

DIRECTORATE OF DISTANCE & CONTINUING EDUCATIONS

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI – 627012

OPEN AND DISTANCE LEARNING(ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023 – 2024)



**M.Sc. CHEMISTRY
COURSE MATERIALS
ALLIED CHEMISTRY – II
JECH41**

By
S. NAGARAJAN
Assistant Professor
Department of Chemistry
Manonmaniam Sundaranar University
Tirunelveli 627012

UNIT-1

Co-ordination Chemistry and Water Technology

Co-ordination Chemistry:

Coordination compounds are formed when central metal ions are surrounded by molecules or ions called ligands through coordinate covalent bonds. These compounds are important in both biological and industrial chemistry. The central metal ion acts as a Lewis acid, and the ligands, which donate electron pairs, act as Lewis bases. Ligands can be neutral (like H_2O , NH_3) or negatively charged (like Cl^- , CN^-). They can also be monodentate (donating one pair), bidentate (two pairs), or polydentate (many pairs, such as EDTA). The coordination number of a complex is the number of ligand donor atoms attached to the metal ion. Complex ions are often enclosed in square brackets, and any counterions are written outside. Chelation is a special case where a ligand forms multiple bonds with the metal ion, enhancing stability. The coordination sphere includes the central metal and the attached ligands. These compounds have varied applications in medicine, catalysis, and material science.

IUPAC Nomenclature of Coordination Compounds

The IUPAC system provides a standard way of naming coordination compounds. The naming starts with the ligands (in alphabetical order), followed by the central metal. Neutral ligands retain their names (e.g., NH_3 is ammine, H_2O is aqua), while anionic ligands end with ‘-o’ (e.g., Cl^- becomes chloro, CN^- becomes cyano). Prefixes such as mono-, di-, tri-, tetra- denote the number of each ligand present. The oxidation state of the central metal is indicated by Roman numerals in parentheses. If the complex is an anion, the metal's name ends in ‘-ate’ (e.g., ferrate for iron). For example, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is named hexaamminecobalt(III) chloride, and $[\text{CuCl}_4]^{2-}$ is tetrachlorocuprate(II). This naming helps chemists clearly identify

the structure and composition of complex compounds and is essential for understanding coordination chemistry.

Werner's Theory

Werner's theory, proposed by Alfred Werner in 1893, laid the foundation of modern coordination chemistry. He introduced the idea of primary and secondary valencies. The primary valency corresponds to the oxidation state and is satisfied by anions like Cl^- or NO_3^- . The secondary valency is the coordination number and is satisfied by ligands, which form coordinate bonds. According to Werner, secondary valencies are directional, leading to specific geometries such as octahedral or tetrahedral. For example, in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, cobalt exhibits three primary valencies (Cl^- ions) and six secondary valencies (NH_3 ligands). He explained the different isomers of complexes and confirmed his ideas by isolating and analyzing compounds. His work earned him the Nobel Prize in Chemistry in 1913. Werner's theory marked a turning point in understanding the structure and bonding of complex compounds.

Effective Atomic Number (EAN) Rule

The Effective Atomic Number (EAN) rule, proposed by Sidgwick, helps predict the stability of coordination compounds. According to the EAN rule, the total number of electrons around the central metal ion (including those from ligands) should match the atomic number of the nearest noble gas. The EAN is calculated by adding the metal's atomic number minus its oxidation state to the electrons donated by the ligands. For example, in $[\text{Ni}(\text{CO})_4]$, nickel has an atomic number of 28 and is in the zero-oxidation state. CO donates two electrons each, giving 8 electrons in total. The EAN becomes $28 + 8 = 36$, equal to krypton, a noble gas. Complexes satisfying the EAN rule are generally stable, although exceptions exist. This rule is particularly useful in predicting the geometry and magnetic properties of coordination compounds.

Pauling's Theory (Valence Bond Theory)

Pauling's theory is based on the Valence Bond Theory (VBT), which explains bonding in coordination complexes through hybridization. The central metal ion uses empty atomic orbitals to accept electron pairs from the ligands. Depending on the ligands and the metal's oxidation state, different types of hybridization occur. For example, d^2sp^3 hybridization gives an octahedral geometry, while dsp^2 leads to square planar geometry. This theory also explains the magnetic properties of complexes. Strong field ligands (like CN^-) cause pairing of electrons, leading to low-spin (diamagnetic) complexes, while weak field ligands (like Cl^-) lead to high-spin (paramagnetic) complexes. For example, $[Ni(CN)_4]^{2-}$ is square planar and diamagnetic, whereas $[NiCl_4]^{2-}$ is tetrahedral and paramagnetic. Though VBT is useful, it does not explain color or spectra, which are better handled by Crystal Field Theory.

Applications to Selected Complexes

Let us look at three important coordination compounds: $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$, and $[Co(CN)_6]^{3-}$. In $[Ni(CO)_4]$, nickel is in zero oxidation state, forming a tetrahedral, diamagnetic complex due to CO being a strong field ligand. This compound is volatile and is used in nickel purification (Mond process). In $[Ni(CN)_4]^{2-}$, nickel is in +2 oxidation state, and CN^- is a strong field ligand, leading to a square planar, diamagnetic structure. $[Co(CN)_6]^{3-}$ is an octahedral complex where cobalt is in the +3 oxidation state. Due to the strong field CN^- ligands, it forms a low-spin, diamagnetic complex. These examples highlight how ligand strength and oxidation state influence geometry, magnetic behavior, and applications of coordination compounds.

Chelation

Chelation is the process where a single ligand forms multiple bonds with a central metal ion, resulting in a ring-like structure. Multidentate ligands like

ethylenediamine (en) and EDTA can bind through two or more donor atoms. These ligands are also called chelating agents. Chelate complexes are generally more stable than their monodentate counterparts due to the chelate effect, which is both thermodynamic and kinetic in nature. This increased stability arises from the entropy gain and the difficulty of breaking multiple bonds simultaneously. Chelating agents are widely used in medicine (e.g., EDTA to treat lead poisoning), agriculture (as micronutrient carriers), and analytical chemistry (in titrations). In biological systems, chelation is essential—for instance, hemoglobin chelates iron, and chlorophyll chelates magnesium. Thus, chelation is a vital concept with numerous practical applications.

Biological Role of Hemoglobin and Chlorophyll

Coordination compounds play a crucial role in biological systems. Hemoglobin, the red pigment in blood, contains iron at the center of a porphyrin ring. This iron ion coordinates with nitrogen atoms in the ring and binds oxygen reversibly, facilitating oxygen transport in the body. Chlorophyll, the green pigment in plants, contains magnesium at the center of a similar porphyrin-like ring. It plays a central role in photosynthesis by capturing sunlight and converting carbon dioxide and water into glucose. These biological complexes show the importance of metal-ligand interactions in life processes. Both systems involve chelation and exhibit complex stability and functionality due to their specific geometry and ligand environment. Understanding these examples helps highlight the relevance of coordination chemistry in health and environment.

Applications in Qualitative and Quantitative Analysis

Coordination compounds are widely used in both qualitative and quantitative chemical analysis. In qualitative analysis, the color changes of complex ions help identify specific metal ions. For example, the deep blue color of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ confirms the presence of Cu^{2+} ions. In quantitative analysis, complexometric

titrations involve the use of ligands like EDTA to determine the concentration of metal ions. The endpoint is detected using indicators such as Eriochrome Black T, which changes color when the metal ion is completely complexed. Such titrations are used to assess water hardness, metal content in alloys, and even trace metals in biological fluids. The specificity and stability of complexes make them ideal for accurate and selective analysis in various fields, including environmental testing, medicine, and industry.

Hardness of Water

Hardness of water refers to the presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water. Hard water does not lather well with soap and causes scaling in boilers and pipes. Hardness is categorized into temporary and permanent. Temporary hardness is caused by bicarbonates of calcium and magnesium, which can be removed by boiling. Permanent hardness is due to chlorides and sulfates, and requires chemical treatment. Hard water affects industrial processes, laundry, and even the taste of food and beverages. Measuring and treating hardness is essential for domestic and industrial water supply systems. The total hardness is usually expressed in parts per million (ppm) of CaCO_3 equivalent. Water softening techniques are employed to remove these ions to make water suitable for use.

Water Hardness Scale		
mg/L & ppm as CaCO_3	dH	Classification
0 - 75	0 - 4	Soft
75 -150	4 - 8.5	Slightly Hard
150 - 300	8.5 - 17	Hard
300+	17+	Very Hard

Determination of Hardness (EDTA Method)

The EDTA method is a widely used titrimetric technique for determining the hardness of water. EDTA (ethylenediaminetetraacetic acid) is a strong complexing agent that binds with Ca^{2+} and Mg^{2+} ions in a 1:1 ratio. The procedure involves titrating the water sample with standard EDTA solution in the presence of Eriochrome Black T indicator. Initially, the solution appears wine red due to the metal-indicator complex. As EDTA binds the metal ions, the color changes to blue at the endpoint. The volume of EDTA used is directly proportional to the concentration of Ca^{2+} and Mg^{2+} in the sample. This method is simple, reliable, and gives accurate results, making it suitable for laboratory and field testing of water hardness.

