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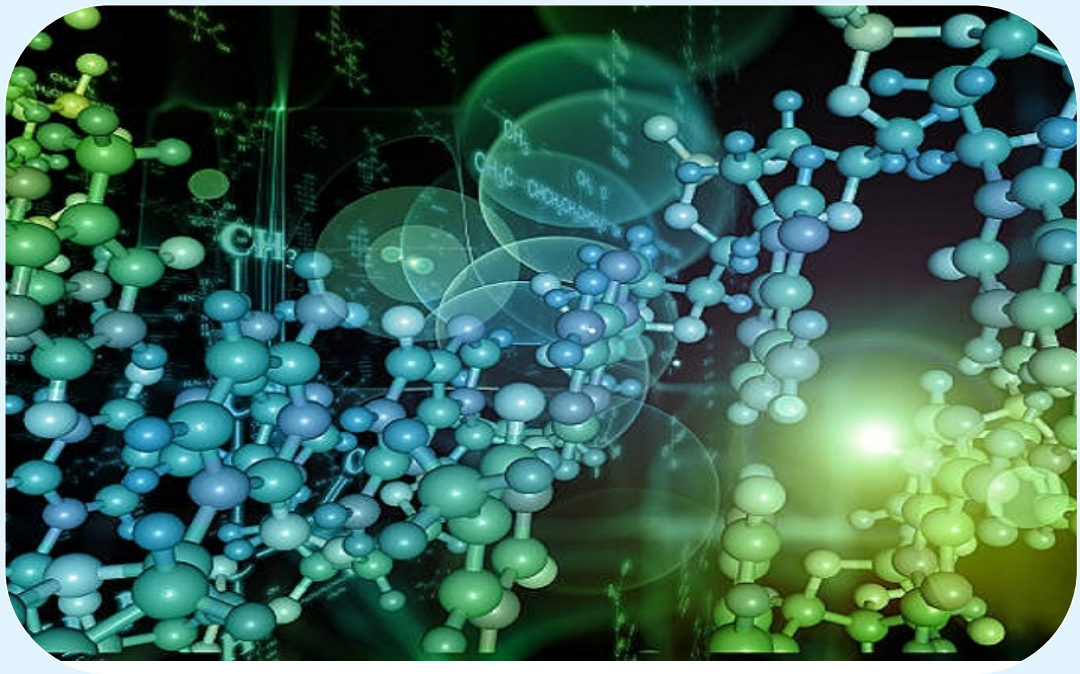
Organic & Physical Chemistry I

Bachelor of Science (B.Sc.)
Semester - 4



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NAAC GRADE A+ ACCREDITED UNIVERSITY

BACHELOR OF SCIENCE
(B.Sc)

Chemistry IV

(Organic and Physical Chemistry-I)

CODE: ODL/MSS/BSCB/403

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The entire syllabus has organized into four modules. Module 01 focuses on organic compounds like alkyl halides, aryl halides, alcohols, and phenols. It covers their structures, synthesismethods, reactivity, and applications. Module 02 explores carbonyl compounds, such asaldehydes and ketones, as well as carboxylic acids and their derivatives, highlighting theirproperties, synthesis, and chemical behavior. Module 03 introduces the concepts of chemicaland phase equilibria, focusing on equilibrium constants, factors that affect equilibrium, andapplications in reversible reactions. Finally, Module 04 covers photochemical reactions andtheir real-world applications, along with the study of liquid-liquid mixtures and the NernstDistribution Law for solute distribution.

BLOCK 1

HALIDES, AND ALCOHOLS

ORGANIC AND PHYSICAL CHEMISTRY

Unit 1Alkyl Halides:

Structure-

1.1 Introduction

Alkyl halides, also known as haloalkanes, are organic compounds in which one or more hydrogen atoms of an alkane are replaced by halogen atoms such as fluorine, chlorine, bromine, or iodine. They are represented by the general formula R–X, where R denotes an alkyl group and X represents a halogen. Depending on the carbon atom to which the halogen is attached, alkyl halides are classified as primary, secondary, or tertiary. They can also be mono-, di-, or poly-halo compounds depending on the number of halogen atoms present. Alkyl halides are generally prepared from alkanes by free radical halogenation, from alcohols by reaction with hydrogen halides or halogenating agents like PCl_3, PBr_3, and $SOCl_2$, and from alkenes by addition of hydrogen halides or halogens. These compounds are typically colorless, insoluble in water but soluble in organic solvents, and their boiling points increase with the size of the halogen atom. Chemically, alkyl halides undergo nucleophilic substitution, elimination, and Grignard reagent formation reactions. They are widely used as solvents, refrigerants, and intermediates in the preparation of pharmaceuticals, dyes, and other organic compounds**.**

1.2 Objective

- Understand the preparation and reactions of alkyl halides.
- Learn about nucleophilic substitution reactions and their mechanisms.

