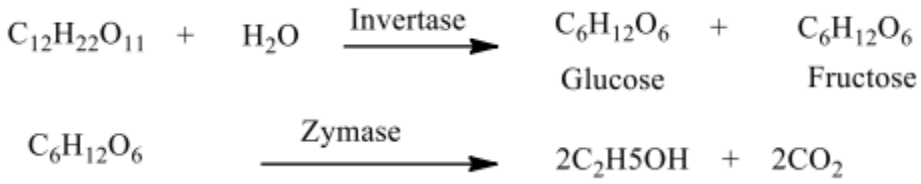
For example, in the case of calcium hydroxide:



- **Reaction with nitric acid; oxidation occurs to provide oxalic acd**

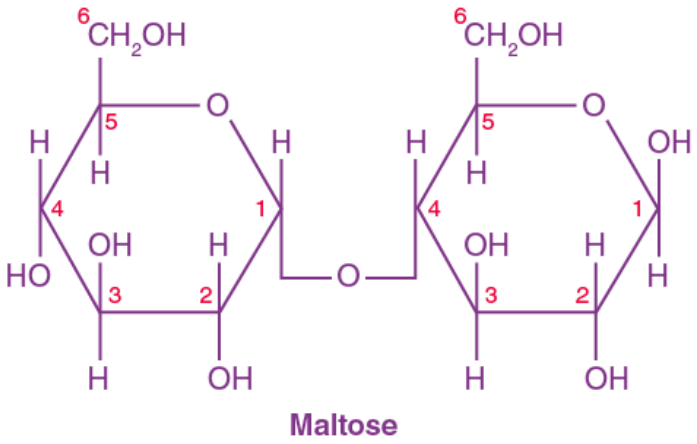


- **Fermentation;** In the fermentation process, yeast plays a crucial role in converting sucrose into ethyl alcohol and carbon dioxide



14.3 Maltose

Maltose is a disaccharide composed of two glucose molecules joined by an α(1→4) glycosidic linkage. This means that the two glucose units are linked together through the first carbon of one glucose molecule to the fourth carbon of the other glucose molecule, with the oxygen bridge forming in an α configuration. Here's a breakdown of the chemistry of maltose. Maltose, also known as malt sugar, has the molecular formula $C_{12}H_{22}O_{11}$. It consists of two glucose units linked together:



Maltose

14.3.1 Properties of Maltose

1. Maltose, a disaccharide comprised of two glucose molecules linked *via* an ‘α(1→4) glycosidic bond’, possesses a free anomeric carbon on one of its glucose units. This configuration allows maltose to undergo mutarotation in solution, resulting in the formation of a dynamic equilibrium between its α and β anomers. Consequently, a solution of maltose contains a mixture of both α-maltose and β-maltose configurations**.**
2. Maltose is classified as a reducing sugar because it contains a free aldehyde group on one of its glucose units. As a reducing sugar, maltose can participate in Maillard reactions, caramelization, and other chemical reactions that involve the reduction of other compounds.
3. Maltose can be hydrolyzed by enzymes such as maltase or α-glucosidase to yield two molecules of glucose. This hydrolysis reaction occurs in the digestive system of humans and other animals, where maltose is broken down into glucose for absorption and energy production
4. Maltose is classified as an oligosaccharide because it consists of two monosaccharide units (glucose molecules) linked together by a glycosidic bond. Its relatively small size compared to polysaccharides allows for easier digestion and absorption in the digestive tract.
5. Maltose is utilized in the food industry as a sweetener, flavor enhancer, and fermentation substrate. It is commonly found in products like candies, malted milk drinks, brewing adjuncts, and specialty food preparations.

6. **Maillard Reaction:** Maltose participates in the ‘Maillard reaction’, a complex series of chemical reactions between ‘amino acids’ and reducing sugars that occur during cooking or heating. This reaction contributes to the browning, flavor, and aroma of cooked foods, such as baked goods and roasted malt in brewing.