Zeolite Method

The Zeolite method is an ion-exchange process used to soften hard water. Zeolites are naturally occurring or synthetic sodium aluminosilicates that exchange sodium ions (Na^+) with calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in hard water. When hard water passes through the zeolite column, hardness-causing ions are replaced by Na^+ , converting hard water into soft water. Over time, the zeolite becomes saturated and is regenerated using a concentrated sodium chloride (NaCl) solution. This method is widely used in industrial and domestic water softening units. It is economical, efficient, and continuous, with the added benefit of easy regeneration. However, it does increase the sodium content of water, which may not be desirable for all applications

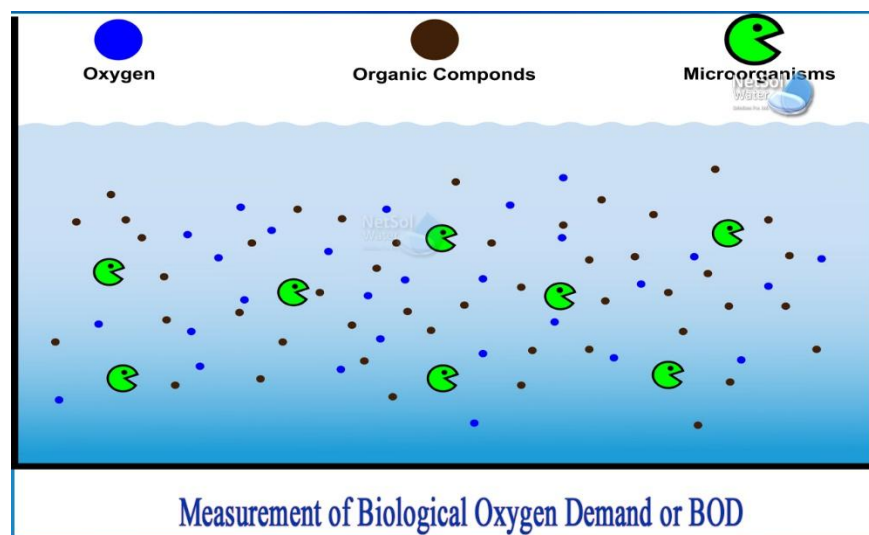
Water Purification Techniques

Water purification is essential for safe drinking and industrial use. The main purification techniques include sedimentation, filtration, disinfection, and advanced methods like reverse osmosis (RO). Sedimentation allows heavy particles to settle under gravity. Filtration removes suspended impurities using sand or membrane

filters. Disinfection, typically with chlorine, ozone, or UV light, kills harmful microorganisms. Reverse osmosis uses a semipermeable membrane to remove dissolved salts and organic molecules. Each method targets specific contaminants and is often used in combination for comprehensive purification. Modern systems integrate these steps in water treatment plants to produce potable and industrial-grade water, ensuring public health and equipment safety.

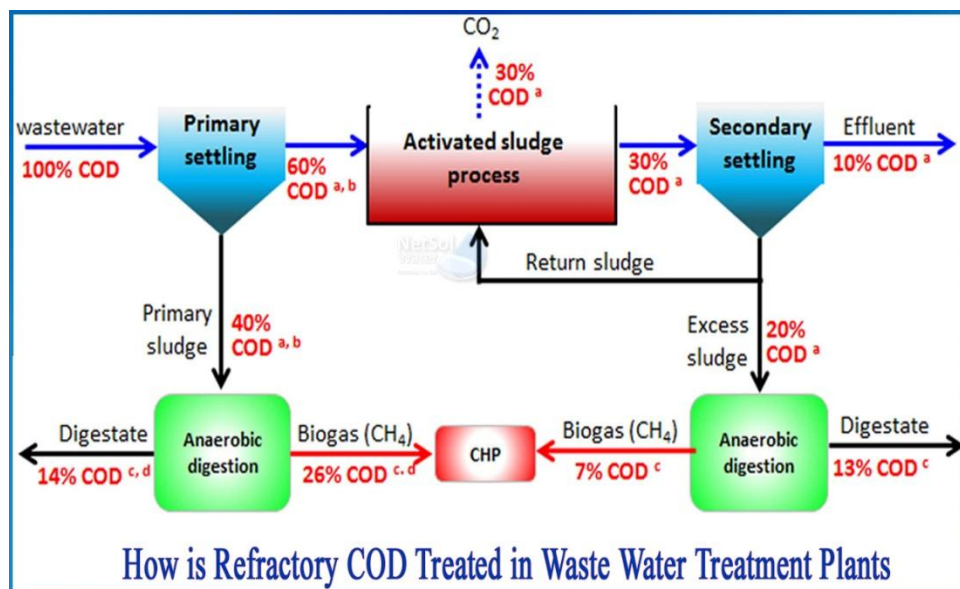
BOD (Biochemical Oxygen Demand)

BOD is a measure of the amount of oxygen required by aerobic microorganisms to decompose organic matter in water over a specific time period (usually 5 days at 20°C). It indicates the degree of organic pollution in water. Higher BOD values mean more organic matter and lower water quality. BOD testing is essential for monitoring wastewater treatment efficiency and the health of natural water bodies. It provides information about the oxygen depletion capacity of water, which is crucial for the survival of aquatic life. BOD is widely used by environmental agencies to set discharge limits and pollution control standards for industries and municipalities.



COD (Chemical Oxygen Demand)

COD is the amount of oxygen required to oxidize all organic and inorganic matter in a water sample using a strong chemical oxidant, such as potassium dichromate. Unlike BOD, which measures biodegradable matter, COD measures total oxygen demand, including non-biodegradable substances. The COD test is quicker (2-3 hours) and more comprehensive. It is an important parameter in wastewater treatment, helping assess the pollution load and design treatment systems. COD values are usually higher than BOD values for the same sample. Regular monitoring of COD ensures compliance with environmental regulations and helps protect aquatic ecosystems from excessive organic pollution.



UNIT-2

Carbohydrates and Amino acids

Carbohydrates: Classification, Preparation and Properties of Glucose, Fructose and Sucrose

Carbohydrates are a major class of biomolecules that serve as a primary source of energy for living organisms. Chemically, carbohydrates are polyhydroxy aldehydes or ketones or compounds that yield such substances upon hydrolysis. They are composed of carbon, hydrogen, and oxygen, with the general formula $C_n(H_2O)_n$. Based on their structure and hydrolysis behavior, carbohydrates are classified into three major types: monosaccharides, disaccharides, and polysaccharides. Monosaccharides are simple sugars that cannot be hydrolyzed further into smaller units. Common examples include glucose and fructose. Disaccharides are formed by the condensation of two monosaccharide units. Examples are sucrose, lactose, and maltose. Polysaccharides are long-chain carbohydrates formed by the polymerization of many monosaccharide units. Examples include starch, cellulose, and glycogen.

Monosaccharides are further divided based on the number of carbon atoms. If the sugar contains an aldehyde group, it is called an aldose, and if it contains a ketone group, it is a ketose. Glucose is an aldohexose, while fructose is a ketohexose. Glucose and fructose are structural isomers as they have the same molecular formula ($C_6H_{12}O_6$) but differ in functional groups. Disaccharides like sucrose are formed when two monosaccharide units are joined by a glycosidic bond with the elimination of one water molecule. These classifications are helpful in understanding the structure, function, and metabolism of carbohydrates in living organisms.

Glucose is the most important and widely distributed monosaccharide. It is found in fruits, honey, and the bloodstream of animals. It is commonly known as grape sugar or blood sugar. Glucose can be prepared in the laboratory by the hydrolysis of starch using dilute acids or enzymes. It can also be obtained by the hydrolysis of sucrose (cane sugar) in the presence of the enzyme invertase. Another method of preparation involves the hydrolysis of cellulose under acidic conditions. Glucose is a white crystalline solid that is sweet in taste and soluble in water. It exhibits reducing properties due to the presence of a free aldehyde group in its open-chain form. It gives a positive Fehling's test and Tollen's test. Glucose undergoes oxidation to form gluconic acid and is reduced to sorbitol. It also forms osazone crystals with phenylhydrazine, which are used for identification.

The molecular structure of glucose exists in both open-chain and cyclic forms. In the open-chain form, glucose has an aldehyde group at carbon-1, while in the cyclic form, it forms a six-membered pyranose ring due to the reaction between the aldehyde group and the hydroxyl group on carbon-5. This results in two anomeric forms: α -glucose and β -glucose. These forms differ in the position of the -OH group at the anomeric carbon and exhibit a phenomenon called mutarotation, where one form gradually changes to the other in aqueous solution until an equilibrium mixture is obtained.

Fructose, another important monosaccharide, is found in fruits, vegetables, and honey. It is the sweetest naturally occurring sugar. Fructose is a ketohexose with a ketone group on the second carbon atom. It can be obtained by the hydrolysis of sucrose using dilute acid or the enzyme sucrase. Like glucose, fructose is also a white crystalline solid and is very soluble in water. In solution, fructose exists in equilibrium between its open-chain form and five-membered furanose ring form. The cyclic structure is formed due to the reaction between the ketone group at carbon-2 and the hydroxyl group at carbon-5.

Fructose exhibits reducing properties despite being a ketose, as it can undergo tautomerization under alkaline conditions to form an aldehyde group, which reacts with Fehling's and Tollen's reagents. Fructose also forms osazone crystals similar to glucose, but the crystals differ in shape, helping in their identification. Like glucose, fructose is also capable of forming glycosidic bonds during the formation of disaccharides.

Sucrose is a disaccharide composed of one molecule each of glucose and fructose linked by an α,β -1,2-glycosidic bond. It is commonly known as cane sugar and is widely used in the food industry. It is extracted from sugarcane or sugar beet and purified by crystallization. Unlike glucose and fructose, sucrose is a non-reducing sugar because the glycosidic bond involves the reducing ends of both monosaccharides, thus blocking their reactivity. As a result, sucrose does not give Fehling's or Tollen's tests. Upon hydrolysis in the presence of dilute acids or the enzyme invertase, sucrose breaks down into glucose and fructose. This reaction is called inversion, and the resulting mixture is known as invert sugar because it rotates plane-polarized light in the opposite direction to that of sucrose.