- Study the nomenclature, preparation, properties, and reactions of alcohols and phenols.
- Explore the mechanismsof important reactions like Williamson's ether synthesis, Fries rearrangement, and Reimer-Tiemann reaction.

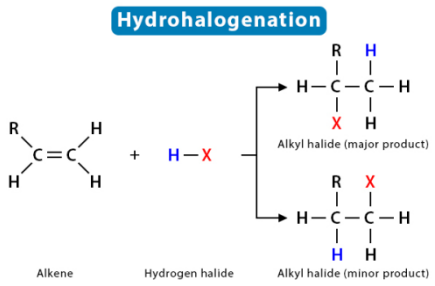
A particularly important class of organic compounds with carbon halogen bonds are the alkyl halides. The chemical reactivity of these compounds gives them the potential to serve as versatile synthetic intermediates in organic chemistry, undergoing a variety of transformation in differing reaction conditions. Theyare easyto prepare from alkenes and alcohols, and they undergo a variety of nucleophilic substitution reactions that enable the introduction of a wide range of functional groups. Mechanism, stereochemistry and factors of these reactions help in predicting the reaction and designing the synthetic pathway. Covering the preparation, nucleophilic substitution reactions, mechanisms and stereochemistry, this in-depth article and infographic also covers the factors that affect the reactivity of alkyl halides.

1.3 Preparation of Alkyl Halides-

Alkyl halides can be synthesized through various methods, with preparation from alkenes and alcohols being among the most common and synthetically useful approaches.

Preparation from Alkenes Alkenes serve as excellent precursors for alkyl halides through addition reactions across the carbon-carbon double bond. These additions typically follow Markovnikov's rule unless specific reagents or conditions are employed to achieve anti-Markovnikov addition.

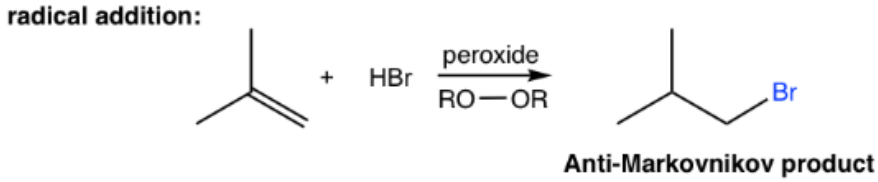
Addition of Hydrogen Halides (HX) The addition of hydrogen halides (HX, where X = Cl, Br, I) to alkenes represents one of the most straightforward methods for preparing alkyl halides. This reaction proceeds via electrophilic



2. Anti-Markovnikov Addition (Peroxide Effect)

1.2 When the addition of HBr is carried out in the presence of peroxides (ROOR), the reaction proceeds via a radical mechanism, resulting in anti-

Markovnikov addition. This phenomenon is known as the peroxide effect or Kharasch effect:



Halogenation of Alkenes

Alkenes react with halogens (X, , where X = Cl, Br) to form vicinal dihalides through ananti addition mechanism. Thisreaction proceeds through acyclic halonium ion intermediate:

For instance, the reaction of ethene with bromine yields 1,2-dibromoethane:

1.4. Halohydrin Formation :Alkenes react with halogens in aqueous medium to form halohydrins, which are compounds containing both a halide and a hydroxyl group on adjacent carbon atoms:

R, C=CR, + X, + H, O '! R, CX-CR, OH + HX

For example, the reaction of propene with bromine in water produces 1-bromo-2-propanol:

CH*f* CH=CH, + Br, + H, O '! CH*f* CHBr-CH, OH + HBr

Preparation from Alcohols

Alcohols serve as excellent precursors for alkyl halides through various substitution reactions. The hydroxyl group (-OH) in alcohols can be replaced by a halogen atom under appropriate conditions.

Reaction with Hydrogen Halides (HX): Alcohols react with hydrogen halides (HX, where X = Cl, Br, I) to form alkyl halides and water:

R-OH + HX '! R-X + H, O The reactivity of alcohols toward hydrogen halides follows the order: tertiary >

2. Reaction with Phosphorus Halides (PX*f* , PX…) Alcohols react with phosphorus halides such as PCl*f* , PCl… , PBr*f* , and PI*f* to form alkyl halides: 3R-OH + PX*f* '! 3R-X + H*f* PO*f* R-OH + PX… '! R-X + POX*f* + HX For instance, the reaction of ethanol with phosphorus tribromide yields bromoethane: 3CH*f* CH, OH + PBr*f* '! 3CH*f* CH, Br + H*f* PO*f*

Phosphorus halides are particularly useful for converting primary and secondary alcohols to alkyl halides without significant rearrangement.

3.**Reaction with Thionyl Chloride (SOCl,):** Alcohols react with thionyl chloride (SOCl,) in the presence of a base such as pyridine to form alkyl chlorides: R-OH + SOCl, '! R-Cl + SO, + HCl

For example, the reaction of 1-butanol with thionyl chloride yields 1-chlorobutane: This method is particularly advantageous because the byproducts (SO, and HCl) are gases that escape from the reaction mixture, driving the equilibrium toward the product.