14.3.2 Production of Maltose:

Maltose was initially discovered by Augustin-Pierre Dubrunfaut, though his findings were not widely embraced. It wasn't until 1872 that the existence of maltose was definitively confirmed by Cornelius O’Sullivan, an Irish chemist. The term "maltose" derives from "malt," indicating its association with this substance, with the addition of the suffix "-ose," designating its classification as a sugar. As a member of a crucial biochemical series of glucose chains, maltose holds significance. It can be synthesized through the hydrolysis of starch using the enzyme diastase. This process breaks down starch into two glucose molecules. Additionally, maltose can be obtained by subjecting starch to high temperatures in the presence of a potent acid for a duration of time. Within living organisms, the enzyme maltase facilitates this reaction, aiding in the conversion of starch into maltose.

14.3.3 Uses of Maltose

- **Food and Beverage Industry:** Maltose is widely used in the food and beverage industry as a sweetener, flavor enhancer, and fermentation substrate. It provides sweetness to products such as candies, malted milk beverages, and confectioneries. Maltose is also a key component in brewing beer, where it serves as a fermentable sugar during the fermentation process, contributing to alcohol production and flavor development.
- **Baking and Cooking:** Maltose is used in baking and cooking to enhance flavor, texture, and browning. It is added to bread dough to improve crust color and flavor, and it is also used in the production of malt extracts and syrups for flavoring various baked goods, sauces, and desserts.
- **Pharmaceutical Industry:** Maltose is utilized in the pharmaceutical industry as an excipient in tablet formulations, where it acts as a binder, filler, or disintegrant. It is also used in the production of liquid medications and as a sweetening agent in chewable tablets and lozenges.
- **Biotechnology and Fermentation:** Maltose is employed in biotechnology and fermentation processes for the production of enzymes, antibiotics, organic acids, and biofuels. It serves as

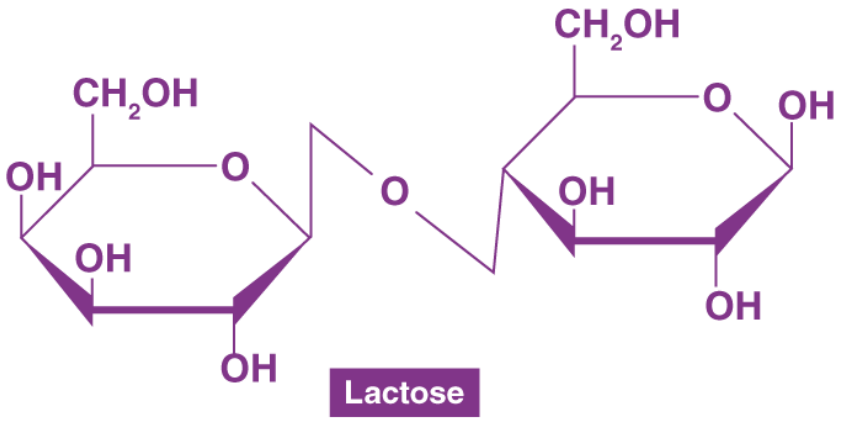
a carbon source for microbial fermentation, enabling the synthesis of various valuable products.

- **Laboratory Applications:** Maltose is used in laboratory settings for biochemical and molecular biology experiments. It is utilized as a substrate for enzyme assays, carbohydrate metabolism studies, and as a culture medium component for microorganism growth.

14.4 Lactose

Lactose is a disaccharide sugar composed of two monosaccharides, galactose and glucose, linked together by a 'β(1→4) glycosidic' bond. It is commonly found in milk and dairy products, where it serves as the primary carbohydrate source. Lactose is notable for its specific chemical and nutritional properties, making it an important component in both food and pharmaceutical industries. Here's a closer look at lactose**:**