Sucrose is a white crystalline solid, highly soluble in water, and has a sweet taste. It is non-reducing, but when hydrolyzed, the resulting mixture becomes reducing due to the presence of glucose and fructose. Sucrose does not exhibit mutarotation, as it does not have a free anomeric

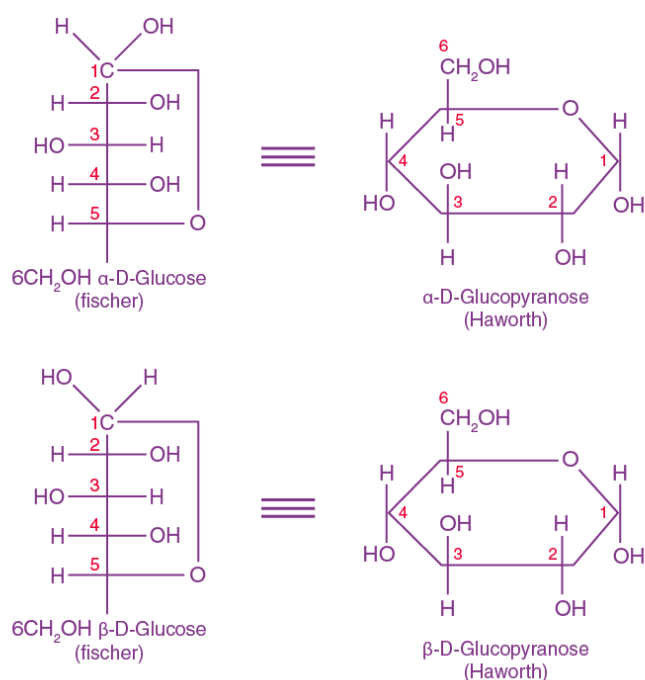
carbon in its structure. It is widely used as a sweetener in food and beverages, and its hydrolysis is a common biological process in the human body.

Open Chain and Ring Structures of Glucose and Fructose

Glucose and fructose are two of the most important monosaccharides in nature. Both have the same molecular formula ($C_6H_{12}O_6$) but differ in structure and functional groups. Glucose is an aldohexose, meaning it contains six carbon atoms and an aldehyde group at the first carbon in its open-chain form. In aqueous solution, glucose exists primarily in a cyclic form, but a small amount is also present as the open-chain structure. In the open-chain form, glucose has an aldehyde group ($-CHO$) at carbon 1 and hydroxyl ($-OH$) groups on the other carbons. The structure allows glucose to undergo oxidation and participate in reactions characteristic of aldehydes, like reducing Fehling's and Tollen's reagents.

However, the most stable and predominant structure of glucose in solution is the pyranose ring form, a six-membered ring. This ring is formed by an internal reaction between the aldehyde group at carbon 1 and the hydroxyl group at carbon 5. This forms a hemiacetal linkage and results in a ring structure that resembles the compound pyran. The ring form exists in two isomeric forms: α -glucose and β -glucose, differing in the position of the $-OH$ group on the first carbon. This interconversion between the α and β forms in solution is known as mutarotation.

Fructose, on the other hand, is a ketohexose with a ketone group at the second carbon in its open-chain structure. Like glucose, it can also exist in both open-chain and ring forms in solution. In its open-chain form, fructose has a ketone group ($=C=O$) on the second carbon atom and hydroxyl groups on the remaining carbons. In aqueous medium, fructose prefers to form a five-membered furanose ring, which is more stable due to lower ring strain. This cyclic structure is formed by a reaction between the ketone group on carbon 2 and the hydroxyl group on carbon 5, resulting in a hemiketal linkage. The cyclic form of fructose also exists in α and β isomers, similar to glucose.



Glucose–Fructose Interconversion

Glucose and fructose can interconvert in aqueous alkaline solutions through an enediol intermediate. This is known as the Lobry de Bruyn–van Ekenstein transformation. In this reaction, glucose isomerizes to fructose and vice versa. The process begins with the enolization of the glucose molecule, where the α -hydrogen adjacent to the aldehyde group is removed to form an enediol intermediate (a compound with hydroxyl groups on adjacent double-bonded carbons). This intermediate can then rearrange to form either glucose, fructose, or even mannose, another isomer.

In biological systems, this conversion is catalyzed by enzymes such as glucose isomerase, which plays an essential role in carbohydrate metabolism. Industrially, this reaction is important in the production of high-fructose corn syrup, where glucose derived from corn starch is enzymatically converted into fructose, making the syrup sweeter and more suitable for food and beverage use. The interconversion is a key example of how simple sugars can transform into each other under certain conditions, highlighting their structural flexibility and importance in biochemical pathways.

Properties of Starch and Cellulose

Starch and cellulose are polysaccharides composed of glucose units but differ significantly in structure and properties. Starch is the primary storage carbohydrate in plants and is composed of two components: amylose and amylopectin. Amylose is a linear polymer of α -D-glucose units connected by α -1,4-glycosidic bonds. It tends to form a helical structure in solution and gives a blue color with iodine. Amylopectin, the branched form, contains both α -1,4 and α -1,6 glycosidic linkages, with branching occurring every 20–25 glucose units. Because of its branched structure, amylopectin is more soluble in water and easily digestible.

Starch is found in high concentrations in cereals, potatoes, and legumes. It is insoluble in cold water but forms a colloidal solution (paste) in hot water. Upon digestion, enzymes such as amylase break down starch into maltose and glucose, providing energy for the body. Starch is non-reducing and does not exhibit any reducing properties unless hydrolyzed into smaller sugars.

Cellulose, on the other hand, is a structural polysaccharide found in the cell walls of plants. It consists of β -D-glucose units linked by β -1,4-glycosidic bonds, which result in a linear, rigid structure. The β -linkage allows hydrogen bonding between adjacent chains, making cellulose highly crystalline, strong, and insoluble in water. Humans and many animals lack the enzyme cellulase, which is required to break the β -1,4 linkages, so cellulose cannot be digested and serves as dietary fiber.

Cellulose does not give any color with iodine and is chemically inert under mild conditions. It is used industrially in the manufacture of paper, textiles (like cotton), and synthetic materials like cellophane and rayon. Despite being composed of the same glucose monomer as starch, its different linkage pattern gives cellulose entirely distinct physical and biological properties. Understanding the differences between these two polysaccharides is essential to appreciate how nature modifies simple units into functionally diverse macromolecules.

Amino acids:

Classification preparation and properties of alanine:

Amino acids are organic molecules that serve as the basic building blocks of proteins. Each amino acid contains at least one amino group ($-\text{NH}_2$) and one carboxylic acid group ($-\text{COOH}$) attached to a central (α) carbon atom. The simplest amino acid is glycine, which has hydrogen as its side chain. Alanine is a naturally occurring, α -amino acid with the chemical formula $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$. It has a methyl group ($-\text{CH}_3$) as its side chain, making it a non-polar, neutral amino acid.

Alanine is classified as an α -amino acid because both the amino and carboxylic groups are attached to the same carbon atom—the α -carbon. Based on the polarity of the side chain, alanine is also categorized as a non-polar and aliphatic amino acid. It is neutral in solution, meaning its side chain does not ionize or react with acids or bases. Alanine is optically active, as the α -carbon is chiral, except in the case of glycine. The naturally occurring form is L-alanine, which is used in protein synthesis in biological systems. The D-form of alanine, though rare in nature, may occur in bacterial cell walls.

Alanine is present in significant quantities in proteins and can also be synthesized in the body from pyruvate via a transamination reaction. It plays an important role in glucose metabolism and is involved in the glucose-alanine cycle, where it helps transport nitrogen from muscle tissues to the liver. The body uses L-alanine as an energy source and for building proteins and enzymes essential for life processes. Due to its simple structure, alanine is also used as a reference point when studying the properties of other amino acids.

In the laboratory, alanine can be synthesized by several methods. One classic method involves treating acetaldehyde (CH_3CHO) with ammonium chloride (NH_4Cl) and potassium cyanide (KCN) to form an α -aminonitrile, which on acidic hydrolysis gives alanine. This method is known as Strecker synthesis. Another method includes the bromination of propionic acid followed by treatment with aqueous ammonia. Alanine can also be synthesized through the reductive amination of pyruvic acid using ammonia and a reducing agent like hydrogen in the presence of a catalyst.

Alanine exhibits typical amphoteric behavior, meaning it can act as both an acid and a base. In aqueous solution, alanine primarily exists in the zwitterionic form, where the amino group is protonated ($-\text{NH}_3^+$) and the carboxyl group is deprotonated ($-\text{COO}^-$). This internal charge separation gives alanine unique solubility and buffering properties. Its isoelectric point (pI) is around 6.0, at which the amino acid has no net charge and does not migrate in an electric field.

Alanine shows various chemical reactions. The carboxylic acid group can undergo reactions like esterification, decarboxylation, and salt formation with bases. The amino group can react with acids to form salts or with acyl chlorides and aldehydes to form amides and Schiff bases, respectively. Alanine also reacts with ninhydrin reagent, producing a characteristic purple color, which is commonly used in detecting amino acids in qualitative analysis.

Being a simple, non-essential amino acid, alanine can be synthesized by the body and is not required in the diet. However, it is widely used in dietary supplements and medical applications. Alanine is also useful in protein structure studies due to its relatively inert and small side chain.