Reaction with Sulfonyl Chlorides :Alcohols can be converted to alkyl halides via tosylate or mesylate intermediates. The alcohol is first converted to a tosylate or mesylate, which then undergoes nucleophilic substitution with a halide ion: This two-step process is particularly useful for converting alcohols that are prone to rearrangement or elimination reactions.

1.4Chemical properties

Nucleophilic Substitution Reactions of Alkyl Halides: Alkyl halides undergo a variety of nucleophilic substitution reactions, wherein the halogen atom is replaced by a nucleophile. These reactions are central to organic synthesis as they allow for the introduction of various functional groups.

Alcohol Formation

Alkyl halides react with aqueous bases such as NaOH or KOH to form alcohols: R-X + OH{ '! R-OH + X{

For example, the reaction of 1-bromobutane with sodium hydroxide yields 1-butanol: CH*f* CH, CH, CH, Br + NaOH '! CH*f* CH, CH, CH, OH + NaBr

This reaction proceeds via an SN2 mechanism for primaryand secondaryalkyl halides, while tertiary alkyl halides may undergo elimination (E2) as a competing reaction.

Nitriles are valuable intermediates in organic synthesis as they can be hydrolyzed to carboxylic acids or reduced to amines.

Isonitrile Formation

Williamson's Ether Synthesis

The Williamsonether synthesis represents one of the most reliablemethods for preparing ethers. In this reaction, an alkyl halide reacts with an alkoxide ion to form an ether:

R-X + R'O{ '! R-O-R' + X{

For example, the reaction of bromoethane with sodium methoxide yields methyl ethyl ether:

CH*f* CH, Br + CH*f* O{ Naz '! CH*f* CH, OCH*f* + NaBr

For optimal results, primary alkyl halides are preferred as they minimize competing elimination reactions. The reaction proceeds via an SN2 mechanism, leading to inversion of configuration at the stereogenic center if present in the alkyl halide.

Mechanism and Stereochemistry of Nucleophilic Substitution Reactions

Nucleophilic substitution reactions of alkyl halides primarily proceed through two distinct mechanisms: SN1 (Substitution Nucleophilic Unimolecular) and SN2 (Substitution Nucleophilic Bimolecular). Understanding these mechanisms is crucial for predicting reaction outcomes, including stereochemistry.

SN2 Mechanism

The SN2 mechanism involves a concerted process where the nucleophile attacks the carbon bearing the halogen from the side opposite to the leaving group, resulting in inversion of stereochemistry. This mechanism occurs in a single step without the formation of intermediates.

Key features of the SN2 mechanism include:

1. Rate Law: The reaction rate depends on the concentrations of both the substrate and the nucleophile, indicating a bimolecular process:

Rate = k[R-X][Nu{]

2. Stereochemistry: The SN2 mechanism proceeds with inversion of configuration at the stereogenic center, often described as an “umbrella-like” inversion or “Walden inversion.” If the reaction occurs at a stereogenic center, the product will have the opposite configuration:

R-X + Nu{ ’! [Nu—C—X]‡ ’! Nu-R + X{

For example, when (R)-2-bromobutane reacts with hydroxide ion, (S)-2-butanol is formed:

(R)-CH*f* CH, CHBrCH*f* + OH{ ’! (S)-CH*f* CH, CHOHCH*f* + Br{

3. Transition State: The transition state involves a pentacoordinate carbon atom with partial bonds to both the nucleophile and the leaving group, resulting in a trigonal bipyramidal geometry.

4. Substrate Reactivity: The reactivityof alkyl halides in SN2 reactions follows the order: methyl > primary > secondary > tertiary. This trend reflects the steric hindrance encountered by the nucleophile during its approach to the carbon center.

SN1 Mechanism

The SN1 mechanism involves a stepwise process where the departure of the leaving group precedes the attack of the nucleophile, resulting in the formation of a carbocation intermediate. This mechanism consists of two distinct steps.

Key features of the SN1 mechanism include:

1. Rate Law: The reaction rate depends only on the concentration of the substrate, indicating a unimolecular process:

Rate = k[R-X]

2. Stereochemistry: The SN1 mechanism typically results in racemization with a slight predominance of inversion due to the presence of the departing leaving group on one face of the planar carbocation, partially hindering nucleophilic attack from that side:

R-X '! Rz + X{ Rz + Nu{ '! R-Nu

For example, when (R)-2-bromobutane undergoes SN1 reaction with water, a mixture of (R)- and (S)-2-butanol is formed, with a slight excess of the (S)-isomer.

3. Carbocation Intermediate: The carbocation intermediate is planar and sp^2- hybridized, allowing the nucleophile to attack from either face. However, the departing leaving group may shield one face, leading to partial inversion.