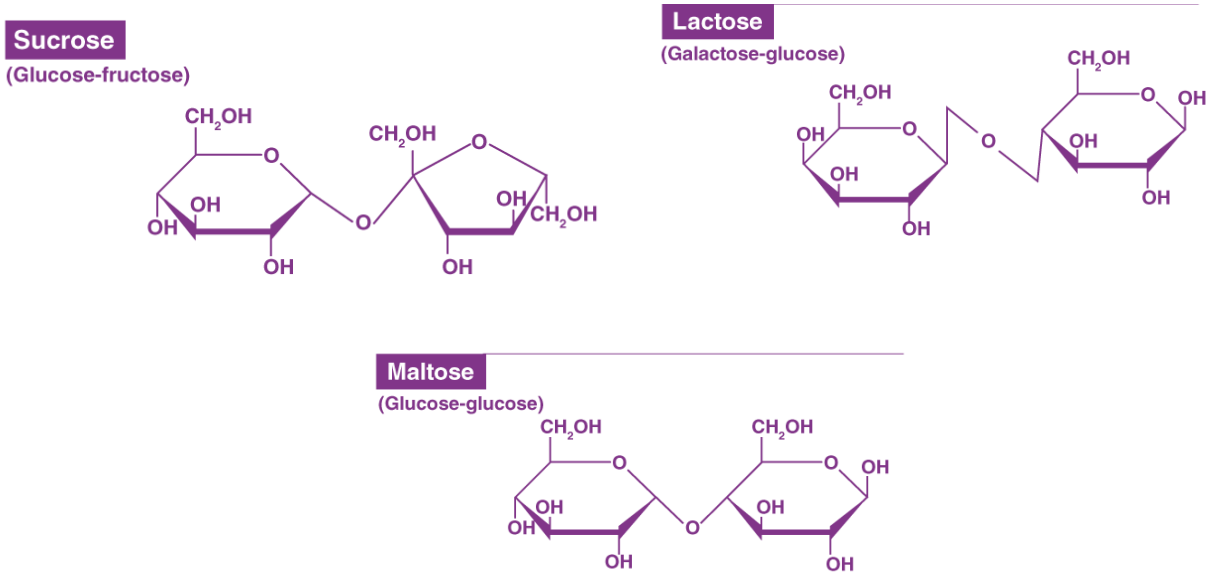
- Lactose has the molecular formula $C_{12}H_{22}O_{11}$ and consists of one molecule of glucose and one molecule of galactose linked together by a β-glycosidic bond.
- The β-glycosidic bond joins the hydroxyl group on the first carbon of glucose with the hydroxyl group on the fourth carbon of galactose.



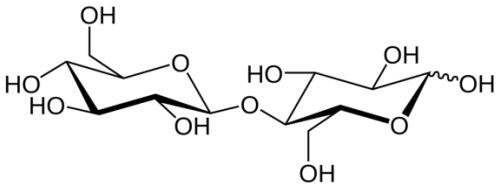
14.5 Difference between, Lactose Maltose and Sucrose

Maltose, sucrose, and lactose are all types of disaccharides, which are composed of two monosaccharide units. While these sugars share similarities in being composed of glucose units, they differ in their additional monosaccharide components.

In the Maltose two glucose moiety, in sucrose one glucose and one fructose molecule and on Lactose, one glucose molecule and galactose links to each other.



14.6 Cellobiose; With the chemical formula $(C_6H_7(OH)_4O)_2O$, is a disaccharide classified as a reducing sugar due to its ability to act as a reducing agent. Its chemical structure results from the condensation of two β-glucose molecules, forming a β(1→4) glycosidic bond. This compound possesses eight free alcohol (OH) groups, one acetal linkage, and one hemiacetal linkage, fostering robust 'inter- and intramolecular hydrogen' bonds. As a result, it appears as a white solid.



Obtaining cellobiose involves enzymatic or acidic hydrolysis of cellulose and cellulose-rich materials like jute, cotton, or paper. Interestingly, cellobiose serves as an indicator carbohydrate for conditions like 'Crohn's disease and malabsorption syndrome'.