In biochemistry laboratories, alanine often serves as a control or baseline compound in the analysis of protein folding, enzyme-substrate interactions, and mutagenesis experiments.

In industrial applications, alanine derivatives are used in the synthesis of pharmaceuticals, biodegradable plastics, and agrochemicals. The understanding of alanine's properties also contributes to the design of synthetic peptides and biopolymers. Its high solubility, stability, and mild reactivity make it an ideal model compound for studying fundamental aspects of amino acid chemistry.

preparation of dipeptides using Bergmann method

The synthesis of peptides, especially dipeptides (compounds made of two amino acid units), is a fundamental aspect of bioorganic and medicinal chemistry. One of the classical approaches to synthesizing dipeptides in the laboratory is known as the Bergmann method. This method was developed by the German chemist Max Bergmann, and it laid the groundwork for modern peptide synthesis. In the Bergmann method, a peptide bond is formed between the carboxylic acid group of one amino acid and the amino group of another, but in a controlled and selective manner using protecting groups. Protecting groups are essential in peptide synthesis because amino acids contain both reactive functional groups ($-\text{NH}_2$ and $-\text{COOH}$), which can lead to unwanted side reactions if not properly managed.

In this method, the amino group of the first amino acid is typically protected using a blocking group such as the benzyloxycarbonyl group (Z-group or Cbz). This group prevents the free amino group from reacting during the initial stages of the reaction. The carboxylic acid group of this protected amino acid is then activated for peptide bond formation. Activation is often done by converting the carboxylic acid to a more reactive intermediate, such as an acid chloride or mixed anhydride, which can readily react with the amino group of a second amino acid. The second amino acid must have its own carboxyl group free for reaction but may have its amino group protected to avoid multiple couplings.

The activated carboxyl group of the first amino acid (with protected amine) is then reacted with the free amino group of the second amino acid (or a protected derivative if selectivity is required). This reaction forms an amide bond, known as the peptide bond, resulting in a protected dipeptide. After the formation of the dipeptide, the protecting group on the amino group is removed using suitable reagents, typically hydrogenation in the presence of a palladium catalyst for benzyloxycarbonyl groups. This final step yields the free dipeptide, where both amino acid units are joined by a single peptide linkage.

The Bergmann method was one of the earliest successful strategies to prepare peptides with defined sequences. Though the procedure may appear cumbersome by modern standards, it was revolutionary in its ability to selectively build peptides of known structure and length. The concept of protection–activation–coupling–deprotection used in this method remains a central principle in peptide chemistry today.

This method allowed chemists to begin studying the structure and function of peptides and small proteins in a laboratory setting, which was previously very difficult using only natural sources. Although the Bergmann method has been largely replaced by more efficient methods like solid-phase peptide synthesis (SPPS) developed by Merrifield, its historical and educational value is immense. It introduced key concepts such as orthogonal protection, stepwise synthesis, and the importance of selectivity in biochemical synthesis.

Furthermore, dipeptides synthesized using the Bergmann method are important in studying protein folding, enzyme-substrate interactions, and metabolic pathways. They can also be used as pharmaceutical intermediates and for preparing artificial enzymes or catalysts. Understanding this method provides students with a foundation in classical organic synthesis as well as insight into how complex biomolecules are built and modified. The method's elegance lies in its strategic use of protection and deprotection to control the reactivity of multifunctional molecules. Overall, the Bergmann method remains a cornerstone of classical peptide synthesis, bridging early biochemical approaches and the advanced synthetic techniques of modern-day science.

RNA and DNA

DNA (Deoxyribonucleic Acid) and RNA (Ribonucleic Acid) are the two primary types of nucleic acids found in living organisms. They are vital biomolecules responsible for the storage, transmission, and execution of genetic information. Both DNA and RNA are made up of repeating units called nucleotides, which are composed of three parts: a nitrogenous base, a pentose sugar, and a phosphate group. However, the key difference between DNA and RNA lies in their sugar component—DNA contains deoxyribose, while RNA contains ribose. Additionally, DNA is generally double-stranded, forming a stable helical structure, while RNA is typically single-stranded.

The nitrogenous bases found in both DNA and RNA are classified into purines (adenine and guanine) and pyrimidines. DNA contains the bases adenine (A), guanine (G), cytosine (C), and thymine (T), whereas RNA contains uracil (U) in place of thymine. In the DNA double helix, the two strands are held together by hydrogen bonds between complementary base pairs: A pairs with

T, and G pairs with C. This structure was famously proposed by Watson and Crick in 1953, and it serves as the foundation for genetic inheritance.

DNA is primarily located in the nucleus of cells (and in mitochondria), where it stores the genetic blueprint of the organism. Its main role is to encode genetic instructions used in the development and functioning of living organisms. During the process of replication, DNA can make identical copies of itself, ensuring that genetic information is passed accurately from one generation to the next.

RNA, on the other hand, plays an active role in the expression of genetic information. It is found in both the nucleus and cytoplasm. There are several types of RNA, each with specific functions. The three major types are messenger RNA (mRNA), transfer RNA (tRNA), and ribosomal RNA (rRNA). mRNA carries genetic instructions from DNA to ribosomes, where proteins are synthesized. tRNA transports amino acids to the ribosome during protein synthesis, and rRNA forms the core structure of ribosomes and catalyzes protein formation.

One important biological process involving both DNA and RNA is transcription, where a segment of DNA is used as a template to synthesize mRNA. This mRNA is then translated during protein synthesis into a chain of amino acids, forming a protein. This flow of genetic information from DNA → RNA → Protein is known as the central dogma of molecular biology.

DNA is a more stable molecule, capable of long-term storage of genetic data, whereas RNA is less stable and designed for short-term roles in gene expression and regulation. Both molecules are essential for life, and any error in their structure or function can lead to genetic disorders or diseases.

UNIT-3

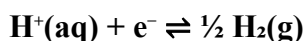
Electrochemistry

Galvanic cells Standard hydrogen electrode calomel electrode

A Galvanic cell (also known as a voltaic cell) is an electrochemical cell that converts chemical energy into electrical energy through a spontaneous redox reaction. It consists of two half-cells, each containing an electrode dipped into an electrolyte solution. The two half-cells are connected by a salt bridge, which allows the movement of ions to maintain electrical neutrality. One half-cell acts as the anode, where oxidation occurs, and the other as the cathode, where reduction takes place. Electrons flow from the anode to the cathode through an external circuit, generating an electric current that can be used to perform work. The cell potential or electromotive force (EMF) of the cell is a measure of the electrical energy produced and is dependent on the nature of the electrodes and the concentrations of the solutions.

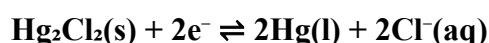
To measure the electrode potential of a half-cell, it must be compared with a reference electrode. The most widely used reference is the Standard Hydrogen Electrode (SHE). The SHE consists of a platinum electrode coated with finely divided platinum black, immersed in 1 M H⁺ ion solution (usually HCl), with hydrogen gas at a pressure of 1 atmosphere continuously bubbled over the electrode. The platinum acts as an inert surface for the exchange of electrons between the hydrogen ions and hydrogen gas.

The half-reaction at the SHE is:



By international agreement, the electrode potential of the SHE is defined as 0.00 volts under standard conditions (298 K, 1 atm, 1 M concentration). This provides a baseline for measuring the standard electrode potentials of other electrodes. When connected to another half-cell, the potential difference can be measured using a voltmeter, and the electrode potential of the unknown electrode can be determined.

Another commonly used reference electrode is the Calomel Electrode. It is a secondary reference electrode, which is more convenient and stable compared to the SHE in practical laboratory work. The Calomel Electrode consists of mercury (Hg) in contact with a paste of mercury(I) chloride (Hg_2Cl_2 , calomel) and immersed in a solution of potassium chloride (KCl). The reaction at the electrode is:



The electrode potential of the calomel electrode depends on the concentration of KCl used. For example, the potential is +0.242 V when saturated KCl is used. It is widely employed as a reference because it is easy to prepare, reproducible, and chemically stable. The calomel electrode is typically connected to other half-cells to measure their electrode potentials in comparison to the known calomel value.

Both the SHE and calomel electrodes play a critical role in electrochemical measurements such as determining standard electrode potentials, studying redox behavior, and calculating cell EMF. These measurements are important in various fields such as analytical chemistry, corrosion science, battery technology, and industrial electrolysis. The combination of a working electrode and a reference electrode allows for accurate determination of unknown potentials, helping in the understanding of electron transfer processes and thermodynamics of redox systems. Thus, the concepts of Galvanic cells and reference electrodes form a fundamental part of electrochemistry in both theoretical and applied sciences.

Standard electrode potentials -electrochemical series

Standard electrode potential (E°) is the measure of the tendency of a half-cell to gain or lose electrons when it is connected to a standard hydrogen electrode under standard conditions. It is expressed in volts (V) and is determined under standard conditions: 1 molar concentration of solution, 1 atmosphere pressure for gases, and a temperature of 25°C (298 K). Each half-cell has a specific tendency to either undergo oxidation (loss of electrons) or reduction (gain of electrons). The standard hydrogen electrode (SHE), with an assigned potential of 0.00 V, is used as the reference electrode to determine these values for other electrodes.