4. Substrate Reactivity: The reactivityof alkyl halides in SN1 reactions follows the order: tertiary > secondary > primary > methyl. This trend corresponds to the stability of the carbocation intermediates: tertiary > secondary> primary
> methyl.

5. Rearrangements: Carbocation intermediates may undergo rearrangements (hydride or alkyl shifts) to form more stable carbocations before nucleophilic attack, potentially leading to unexpected products.

Factors Affecting SN1 and SN2 Reactions

Several factors influence the rates and outcomes of SN1 and SN2 reactions, determining which mechanism predominates under given conditions.

Nature of the Substrate

The structure of the alkyl halide significantly impacts the reaction mechanism:

1. Steric Hindrance: Increasing steric hindrance around the reaction centerfavors SN1 over SN2:

- Primary alkyl halides predominantly undergo SN2 reactions due to minimal steric hindrance.
- Secondary alkyl halides can undergo both SN1 and SN2 reactions depending on other factors.
- Tertiary alkyl halides predominantly undergo SN1 reactions due to significant steric hindrance that impedes nucleophilic attack in an SN2 fashion.

2. Carbocation Stability: The stability of the potential carbocation intermediate strongly influences the likelihood of an SN1 mechanism:

- Tertiary carbocations are relatively stable due to hyperconjugation and inductive effects from alkyl groups.
- Secondary carbocations are moderately stable.

- Primary carbocations are highly unstable and generally do not form under normal conditions.
- Methyl carbocations are extremely unstable and essentially do not form.

3. Leaving Group Ability: The ability of the halide to depart as a leaving group affects both mechanisms:

- The leaving group ability of halides follows: I{ > Br{ > Cl{ > F{ , corresponding to their decreasing polarizabilityand increasing basicity.
- Better leaving groups facilitate both SN1 and SN2 reactions but have a more pronounced effect on SN1 reactions as the rate-determining step involves leaving group departure.

Nature of the Nucleophile

The characteristics of the nucleophile significantly impact the reaction pathway:

1. Nucleophilicity: Stronger nucleophiles favor SN2 reactions:

• Nucleophilicity generally follows the trend: R*f* P > R*f* N > RS{ > I{ > CN{ > Br{ > HO{ > Cl{ > F{ > ROH > H, O

• Factors affecting nucleophilicity include:

Ø Basicity: Higher basicity often correlates with higher nucleophilicity, especiallywithin the same row of the periodic table.

Ø Polarizability: More polarizable species tend to be better nucleophiles, especially in aprotic solvents.

Ø Charge: Negatively charged species are generally stronger nucleophiles than their neutral counterparts (e.g., HO{ > H, O).

2. Steric Bulk: Bulkynucleophiles favor SN1 reactions as theyencounter greater steric hindrance in approaching the carbon center in an SN2 fashion.

3. Concentration: Higher nucleophile concentration favors SN2 reactions as the rate of SN2 reactions depends on nucleophile concentration, while SN1 reactions are independent of it.

Solvent Effects

The solvent plays a crucial role in determining the reaction mechanism:

1. Polar Protic Solvents (e.g., water, alcohols, carboxylic acids):

• Favor SN1 reactions by:

Ø Stabilizing the carbocation through solvation

Ø Stabilizing the leaving group through hydrogen bonding

Ø Decreasing nucleophilicitythrough hydrogen bonding with the nucleophile

• Examples include water, methanol, ethanol, and formic acid.

2. Polar Aprotic Solvents (e.g., acetone, DMF, DMSO, acetonitrile):

• Favor SN2 reactions by: Ø Not forming hydrogen bonds with nucleophiles, leaving them “naked” and more reactive

Ø Solvating cations effectively, increasing nucleophile reactivity

- Examples include dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, and acetonitrile.

3. Nonpolar Solvents (e.g., hexane, benzene, carbon tetrachloride):

- Generally disfavor both SN1 and SN2 reactions due to poor solvation of ionic species
- May support SN2 reactions with strong, neutral nucleophiles

Temperature Effects: Temperature influences the competition between SN1 and SN2 mechanisms:

1. Higher Temperatures:

- Generally favor SN1 reactions due to the higher activation energy associated with bond breaking in the rate-determining step.
- Also favor competing elimination reactions (E1 and E2) over substitution reactions.

2. Lower Temperatures:

- Generally favor SN2 reactions, especially with good nucleophiles and primary or secondary substrates.
- Minimize competing elimination reactions.

Competitive Elimination Reactions Substitution reactions often compete with elimination reactions:

1. E1 (Elimination Unimolecular):
- Competes with SN1 and involves the same carbocation intermediate
- Favored by higher temperatures, stronger bases, and bulkier substrates
- Results in the formation of alkenes

2. E2 (Elimination Bimolecular):
- Competes with SN2 and involves a concerted mechanism
- Favored by strong, sterically hindered bases, higher temperatures, and tertiary substrates
- Results in the formation of alkenes with predominantlyanti elimination

The competition between substitution and elimination can be controlled by adjusting reaction conditions:

- To favor substitution: Use weaker bases/better nucleophiles, lower temperatures, and polar aprotic solvents.
- To favor elimination: Use stronger bases, higher temperatures, and bulkier bases.