Through treatment with acetic anhydride and sulfuric acid, cellobiose can be modified to produce cellobiose acetoacetate. This derivative loses its hydrogen bond donor property while retaining

its ability to accept hydrogen bonds, and it exhibits increased solubility in nonpolar organic solvents.

14.7 Polysaccharides

These are neutral polymeric compounds formed by the linkage of hundreds or even thousands of monosaccharide units via glycosidic bonds. They share the general formula $(C_5H_{10}O_5)n$, where 'n' represents a very large value. These compounds, typically colorless and tasteless, exhibit insolubility in water. They serve crucial functions in both plant and animal life, acting as storage forms of food and providing structural support.

Polysaccharides are primarily composed of pentoses or hexoses. The significant ones include cellulose, starch, **glycogen, and dextrins.**

14.7.1 Starch

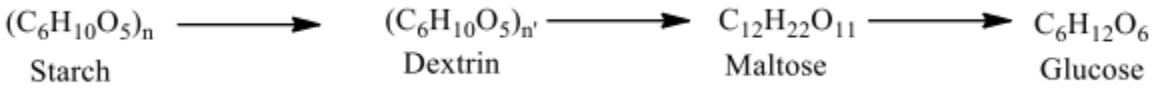
Starch is a polysaccharide carbohydrate composed of glucose units linked together by glycosidic bonds. It serves as the primary storage form of energy in plants, fulfilling a role analogous to glycogen in animals. Starch is abundant in staple foods such as grains, potatoes, and legumes, making it a crucial component of the human diet. Some properties of starch are as

- **Appearance:** Starch typically appears as a fine white powder or granules. The size, shape, and appearance of starch granules vary depending on the plant source (e.g., wheat, corn, potatoes) and processing methods.
- **Solubility:** Starch is insoluble in cold water but can swell and absorb water when heated, forming a colloidal dispersion or gel. The degree of solubility depends on factors such as temperature, particle size, and the presence of other substances.
- **Gelatinization:** When starch is heated in the presence of water, the hydrogen bonds between starch molecules break, allowing water molecules to penetrate the granules. This process, known as gelatinization, causes the starch granules to swell and absorb water, resulting in the formation of a viscous paste or **gel.**

14.7.2 Chemical Reactions

(i) It transforms into dextrin at temperatures between 200 and 2500. Higher temperatures cause charring to occur.

(ii) When starch was cooked with weak acids, glucose was eventually produced.



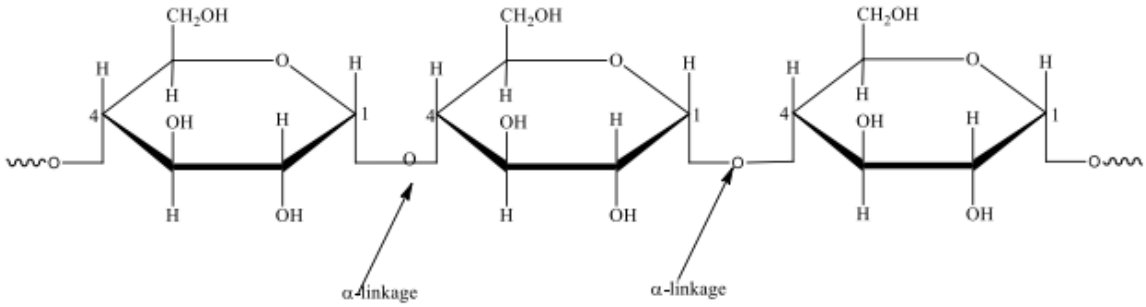
Maltose is produced when the enzyme diastase is hydrolyzed.

(iii) When an iodine solution is added, the starch solution becomes blue. When heated, the blue color fades; when cooled, it returns. Actually, amylase is the enzyme that gives iodine its color; amylopectin provides iodine its reddish-brown shade.

(iv) A non-reducing sugar is starch. Neither 'Fehling's solution nor Tollen's reagent' are diminished by it. Additionally, it does not form an osazone, indicating that all of the glucose units' (C1) hemiacetal hydroxyl groups are bound by glycosidic connections and are not free.