Half Reaction	Standard Potential (V)
<div style="display: flex; align-items: center;"> <div style="writing-mode: vertical-rl; transform: rotate(180deg); margin-right: 10px;">↑ stronger oxidizing agent</div> <div style="background-color: #f08080; padding: 5px; text-align: center;"> F₂ Pb⁴⁺ Cl₂ O₂ Ag⁺ Fe³⁺ Cu²⁺ 2H⁺ Pb²⁺ Fe²⁺ Zn²⁺ Al³⁺ Mg²⁺ Li⁺ </div> </div>	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> + 2e⁻ + 2e⁻ + 2e⁻ 4H⁺ + 4e⁻ + 1e⁻ + 1e⁻ + 2e⁻ + 2e⁻ + 2e⁻ + 2e⁻ + 2e⁻ + 3e⁻ + 2e⁻ + 1e⁻ </div> <div style="margin-right: 10px;"> ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ ⇌ </div> <div style="display: flex; align-items: center;"> <div style="background-color: #4169e1; padding: 5px; text-align: center; writing-mode: vertical-rl; transform: rotate(180deg); margin-right: 10px;">↓ stronger reducing agent</div> <div style="background-color: #e0e0ff; padding: 5px; text-align: center;"> 2F⁻ Pb²⁺ 2Cl⁻ 2H₂O Ag Fe²⁺ Cu H₂ Pb Fe Zn Al Mg Li </div> <div style="margin-left: 10px;"> +2.87 +1.67 +1.36 +1.23 +0.80 +0.77 +0.34 0.00 -0.13 -0.44 -0.76 -1.66 -2.36 -3.05 </div> </div> </div>

If a half-cell shows a positive E° value, it means it has a greater tendency to gain electrons (get reduced) compared to hydrogen and is called a strong oxidizing agent. Conversely, a negative E° value means the half-cell has a greater tendency to lose electrons (get oxidized), making it a strong reducing agent. For example, fluorine has a high positive standard reduction potential (+2.87 V), making it a very powerful oxidizing agent, whereas lithium, with a highly negative potential (–3.04 V), is an excellent reducing agent. The arrangement of various elements and ions based on their standard electrode potentials is known as the Electrochemical Series. It is a list of chemical species ordered from the most negative to the most positive standard reduction potentials. At the top of the series are strong reducing agents like lithium, potassium, and calcium, while at the bottom are strong oxidizing agents like fluorine, chlorine, and gold ions. This series is extremely useful for predicting the feasibility of redox reactions, as a species higher in the series can reduce another that is lower in the series.

The electrochemical series helps us in understanding which metals will displace others from their salt solutions. For instance, since zinc has a more negative E° value than copper, zinc can displace copper from copper sulfate solution. This principle is also used in constructing Galvanic cells,

where the cell voltage is calculated using the formula:

$$\text{EMF} = E^{\circ} (\text{cathode}) - E^{\circ} (\text{anode}).$$

A positive EMF indicates a spontaneous redox reaction.

The electrochemical series also plays a key role in corrosion science, battery design, and electroplating. For example, metals like iron that are higher in the series corrode easily, while metals like gold and platinum are highly resistant to corrosion. In electroplating, a metal with a more negative potential is deposited on one with a less negative one to protect it from corrosion or to improve appearance.

Furthermore, this series is crucial in electrolysis, helping to determine which ion will be discharged at the electrodes. It is also applied in analytical chemistry, where redox titrations depend on the relative potentials of the reacting species. In conclusion, standard electrode potentials and the electrochemical series form the foundation of electrochemical understanding, and their applications extend across industries, laboratories, and modern technologies. They enable chemists to predict and control redox behavior in a wide variety of chemical systems.

Strong and weak electrolytes ionic product of water pH, pKa, pKb

Electrolytes are substances that dissociate into ions when dissolved in water and conduct electricity through the solution. They are classified as strong electrolytes and weak electrolytes based on the extent of ionization. Strong electrolytes completely dissociate into ions in aqueous solution. Examples include hydrochloric acid (HCl), sodium chloride (NaCl), and sulfuric acid (H₂SO₄). These substances produce a large number of free ions, making the solution a good conductor of electricity. On the other hand, weak electrolytes only partially dissociate in solution, producing fewer ions. Examples include acetic acid (CH₃COOH), ammonia (NH₃), and carbonic acid (H₂CO₃). Due to limited ionization, they are poor conductors of electricity.

The ionic product of water is a key concept in understanding the behavior of acids and bases. Water undergoes a very slight self-ionization, where a small number of water molecules dissociate into hydrogen ions (H⁺) and hydroxide ions (OH⁻). This equilibrium can be represented as:



At 25°C, the concentrations of H^+ and OH^- in pure water are each $1 \times 10^{-7} \text{ mol/L}$, and their product is known as the ionic product of water (K_w):

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2/\text{L}^2$$

This value is constant at a given temperature and is used to determine the concentrations of H^+ and OH^- in acidic, neutral, or basic solutions.

The pH of a solution is a measure of its hydrogen ion concentration and indicates whether a solution is acidic or basic. It is defined as:

$$\text{pH} = -\log[\text{H}^+]$$

For pure water, $[\text{H}^+] = 1 \times 10^{-7}$, so $\text{pH} = 7$, which is considered neutral. A pH less than 7 indicates an acidic solution, while a pH greater than 7 indicates a basic (alkaline) solution. The pH scale typically ranges from 0 to 14 and is logarithmic, meaning that each unit change represents a tenfold change in acidity or basicity.

Related to pH are the terms pK_a and pK_b , which are the negative logarithms of the acid dissociation constant (K_a) and base dissociation constant (K_b), respectively. These constants measure the strength of acids and bases. The lower the pK_a , the stronger the acid, and similarly, a lower pK_b indicates a stronger base. The relationship between pK_a and the strength of an acid is:

$$\text{pK}_a = -\log K_a$$

Stronger acids have higher K_a values and thus lower pK_a values. This helps in comparing weak acids and predicting the direction of acid-base reactions.

For weak bases, the strength is measured using the base dissociation constant, K_b , and its logarithmic form, pK_b :

$$\text{pK}_b = -\log K_b$$

Moreover, for conjugate acid–base pairs, the relationship between pK_a and pK_b is given by:

$$pK_a + pK_b = 14 \text{ (at } 25^\circ\text{C)}$$

This relation helps us calculate one if the other is known. These concepts are especially useful in buffer preparation, titration calculations, and pharmaceutical chemistry, where control of acidity or basicity is crucial.

In summary, the distinction between strong and weak electrolytes explains ion behavior in solution, while the concepts of K_w , pH, pK_a , and pK_b provide a quantitative understanding of acid-base strength and solution chemistry. Mastery of these ideas is essential for understanding chemical equilibria, biochemical processes, and environmental chemistry.

Conductometric Titrations and pH Determination by Colorimetric Method

Conductometric titrations are a type of titration in which the electrical conductivity of a solution is measured continuously as the titration proceeds. The conductivity of a solution depends on the presence and mobility of ions. During a titration, the ionic composition of the solution changes as the titrant reacts with the analyte, leading to changes in conductivity. This change is plotted as a graph of conductivity versus volume of titrant added. The point at which a sharp change in conductivity is observed is considered the endpoint of the titration.

This technique is particularly useful for titrations involving weak acids or weak bases, where traditional indicators do not give a sharp color change. For example, in the titration of a strong acid (HCl) with a strong base (NaOH), the conductivity initially decreases due to the replacement of highly mobile H^+ ions with less mobile Na^+ ions. At the equivalence point, all H^+ ions have been neutralized. After this, the addition of excess NaOH increases the conductivity due to the presence of OH^- ions. The graph shows a V-shaped curve, and the minimum point indicates the endpoint.

In the case of weak acid–strong base titration (e.g., acetic acid vs. NaOH), the conductivity first increases slowly due to the low ionization of acetic acid. As NaOH is added, acetate ions are formed, and after the equivalence point, OH^- ions dominate, sharply increasing the conductivity. Conductometric titrations are advantageous because they can be performed even with colored or turbid solutions, and without the need for indicators, which may interfere with the reaction.

On the other hand, pH determination by the colorimetric method involves the use of pH indicators, which are organic compounds that exhibit color changes at specific pH ranges. This method is simple and widely used for quick estimation of pH in various chemical and biological systems. Indicators are weak acids or bases themselves and change color depending on the hydrogen ion concentration of the solution. For instance, phenolphthalein is colorless in acidic medium and turns pink in basic solution ($\text{pH} > 8.2$). Methyl orange turns red in acidic medium and yellow in basic conditions.

In the colorimetric method, a few drops of a suitable indicator are added to the solution whose pH is to be determined. The resulting color is compared with a standard pH color chart to estimate the pH range. This method is not highly precise but is very useful for approximate measurements, especially in educational labs or fieldwork. For more accurate determination, universal indicators—a mixture of several indicators—can be used, which provide a broad range of color changes corresponding to pH values from 1 to 14.

While the colorimetric method gives only an approximate pH, it is very effective in acid-base titrations, soil testing, and biochemical experiments. However, for very precise measurements, pH meters or electrometric methods are preferred.

A buffer solution is a special type of solution that resists significant changes in its pH upon the addition of small amounts of an acid or a base. It usually consists of a weak acid and its conjugate base, or a weak base and its conjugate acid. Buffer solutions maintain a stable pH and are essential in many chemical and biological systems. For example, a common acidic buffer is a solution of acetic acid and sodium acetate, and a basic buffer can be made from ammonium hydroxide and ammonium chloride.

Buffer action is explained by Le Chatelier's principle. When a small amount of acid (H^+ ions) is added, the base component of the buffer neutralizes it. When a small amount of base (OH^- ions) is added, the acid part of the buffer neutralizes it. This equilibrium-based system helps in stabilizing the hydrogen ion concentration. Buffers are quantitatively described by the Henderson–Hasselbalch equation, which relates the pH of the buffer to the pK_a of the acid and the ratio of salt to acid concentration.