1.5 Physical properties

1. State and Appearance:Lower alkyl halides like methyl chloride and ethyl chloride are gases, while higher members such as bromo- and iodoalkanes are liquids or solids. Most alkyl halides are colorless, though some like bromo- and iodo-compounds may appear yellowish due to light decomposition.
2. Odour:They generally have sweet or chloroform-like odours, but prolonged exposure can be harmful or irritating.
3. Solubility:Alkyl halides are insoluble in water because they cannot form hydrogen bonds with water molecules. However, they are soluble in organic solvents like ether, benzene, and chloroform.
4. Density:The density increases with the molecular weight of the halogen atom (I > Br > Cl > F). Usually, iodoalkanes are the heaviest, and fluoroalkanes are the lightest. Most chloroalkanes are heavier than water, while fluoro- and some bromo-alkanes are lighter.
5. Boiling Point:Boiling points increase with an increase in molecular mass and the size of the halogen.For isomeric alkyl halides, the boiling point decreases with increasing branching of the alkyl group.For the same alkyl group:R–I > R–Br > R–Cl > R–F(because of increasing van der Waals forces with atomic size).
6. Polarity:Alkyl halides are polar molecules due to the difference in electronegativity between carbon and halogen atoms, resulting in a C–X dipole.
7. Refractive Index:The refractive index of alkyl halides increases with the number and atomic weight of halogen atoms present.

1.6 Applications of Alkyl Halide Reactions

Understanding the preparation and reactivity of alkyl halides enables their effective use in various synthetic applications:

1. Synthetic Intermediates: Alkyl halides serve as versatile intermediates in the synthesis of various organic compounds, including alcohols, ethers, esters, amines, and nitriles.

2. C-C Bond Formation: Alkyl halides participate in numerous carbon-carbon bond-forming reactions, such as the Wurtz reaction, Grignard reaction, and various coupling reactions.

3. Pharmaceuticals: Many pharmaceutical compounds are synthesized using alkyl halide intermediates due to their versatile reactivity.

4. Agrochemicals: Numerous pesticides, herbicides, and fungicides contain halogenated compounds or are synthesized using alkyl halide intermediates.

5. Materials Science: Halogenated polymers and materials exhibit unique properties, making them valuable in various applications.

Alkyl halides are one of the main classes of organic compounds with broad synthetic applications. Their synthetic availability from alkenes and alcohols affords simple procedures for the installation of halogen atoms into organic structures. In fact there are full series of nucleophilic substitution reactions performed on alkyl halides which enables the formation of alcohols, esters, nitriles, isonitriles and Williamson's ether synthesis etc. Mechanistic understanding and stereochemistry of SN1 and SN2 reactions. The driving forces behind these reactions—and substrate structure, nucleophile properties, and solvent and temperature effects—give chemists the ability to tune reaction conditions to favour the pathway of choice. As an organic chemist, the more you learn about the fundamental principles that govern alkyl halide chemistry, the more you will be able to leverage these remarkable intermediates for the development of the intricate molecules utilized in human societyrangingfrom medicines to agrochemicals to the plastics that deliver them. LINOWSKI, DR; Strength during the trauma response and symptom severity related to adolescent enhancement and incrementation of drug-seeking behavior.

Check your Progress

1.What is the difference between primary, secondary, and tertiary alkyl halides in terms of structure and reactivity?

.....
.....

2. What is the difference between primary, secondary, and tertiary alkyl halides in terms of structure and reactivity?

……
……
……

1.7 Summary:

Alkyl halides are organic compounds where a halogen replaces hydrogen in an alkane; they are classified as primary, secondary, or tertiary based on the carbon attached to halogen; the C–X bond is polar and reactivity order is RI > RBr > RCl > RF; they mainly undergo nucleophilic substitution and elimination reactions; and they are widely used as solvents, refrigerants, and synthetic intermediates.

1.8 Exercise questions:

Q1. Which is a primary alkyl halide?

a) CH_3Cl b) $(CH_3)_3CCl$ c) $CH_3CHClCH_3$ d) $CH_2=CHCl$

Q2. Correct C–X bond strength order?

a) C–I > C–Br > C–Cl > C–F

b) C–F > C–Cl > C–Br > C–I

c) C–Cl > C–F > C–Br > C–I

d) C–Br > C–I > C–F > C–Cl

Q3. Most easily displaced halogen?

a) F b) Cl c) Br d) I

Q4. General formula of monohaloalkanes?

a) C_nH_{2n+2} b) $C_nH_{2n+1}X$ c) $C_nH_{2n}X$ d) $C_nH_{2n-2}X$

Q5. Common refrigerant?

a) Ethyl chloride b) Methyl iodide c) Freons d) Vinyl chloride

Short answer type questions-

1. What are alkyl halides? Give two examples.
2. Write the general formula of alkyl halides.
3. Classify alkyl halides based on the type of carbon atom attached to the halogen.