The polymer of α-D-glucose known as starch is made up of two parts: 80–85% amylopectin and 15–20% amylase.

(i) Amylase The farction is white and soluble. It's a linear polymer of glucose α-D. As indicated below, it has between 200 and 1000 α-D-glucose units, which are connected to one another by α-glycosidic linkage involving 'C-1' of one glucose and 'C-4' of the subsequent one.



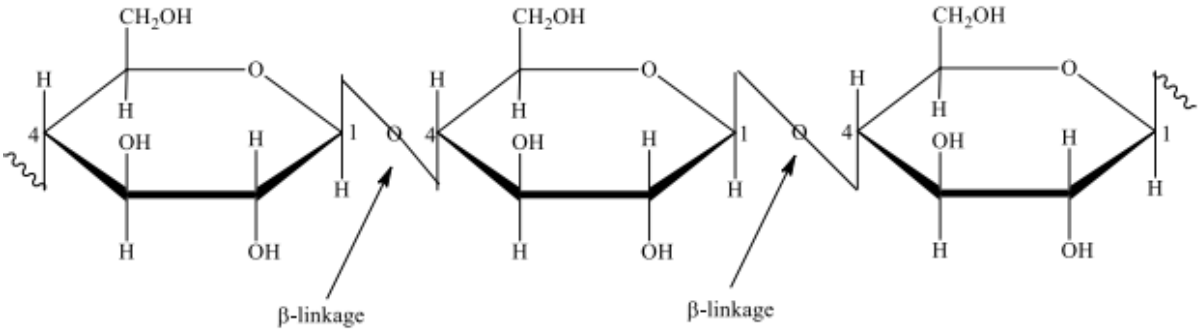
Amylose

(ii) Amylopectin. It is an insoluble fraction in water. It is a highly branching chain polymer that does not turn blue when exposed to iodine. It is composed of many short chains, each containing 25–30 D-glucose units. In this instance, α-linkages connecting C-1 of one α-D-glucose unit and C-4 of the other comprise the primary chain. C-1-C-6 α-linkage connects the C-1 of the terminal

glucose in each chain to the C-6 of the other glucose unit in the subsequent chain. A very branching structure results from this.

14.8 Cellulose

Cellulose is a 'polysaccharide carbohydrate' consisting of linear chains of β-glucose units linked together by β(1→4) glycosidic bonds. It is the main structural component of the cell walls in plants, providing strength, rigidity, and structural support to plant cells and tissues.



Cellulose

Structure D-glucose units make up the straight chain carbohydrate known as cellulose. β-glycosidic bonds connect the C-1 of one glucose unit to the C-4 of the subsequent glucose unit, forming these units. There are 300–2500 D-glucose units per gram of cellulose.

14.8.1Manufacture of Cellulose

97% of cotton wool is made of cellulose. After removing the waxes and lipids that come with it, it is prepared for usage. Wood provides the cellulose needed to make paper. By digesting the wood chips under pressure using a calcium hydrogen sulfite solution, lignin and other resinous compounds that are present along with cellulose are eliminated. The cellulose separates into insoluble fibers that need to be dried, bleached, and cleaned with water.

14.8.2 Some properties of Cellulose

Appearance: Cellulose is typically found in the form of long, fibrous strands or fibers. These fibers may be bundled together to form larger structures such as plant cell walls or textiles.

Texture: Cellulose fibers have a fibrous texture and are often described as being tough and rigid. They contribute to the firmness and texture of plant tissues.

Solubility: Cellulose is insoluble in water and most organic solvents due to the strong hydrogen bonds between its glucose units. This insolubility contributes to its structural integrity and stability.

Strength: Cellulose is known for its high tensile strength, making it one of the strongest natural fibers. This strength is due to the arrangement of cellulose molecules in a parallel orientation within cellulose fibers, which allows for strong intermolecular hydrogen bonding.