In biological systems, buffer solutions play a crucial role in maintaining the pH required for enzymatic activity and metabolic processes. The human blood has a natural buffer system consisting of carbonic acid (H_2CO_3) and bicarbonate ion (HCO_3^-), which maintains the blood pH around 7.4. Even slight deviations from this pH range can be dangerous, making the buffer system

essential for survival. Similarly, cellular fluids have phosphate and protein-based buffers that help maintain intracellular pH.

Buffer solutions are also important in pharmaceutical formulations, biochemical assays, and industrial fermentation processes. In laboratories, buffer solutions are used to calibrate pH meters and to carry out reactions at controlled pH conditions. They are indispensable in electrophoresis, chromatography, and many diagnostic tests.

Electroplating – Nickel and Chrome Plating

Electroplating is a process in which a metal is deposited onto the surface of another material using electrolysis. It is widely used for decorative, protective, and functional purposes. In this process, the object to be plated is made the cathode, and the metal to be deposited is made the anode, both immersed in an electrolyte solution containing a salt of the plating metal. When an electric current is passed, metal ions from the electrolyte are reduced and deposited on the cathode surface.

Nickel electroplating is one of the most common forms. It is used to give a bright, corrosion-resistant, and wear-resistant coating. The electrolyte typically used is a solution of nickel sulfate (NiSO_4), often mixed with nickel chloride and boric acid to control pH. The anode is usually made of pure nickel. Nickel plating is applied on materials like iron, steel, and brass for applications in hardware tools, kitchen utensils, and automobile parts.

Chrome plating, or chromium electroplating, provides a hard, bright, and highly corrosion-resistant surface. It is used extensively in the automotive industry, especially for bumpers, grills, and handlebars. The electrolyte used in chrome plating is usually chromic acid (H_2CrO_4). Since chromium ions are toxic, the process must be carefully monitored to prevent environmental and health hazards. The plating is done over a layer of nickel for better adhesion and appearance.

Both nickel and chrome plating enhance the aesthetic appeal, durability, and corrosion resistance of metal surfaces. However, environmental regulations now emphasize waste treatment and pollution control, especially for chromium plating, due to the hazardous nature of hexavalent chromium.

Types of cells-fuel

Electrochemical cells are devices that convert chemical energy into electrical energy or vice versa. They are broadly classified into galvanic cells (or voltaic cells) and electrolytic cells. In galvanic cells, spontaneous redox reactions generate electricity. Examples include the Daniell cell, dry

cells, and lead-acid batteries. In contrast, electrolytic cells use an external electric current to drive non-spontaneous chemical reactions, such as in electroplating or electrolysis of water.

A special and important category of electrochemical cells is fuel cells. Fuel cells are devices that convert the chemical energy of a fuel directly into electrical energy through redox reactions, without combustion. The most common example is the hydrogen-oxygen fuel cell, where hydrogen gas is oxidized at the anode and oxygen is reduced at the cathode. The only by-product is water, making fuel cells highly eco-friendly. These cells are efficient, clean, and widely used in spacecraft, electric vehicles, and backup power systems.

Fuel cells differ from traditional batteries in that they require a continuous supply of fuel and oxidant to operate. As long as the reactants are provided, the cell can produce electricity. There are various types of fuel cells, such as alkaline fuel cells (AFC), proton-exchange membrane fuel cells (PEMFC), and solid oxide fuel cells (SOFC), each with specific advantages and operating conditions. The development of fuel cells is a key component of sustainable and renewable energy research.

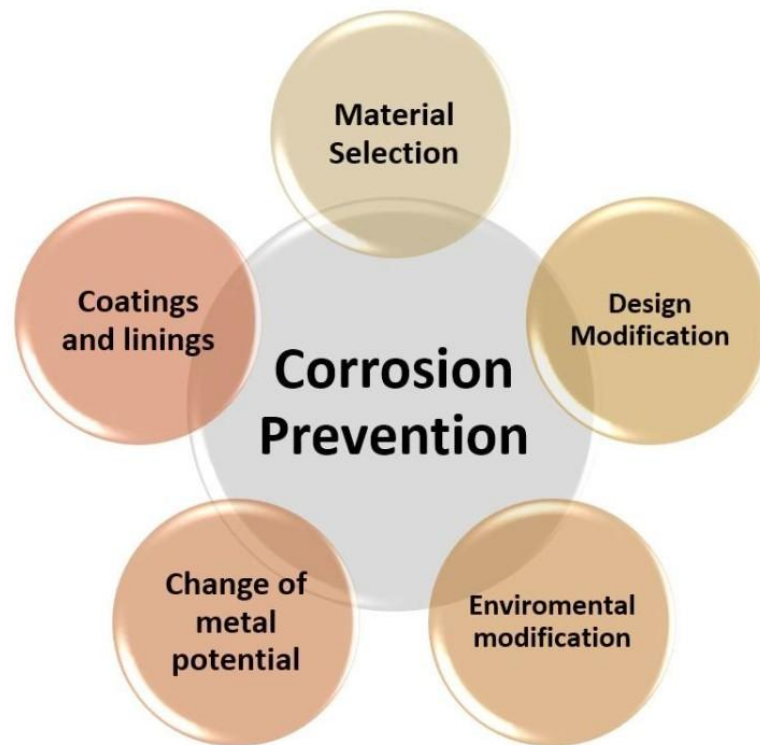
On the other hand, one of the major issues related to metals is corrosion, which is the gradual deterioration of a metal due to chemical or electrochemical reaction with its environment. The most common form is rusting of iron, which occurs in the presence of oxygen and moisture, forming iron oxide. Corrosion not only affects the appearance of metals but also leads to loss of strength, safety hazards, and economic damage.

Corrosion and its prevention

Corrosion is an electrochemical process involving anodic oxidation and cathodic reduction. At the anode, iron loses electrons and forms Fe^{2+} , while at the cathode, oxygen is reduced in the presence of water. Several types of corrosion exist, including uniform corrosion, galvanic corrosion, pitting, and stress corrosion cracking.

To protect metals from corrosion, several prevention methods are employed. Barrier protection involves coating the metal with paints or plastics to prevent exposure to air and water. Galvanization is a method where iron is coated with a layer of zinc, which serves as a sacrificial anode and protects the iron underneath. Cathodic protection is an advanced technique where the metal to be protected is made the cathode of an electrochemical cell, thus preventing its oxidation. Alloying (e.g., adding chromium to make stainless steel) also improves corrosion resistance.

In industrial and marine environments, proper corrosion protection is critical for maintaining the longevity of structures like bridges, pipelines, and ships. Understanding the types of cells and their applications, especially fuel cells and corrosion prevention, is essential for sustainable technology and infrastructure development.



UNIT-4

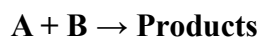
Kinetics and Catalysis

Order and molecularity

Order of Kinetics: Order and Molecularity

In chemical kinetics, the rate of a reaction refers to how quickly reactants are converted into products. The study of reaction rates provides valuable insights into the reaction mechanism and helps in optimizing conditions for industrial and laboratory processes. Two important terms in this context are order of a reaction and molecularity.

The order of a reaction is an experimentally determined value that indicates the power to which the concentration of a reactant is raised in the rate law expression. For a general reaction:



the rate law is given as:

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

where m and n are the reaction orders with respect to A and B, respectively, and their sum ($m + n$) is the overall order of the reaction.

The order can be zero, first, second, or fractional, depending on how the rate depends on the concentration. For example, in a zero-order reaction, the rate is independent of the concentration of reactants. In a first-order reaction, the rate is directly proportional to the concentration of one reactant. A second-order reaction may depend on either the square of one reactant's concentration or the product of two different reactant concentrations.

The units of the rate constant (k) vary with the order of the reaction. For example:

- Zero order: k has units of $\text{mol L}^{-1} \text{s}^{-1}$,

- First order: s^{-1} ,
- Second order: $\text{L mol}^{-1} \text{s}^{-1}$.

The order of a reaction is determined experimentally using methods such as the method of initial rates or the integrated rate law method. It gives no information about the mechanism or the number of molecules involved in the actual collision step.

In contrast, molecularity is the number of reactant molecules taking part in an elementary step of a reaction. It is always a whole number: unimolecular, bimolecular, or trimolecular, referring to one, two, or three molecules colliding simultaneously in the elementary reaction. For instance, a reaction step involving only the decomposition of a single molecule is unimolecular.

Unlike order, molecularity is theoretical and is assigned only to elementary reactions. It is not applicable to complex reactions or the overall reaction unless it proceeds in a single step. Also, molecularity can never be zero or fractional, unlike the order of reaction.

A major difference between the two is that order is derived from experiments, while molecularity is derived from the reaction mechanism. In a complex reaction involving multiple steps, the rate-determining step governs the observed kinetics, and the overall order may differ from the total molecularity of the reaction.

Integrated rate expression for I and II (2A Products) order reactions

In chemical kinetics, the integrated rate law expresses how the concentration of a reactant changes over time. It is derived by integrating the differential form of the rate law. These expressions help in determining the order of reaction, rate constant, and half-life using experimental data. The two most commonly encountered reaction types are first-order and second-order reactions.

First Order Reactions

For a first-order reaction:



The rate law is:

$$\text{Rate} = -\text{d}[\text{A}]/\text{dt} = k[\text{A}]$$

Rearranging and integrating:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

This gives the **integrated rate equation**:

$$\ln[A] = \ln[A]_0 - kt$$

or

$$\ln \left(\frac{[A]_0}{[A]} \right) = kt$$

Where,

$[A]_0$ is the initial concentration,

$[A]$ is the concentration at time t ,

k is the rate constant,

t is the time.