4. Why are alkyl halides insoluble in water?
5. Arrange the following in order of increasing boiling point: CH_3F, CH_3Cl, CH_3Br, CH_3I.
6. What is the IUPAC name of $CH_3CH_2CH_2Br$?
7. How will you prepare ethyl bromide from ethanol?
8. What happens when ethyl chloride reacts with aqueous KOH?
9. What happens when alkyl halides react with alcoholic KOH?
10. Why do tertiary alkyl halides undergo SN1 reactions more easily than primary ones?

Long answer types questions-

1. Explain the **classification of alkyl halides** with suitable examples.
2. Describe **three methods of preparation** of alkyl halides with balanced chemical equations.
3. Discuss the **physical properties of alkyl halides** and explain how these vary with molecular mass.
4. Explain the **chemical reactions** of alkyl halides with suitable examples (substitution, elimination, and Grignard reagent formation).
5. Compare the **reactivity of primary, secondary, and tertiary alkyl halides** towards nucleophilic substitution reactions.

1.9 Reference and suggestive readings

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Unit – 2 Aryl Halides:

Structure

2.1 Introduction Aryl halides are aromatic compounds where one or more hydrogen atoms directly bonded to an aromatic ring system are variable for halogen atoms (fluorine, chlorine, bromine, or iodine). The simplest aryl halide is halobenzene, in which one of the hydrogen atoms in a benzene ring is replaced by a halogen atom. They serve as important building blocks in organic synthesis for a range of transformations. They have unique reactivitypatterns due to the presence of the aromatic ring system affecting the carbon-halogen bond, unlike the reactivity of alkyl halides. Aryl halides are a prime example of a class of compounds whose chemistry is dominated by a resonance- stabilized aromatic ring that affects bond strength, nucleophilic reactivity, and involvement in a range of mechanistic pathways. Chlorobenzene is the first chlorinated aromatic compound and should be taken as a prototypical example for this class of compounds in terms of its chemical reactivity.

Preparation of Chlorobenzene There are several methods of synthesizing chlorobenzene; the most important industrial and laboratory procedures are aromatic halogenation and the Sandmeyer reaction.

Aromatic Halogenation

1.Electrophile Generation: The Lewis acid catalyst (FeCl) interacts with molecular chlorine (Cl,) to generate a more electrophilic species, enhancing the polarization of the Cl-Cl bond and creating an electrophilic Clz species:

2.Electrophilic Attack: The electrophilic Clz attacks the ð-electron system of benzene, forming a resonance-stabilized carbocation intermediate (arenium ion or ó-complex):

3.Deprotonation: The carbocation intermediate loses a proton to a base (typically [FeCl,,]{) to restore aromaticity: This methodis effective but haslimitations including lack of regioselectivityin substituted benzenes, potential for multiple halogenation, and the production of HCl as a byproduct, which can be corrosive and environmentally problematic.

Sandmeyer Reaction: The Sandmeyer reaction provides a more controlled method for synthesizing aryl halides, including chlorobenzene. This reaction involves the conversion of an aromatic diazonium salt to an aryl halide. The process typically follows these steps:

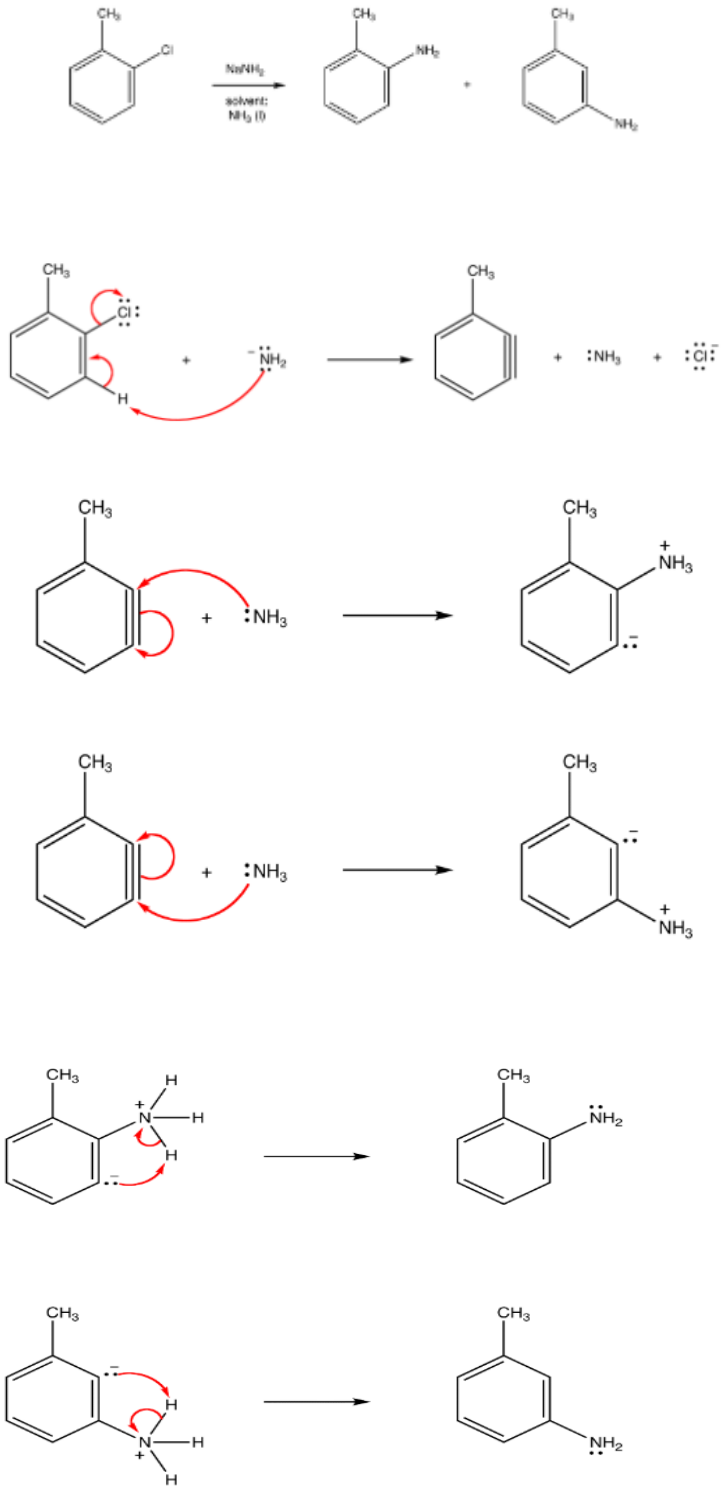
1.Diazotization: Aniline (or another primary aromatic amine) is treated with sodium nitrite (NaNO,) in the presence of a strong acid (usually HCl) at low temperatures (0-5°C) to form a diazonium salt:

C† H… NH, + NaNO, + 2HCl '! C† H… N, z Cl{ + NaCl + 2H, O

2.Halogenation: The diazonium salt is then treated with copper(I) chloride (CuCl) to form chlorobenzene:

- Superior region selectivity, as the position of halogenation is determined by the initial position of the amino group
- Versatility in introducing various functional groups (not just halogens)
- Milder reaction conditions compared to direct halogenation However, the Sandmeyer reaction has drawbacks such as:
- A multi-step process requiring careful temperature control
- Formation of unstable and potentially explosive diazonium intermediates
- Necessity of copper catalysts, which can be environmentally concerning Aromatic Nucleophilic Substitution Involving Benzyne Mechanism Base does not form on the side of solvent non-volatile - to that a method use derives on nucleophilic substitutions because that are obtained the more positive charge on the second carbon of the aryl haloginol takes place because that as that solvent is less volatile. Anotable way is via benzyne mechanism, which takes place using very strong bases like with potassium amide (KNH,) or sodium amide (NaNH,) in liquid ammonia.

The Benzyne Mechanism: The benzyne mechanism of aromatic nucleophilic substitution in chlorobenzene using KNH, /NH*f* proceeds through the following steps:



Several key characteristics of the benzyne mechanism include:

• Regioselectivity: Since the nucleophile can attack either carbon of the triple bond in the benzyne intermediate, the reaction often leads to a mixture of products when substituted aryl halides are used. For monosubstituted benzenes,

meta-substitution is preserved, while ortho and para substitutions can interchange.

- Base Strength Requirement: The mechanism requires extremely strong bases (like KNH,) to abstract a proton from the relatively non-acidic benzene ring.
- Temperature Considerations: The reaction typically requires low temperatures due to the use of liquid ammonia as a solvent.
- Evidence for Benzyne: The existence of benzyne intermediates has been confirmed through various experimental methods, including trapping experiments and isotopic labeling studies.

Applications and Limitations of the Benzyne Mechanism

The benzyne mechanism provides a valuable route for nucleophilic substitution in aryl halides that are otherwise resistant to such transformations. However, it has several limitations:

- Limited Substrate Scope: The reaction works best with aryl halides that possess hydrogen atoms at the ortho positions.
- Regioselectivity Issues: The reaction often produces a mixture of isomers due to the lack of regioselectivity in the nucleophilic addition step.
- Harsh Conditions: The requirement for extremely strong bases and low temperatures limits practical applications.

- Competing Reactions: Side reactions, including polymerization of the highly reactive benzyne intermediate, can reduce yields.

Despite these limitations, benzyne chemistry has found applications in the synthesis of complex aromatic compounds, particularlythose with substituents thatwould be difficult to introduce through conventional methods.