Thermal Stability: Cellulose has good thermal stability and can withstand high temperatures without decomposing. This property makes cellulose suitable for various industrial applications, including papermaking and textile manufacturing.

Hydrolysis; D-glucose is produced when diluted acids are heated to hydrolyze cellulose. In cases when hydrolysis is not completed, cellobiose is generated.
Digestion enzymes called cellulases are found in cattle, goats, and other ruminants. These enzymes hydrolyze cellulose to produce glucose. As so, these can consume cellulose directly. Because they do not have the essential digestive tract enzymes, humans and many other mammals are unable to utilise cellulose as food.

Summary

Disaccharides, composed of two units of monosaccharides joined by glycosidic linkage, are the carbohydrates that, upon hydrolysis, yield two same or different monosaccharides. In contrast, polysaccharides are neutral polymeric compounds wherein hundreds or even thousands of monosaccharide units are linked together by glycosidic linkages.

Keywords

Disaccharide: A carbohydrate formed by the condensation of two monosaccharides with the elimination of a molecule of water.

Sucrose: A disaccharide composed of glucose and fructose units, commonly known as table sugar.

Lactose: A disaccharide composed of glucose and galactose units, found in milk.

Maltose: A disaccharide composed of two glucose units, formed during the digestion of starch.

Glycosidic Bond: The covalent bond formed between two monosaccharides by a dehydration reaction.

Starch: A polysaccharide composed of glucose units, used by plants for energy storage.

Cellulose: A polysaccharide composed of glucose units, forms the structural component of plant cell walls.

MCQ

1. What is the chemical bond that joins two monosaccharides to form a disaccharide?

A) Ester bond

B) Glycosidic bond

C) Peptide bond

D) Ionic bond **Answer: B) Glycosidic bond**

2. Which of the following is NOT a disaccharide?

A) Sucrose

B) Maltose

C) Lactose

D) Starch **Answer: D) Starch**

3. Lactose is composed of which two monosaccharides?

A) Glucose and fructose

B) Glucose and galactose

C) Glucose and maltose

D) Glucose and sucrose **Answer: B) Glucose and galactose**

4. What is the main structural difference between starch and cellulose?

A) Starch is branched, while cellulose is linear.

B) Starch is linear, while cellulose is branched.

C) Starch is composed of glucose, while cellulose is composed of fructose.

D) Starch is found in animals, while cellulose is found in plants.

Answer: A) Starch is branched, while cellulose is linear.

5. Which of the following is a component of plant cell walls that humans cannot digest?

A) Starch

B) Maltose

C) Cellulose

D) Sucrose **Answer: C) Cellulose**

Short Answer question

1. Describe the formation of a disaccharide.
2. What are the main differences between sucrose, lactose, and maltose?
3. Compare and contrast starch and cellulose in terms of structure and function.
4. Differentiate between amylose and amylopectin in terms of structure
5. What is cellulose, and where is it found in nature?

REFERENCES

1. Castellan, G. W. (2004), Physical Chemistry, Narosa.
2. Kapoor, K.L. (2015),A Textbook of Physical Chemistry, Vol 1, 6th Edition, McGraw Hill Education.
3. Kapoor, K.L.(2015), A Textbook of Physical Chemistry, Vol 2, 6th Edition, McGraw Hill Education.
4. B.R. Puri, L.R. Sharma, M.S. Pathania, (2017),Principles of Physical Chemistry, Vishal Publishing Co.
5. Finar, I. L. Organic Chemistry (Volume 1 & 2), Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
6. Morrison, R. N.; Boyd, R. N. Organic Chemistry, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education). Page 12 of 96 B.Sc. Physical Science
7. Bahl, A; Bahl, B. S. (2012), Advanced Organic Chemistry, S. Chand.
8. Mc Murry, J.E. Fundamentals of Organic Chemistry, 7th Ed. Cengage Learning India Edition, 2013.
9. Sykes, P. A Guidebook to Mechanism in Organic Chemistry, Orient Longman, New Delhi.