A plot of $\ln[A]$ vs. time t gives a straight line with a **slope of $-k$** .

The **half-life** ($t_{1/2}$) for a first-order reaction is:

$$t_{1/2} = \frac{0.693}{k}$$

Note: The half-life is independent of concentration for first-order reactions.

Second Order Reactions ($2A \rightarrow \text{Products}$)

For a second-order reaction:



The rate law is:

$$\text{Rate} = -d[A]/dt = k[A]^2$$

Rearranging and integrating:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

This gives the **integrated rate equation**:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Where:

- $[A]_0$ is the initial concentration,
- $[A]$ is the concentration at time t ,
- k is the second-order rate constant.

A plot of $1/[A]$ vs. time t gives a straight line with a **slope of k** .

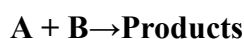
The **half-life** ($t_{1/2}$) for a second-order reaction is:

$$t_{1/2} = \frac{1}{k[A]_0}$$

pseudo first order reaction

In chemical kinetics, a pseudo first order reaction is a reaction that is not truly first order but appears to follow first-order kinetics under specific conditions. This usually happens when a reaction involves two or more reactants, but the concentration of one reactant is present in large excess compared to the other. As a result, the concentration of the excess reactant remains nearly constant throughout the reaction, and its effect on the rate is absorbed into the rate constant.

Let us consider a general second-order reaction involving two reactants A and B:



The rate law is:

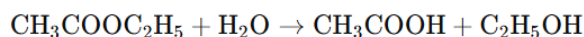
$$\mathbf{Rate = k[A][B]}$$

If B is taken in large excess, then $[B]$ does not change appreciably during the reaction. Therefore, $[B]$ can be treated as a constant. The rate law becomes:

$$\text{Rate} = k[A][B] \approx k'[A]$$

where $k'=k[B]$ is a new constant. Now, the rate law is of the form of a **first-order reaction**, i.e.,

$$\text{Rate}=k'[A]$$



Such a reaction behaves like a first-order reaction even though it is fundamentally second-order. Therefore, it is called a pseudo first-order reaction.

One of the most common examples of a pseudo first-order reaction is the acid hydrolysis of esters. Consider the hydrolysis of ethyl acetate in the presence of excess water:

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$$

This reaction is actually second-order, but since water is present in a large excess (e.g., as solvent), its concentration remains constant. Thus, the reaction follows pseudo first-order kinetics:

Another example is the inversion of cane sugar (sucrose) in the presence of acid:



Since water is again in excess, the rate depends only on the concentration of sucrose.

The integrated rate law for a pseudo first-order reaction is the same as for a first-order reaction:

$$\ln \left(\frac{[A]_0}{[A]} \right) = k't$$

Key features of pseudo first-order reactions:

- Useful in simplifying complex kinetics.
- Common in aqueous and biochemical reactions.
- Enable easier calculation of rate constants and activation energy.

Understanding pseudo first-order reactions is important because many real-world chemical and biological processes occur in environments where one reactant (like water or enzyme) is in large excess, allowing simplification of kinetic analysis.

Methods of determining order of a reaction Half-life period

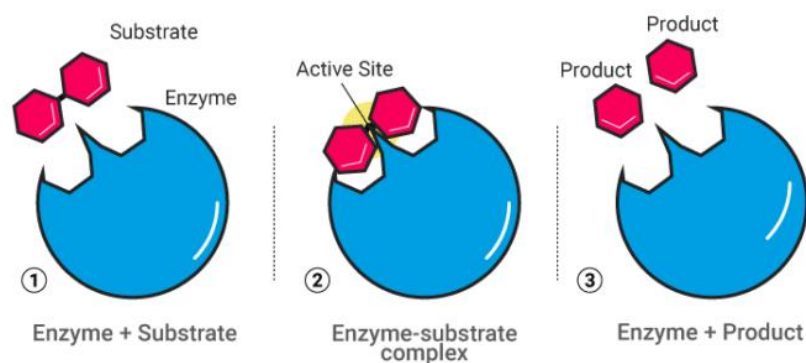
Understanding the order of a chemical reaction is essential in kinetics because it gives insight into how the rate depends on the concentration of the reactants. One effective and commonly used technique to determine the order of a reaction is the half-life period method. This method involves measuring the time required for a reactant's concentration to decrease to half of its original value. This time is referred to as the half-life or $t_{1/2}$. By studying how the half-life changes with varying initial concentrations, one can determine the order of the reaction in a simple and straightforward manner.

For a first-order reaction, the half-life remains constant, regardless of the initial concentration of the reactant. This unique feature of first-order kinetics is very useful and allows chemists to quickly confirm whether a reaction is first order. In contrast, for a zero-order reaction, the half-life is directly proportional to the initial concentration. That means, as the initial amount of the reactant increases, the half-life also increases. On the other hand, for a second-order reaction, the half-life is inversely proportional to the initial concentration. In such cases, if the concentration is high, the half-life becomes shorter, and if the concentration is low, the half-life becomes longer.

The procedure typically involves performing the reaction multiple times with different initial concentrations and measuring how long it takes in each case for the concentration to fall to half. The experimental data are then compared. If the half-life does not change with different initial concentrations, the reaction is likely to be first order. If the half-life increases with concentration, the reaction may be zero order, and if it decreases, the reaction may be second order. This method avoids the need for complicated rate equations and is particularly useful when the integrated form of the rate law is difficult to apply.

The half-life method is widely used in both laboratory experiments and industrial applications. It is especially beneficial for studying reactions that proceed slowly or where direct rate measurements are difficult. This method is also commonly applied in fields like radioactive decay studies, pharmacokinetics, and environmental chemistry. Though the half-life method is very useful, it works best when the reaction is simple and involves only one reactant. In more complex reactions involving multiple steps or intermediate species, other methods such as the method of initial rates or graphical analysis may be more appropriate.

Catalysis



Catalysis is a fundamental concept in chemistry where the speed of a chemical reaction is increased by a substance called a catalyst, which itself remains chemically unchanged at the end of the reaction. Catalysts work by lowering the activation energy required for the reaction to proceed, allowing the process to occur faster and often under milder conditions. Catalysis is broadly classified into two main types: homogeneous catalysis and heterogeneous catalysis, based on the physical state of the catalyst and the reactants.

Homogeneous and Heterogeneous

In homogeneous catalysis, the catalyst and the reactants are present in the same phase, usually in the liquid or gas state. Since all species are in the same phase, the interaction between the catalyst and the reactants is more direct and uniform. A common example is the acid-catalyzed hydrolysis of esters, where both the ester and acid catalyst are in the aqueous phase. Another example is the oxidation of sulfur dioxide in the presence of nitric oxide, where both the catalyst and reactants are gases. Homogeneous catalysts often lead to faster reactions and better control, but their separation from the product mixture can be difficult.

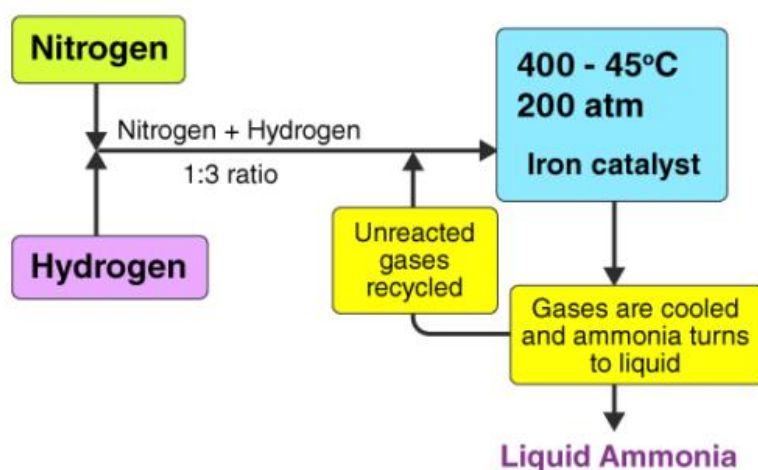
In heterogeneous catalysis, the catalyst is in a different phase from the reactants, typically a solid catalyst interacting with gaseous or liquid reactants. The reaction takes place on the surface of the solid catalyst. This method is widely used in industrial processes due to ease of catalyst recovery and reuse. The reactants get adsorbed on the catalyst surface, react to form the product, and then desorb, leaving the surface ready for the next cycle. Heterogeneous catalysis is used in many applications such as hydrogenation, ammonia synthesis, and oxidation processes.

Two important industrial processes that rely heavily on catalysts are the Contact process and the Haber process. In the Contact process, which is used for the manufacture of sulfuric acid, the key step involves the oxidation of sulfur dioxide to sulfur trioxide. This step uses vanadium pentoxide (V_2O_5) as the heterogeneous catalyst. Vanadium pentoxide provides a large surface area for the reaction and operates efficiently at high temperatures, making the process economically viable.

Haber process

The Haber process is used for the synthesis of ammonia from nitrogen and hydrogen gases. This process uses finely divided iron as the heterogeneous catalyst, often promoted with small amounts of potassium and aluminum oxides to increase its efficiency. The catalyst allows the strong nitrogen-nitrogen triple bond to break more easily, facilitating the reaction under conditions of high temperature and pressure. The Haber process is one of the most important industrial reactions as ammonia is a key raw material for fertilizers and chemicals.

In conclusion, catalysis plays a critical role in both laboratory and industrial chemistry. Understanding the difference between homogeneous and heterogeneous catalysis allows chemists to choose the appropriate conditions for maximum efficiency. The use of specific catalysts in the Contact and Haber processes highlights the practical importance of catalysis in producing essential chemicals on a large scale.



Concept of energy of activation and Arrhenius equation

In chemical kinetics, not all collisions between reactant molecules lead to the formation of products. For a chemical reaction to occur, the reacting molecules must collide with enough energy to overcome a certain minimum energy barrier. This minimum energy required for the reaction to take place is called the **energy of activation**, often denoted as activation energy. It represents the difference in energy between the reactants and the transition state or activated complex. Only those molecules which possess energy equal to or greater than the activation energy during collision are able to transform into products. This concept helps explain why some reactions are fast, while others are slow, even if the reactants are present in similar conditions.

The **Arrhenius equation** provides a mathematical relationship between the rate constant of a reaction and the temperature at which the reaction occurs. The equation shows that the rate of a chemical reaction increases exponentially with an increase in temperature. This is because higher temperatures provide the molecules with more kinetic energy, thus increasing the number of effective collisions. The Arrhenius equation also includes a factor known as the frequency factor or pre-exponential factor, which accounts for the number of collisions and the proper orientation required for reaction.

According to the Arrhenius theory, a graph can be plotted between the logarithm of the rate constant and the reciprocal of the temperature (in Kelvin). The result is a straight line, and the slope of this line is related to the activation energy of the reaction. From the slope, we can calculate the activation energy, which gives valuable insight into how sensitive a reaction is to changes in temperature. If the activation energy is high, a small increase in temperature can lead to a large increase in reaction rate. Conversely, reactions with low activation energy are less sensitive to temperature changes.

The concept of activation energy helps in understanding why catalysts are effective. Catalysts work by lowering the activation energy of a reaction pathway, making it easier for reactant molecules to be converted into products. This means that even at lower temperatures, the reaction can proceed faster when a catalyst is present. The Arrhenius equation also allows scientists to compare the effect of temperature changes on different reactions and to predict the behavior of reactions under various thermal conditions.

In practical applications, the Arrhenius equation is useful in industries to design reactors, predict shelf life of products, and in biological systems to understand enzyme-catalyzed reactions. It plays an important role in areas such as pharmaceuticals, food processing, and materials science. By understanding both the concept of activation energy and the Arrhenius equation, chemists are better equipped to control the speed and efficiency of chemical reactions.

UNIT-5

Photochemistry

Grothus Drapper's law

The Grotthuss–Draper law is one of the fundamental principles in photochemistry and is often referred to as the first law of photochemistry. It was proposed independently by two scientists, Theodor Grotthuss and John William Draper, in the 19th century. The law states that only the light that is absorbed by a substance can bring about a photochemical change. In other words, for a chemical reaction to occur under the influence of light, the reacting substance must first absorb the radiation.

This law implies that the mere exposure of a chemical system to light is not sufficient to initiate a photochemical reaction. The wavelength or frequency of light must be appropriate and must match the energy required by the molecules to get excited. Once the light is absorbed, the molecules are promoted from a ground state to an excited state, and only in this excited state can they participate in chemical transformations.

For example, in photosynthesis, only certain wavelengths of visible light are absorbed by chlorophyll, leading to the formation of energy-rich molecules. Similarly, in photographic films or solar cells, the material must absorb light of suitable energy to trigger the desired effect. If the light passes through the substance without being absorbed, no photochemical reaction will take place, regardless of the light's intensity or duration.

This law helps distinguish photochemical processes from thermal reactions, where energy is supplied in the form of heat. In photochemical reactions, the energy is supplied in the form of photons (light particles), and the success of the reaction depends on how well the reactants absorb the photons. Therefore, the absorption spectrum of a substance plays a critical role in determining its photochemical behavior.

The Grotthuss–Draper law forms the basis for the study of light-induced reactions in chemistry, biology, and environmental science. It is particularly important in designing efficient light-based technologies like UV disinfection, solar energy conversion, and the development of light-sensitive drugs. Without absorption, there can be no initiation of photochemical processes, making this law essential to all studies in the field of photochemistry.

Stark-Einstein's law of photochemical equivalence

The Stark–Einstein law, also known as the second law of photochemistry, is a fundamental principle that explains how light energy is used in photochemical reactions. Proposed independently by Johannes Stark and Albert Einstein, the law states that for each photon of light absorbed by a chemical system, only one molecule is activated for a primary photochemical reaction. This means that one quantum of light activates one molecule, leading to a one-to-one relationship between absorbed photons and reacting molecules in the initial step of the reaction.

This law applies to the primary process of a photochemical reaction, which is the step where the molecule absorbs energy and becomes excited. After excitation, the molecule may undergo further chemical changes, known as secondary processes, which can involve more complex mechanisms. The Stark–Einstein law focuses only on the first, light-absorbing step and not on the subsequent reactions.

To better understand this, it is important to recognize that light behaves like particles called photons, and each photon carries a specific amount of energy depending on its wavelength. When a molecule absorbs a photon, it gains the photon's energy and moves from a lower energy level (ground state) to a higher energy level (excited state). This excited molecule is now capable of undergoing various transformations, such as bond breaking, bond formation, isomerization, or energy transfer.

In many photochemical reactions, especially those involving simple molecules, the Stark–Einstein law holds true with high accuracy. However, in some complex reactions, one absorbed photon may lead to a chain of chemical changes, resulting in the transformation of multiple molecules. In such cases, the law appears to be violated, but actually, the primary photochemical event still follows the law; it is the secondary chain reactions that amplify the overall effect.

Quantum yield Hydrogen -chloride reaction

This law is essential in calculating the quantum yield of a reaction, which is defined as the number of molecules reacting per photon absorbed. A quantum yield close to one indicates high efficiency, while values much greater than one suggest the presence of chain reactions. Photochemical studies in fields such as photosynthesis, vision, polymerization, and photodynamic therapy rely on this principle to understand how efficiently light energy is being converted into chemical change.

Quantum yield is a key concept in photochemistry that measures the efficiency of a photochemical reaction. It is defined as the number of molecules that undergo chemical change for every photon of light absorbed. In most primary photochemical processes, the quantum yield is expected to be

close to one, meaning one molecule reacts per photon absorbed. However, in some reactions, especially chain reactions, the quantum yield can be much greater than one, indicating that a single photon triggers a chain of events leading to the reaction of many molecules.

One of the most famous examples of high quantum yield is the photochemical reaction between hydrogen and chlorine gases to form hydrogen chloride (HCl). When a mixture of hydrogen and chlorine is exposed to light, especially ultraviolet light, a single photon can initiate the reaction. The light breaks a chlorine molecule (Cl_2) into two chlorine atoms ($\text{Cl}\cdot$), each of which is highly reactive. These chlorine atoms react with hydrogen molecules to form hydrogen chloride and generate new reactive atoms, leading to a chain reaction. For every photon absorbed, hundreds or even thousands of HCl molecules may be produced.

This happens because the initial photochemical event the splitting of Cl_2 is followed by a series of fast and repeating chemical steps where reactive intermediates regenerate and propagate the reaction. Since these steps don't require additional light absorption, the reaction continues on its own after the first photon initiates it. As a result, the quantum yield for the $\text{H}_2\text{--Cl}_2$ reaction can be several thousand, meaning that the efficiency is extremely high. This is a classic example of how a photochemical reaction can be initiated by light but sustained by chemical processes.

The high quantum yield observed in the hydrogen-chlorine reaction is important for understanding chain reactions in photochemistry and also in industrial and atmospheric chemistry. It shows that the initial energy input from light can trigger large-scale transformations, and this principle is used in designing photochemical reactors and in studying environmental processes like photochemical smog formation.

Phosphorescence

Phosphorescence is a type of photoluminescence in which a substance absorbs energy from light and then emits it slowly over time, even after the light source has been removed. This phenomenon occurs when the excited electrons get trapped in a metastable state and slowly return to the ground state, releasing light gradually. It differs from fluorescence because it has a longer afterglow. A common example is glow-in-the-dark paints or objects, which continue to emit light in darkness after exposure to sunlight or artificial light.

Fluorescence

Fluorescence is the immediate emission of light by a substance that has absorbed light or electromagnetic radiation. The process involves excitation of electrons to a higher energy level

followed by a rapid return to the ground state, emitting visible light in the process. Fluorescence stops almost immediately when the light source is removed. A good example is the fluorescent dye used in laboratory stains or the bright colors seen under UV light in some minerals or detergents.

Chemiluminescence

Chemiluminescence is the emission of light as a result of a chemical reaction without the involvement of heat or light absorption. The energy released during the reaction excites electrons, which then emit visible light upon returning to the ground state. This phenomenon is observed in glow sticks, where two chemicals react when mixed to produce a glowing effect. Another example is the bioluminescence of fireflies, which emit light through a chemical reaction involving luciferin and enzymes.

Photosensitization

Photosensitization is a process in which a substance known as a photosensitizer absorbs light and transfers the absorbed energy to another molecule, initiating a chemical reaction in that molecule. The photosensitizer itself remains unchanged during the process. This is commonly used in photodynamic therapy for cancer treatment, where a dye absorbs light and generates reactive oxygen species that kill cancer cells. Another example is the sensitization of silver halide crystals in photographic films.

Photosynthesis

Photosynthesis is a natural photochemical process through which green plants, algae, and some bacteria convert carbon dioxide and water into glucose and oxygen using sunlight. This process occurs in the chloroplasts of plant cells, where chlorophyll absorbs solar energy and initiates the reaction. The general equation for photosynthesis is:



Photosynthesis is essential for life on Earth as it is the primary source of oxygen and the foundation of the food chain.