Reactivity and Relative Strength of C-Halogen Bonds

The reactivity of halogenated compounds is intimately connected to the strength of the carbon-halogen bond. Understanding the relative bond strengths in different classes of halogenated compounds—aryl halides, alkyl halides, and vinyl halides—provides critical insights into their chemical behavior.

Carbon-Halogen Bond Strength in Different Classes The carbon-halogen bond strengths follow this general order: Aryl-X > Vinyl-X >Alkyl-X

Where X represents a halogen atom (F, Cl, Br, or I).

This ordering can be explained by considering the hybridization state of the carbon atom and the influence of resonance effects:

1. Aryl Halides (C† H… -X):

- The carbon-halogen bond is formed between an sp^2 hybridized carbon of the aromatic ring and the halogen.
- The bond is strengthened byresonance interaction between the ð-electrons of the aromatic ring and the p-orbitals of the halogen.
- This resonance contribution gives the carbon-halogen bond partial double- bond character, increasing its strength.
- The electron-withdrawing nature of the aromatic ring also reduces electron densityat the carbon-halogen bond, decreasing its polarization and making it less susceptible to nucleophilic attack.

2. Vinyl Halides (CH, =CH-X):

- The carbon-halogen bond involves an sp^2 hybridized carbon.
- There is some resonance stabilization due to the interaction between the ð-bond and the p-orbitals of the halogen, though less extensive than in aryl halides.
- This limited resonance contribution still provides some additional bond strength compared to alkyl halides.

3. Alkyl Halides (R-X):

- The carbon-halogen bond involves an sp^3 hybridized carbon.
- No resonance stabilization is possible.
- The bond is more polarized due to the electronegativity difference between carbon and halogen, making it more susceptible to nucleophilic attack.

Quantitative Bond Strength Comparison

In terms of bond dissociation energies:

1. Aryl-Cl Bond: ~96 kcal/mol
2. Vinyl-Cl Bond: ~94 kcal/mol
3. Alkyl-Cl Bond: ~85 kcal/mol

Similar trends are observed for other halogens, though the absolute values differ.Effect of Halogen Identity on Bond Strength Within each class of halogenated compounds, the carbon-halogen bond strength follows the order:
C-F > C-Cl > C-Br > C-I This ordering correlates with the electronegativity and atomic size of the halogens

- Carbon-fluorine bonds are the strongest due to fluorine's high electronegativity and small size, allowing for effective orbital overlap.
- As atomic size increases down the halogen group, orbital overlap becomes less effective, and bond strength decreases.

Implications for Reactivity

The differences in carbon-halogen bond strengths have significant implications for the reactivity of these compounds:

1. Nucleophilic Substitution (S™ 2 and S™ 1):

- Alkyl halides readily undergo nucleophilic substitution due to their weaker C-X bonds and the accessibility of the ó* antibonding orbital.
- Aryl halides are highly resistant to nucleophilic substitution under standard conditions due to their stronger C-X bonds, the steric hindrance provided by the aromatic ring, and the lack of accessibility to the ó* antibonding orbital.
- Vinyl halides show intermediate reactivity but are generally resistant to standard nucleophilic substitution conditions.

2. Elimination Reactions:

- Alkyl halides readily undergo elimination reactions (E1 and E2).
- Aryl halides require special conditions, such as very strong bases (as in the benzyne mechanism), to undergo elimination.
- Vinyl halides can undergo elimination but typically require stronger bases compared to alkyl halides.

3. Reduction Reactions:

- The ease of reduction follows the order: Alkyl-X > Vinyl-X > Aryl- X, directly correlating with the inverse of bond strength.

4. Metal-Catalyzed Coupling Reactions:

- Aryl and vinyl halides participate effectivelyin various metal-catalyzed coupling reactions (Suzuki, Heck, Stille, etc.).
- In these reactions, the reactivity generally follows the order: Aryl-I > Aryl-Br >Aryl-Cl, reflecting the ease of oxidative addition which is inversely related to bond strength.

Role of Bond Strength in Reaction Mechanisms

The strength of the carbon-halogen bond plays a crucial role indetermining the dominant reaction mechanisms for different classes of halogenated compounds:

1. Alkyl Halides:

• Weaker C-X bonds and higher polarization favor both S™ 2 and S™ 1 mechanisms.

• Primary alkyl halides typically react via S™ 2, while tertiary alkyl halides favor S™ 1.

2. Aryl Halides:

• Stronger C-X bonds and resonance stabilization generally make conventional S™ 2 or S™ 1 mechanisms unfavorable.

• Instead, these compounds often react via:

Ø Addition-elimination mechanisms (nucleophilic aromatic substitution) when strong electron-withdrawing groups are present at ortho/para positions

Ø Benzyne mechanisms with very strong bases Ø Metal-catalyzed coupling reactions

3. Vinyl Halides:

• Like aryl halides, vinyl halides are resistant to standard nucleophilic substitution.

• They typically react via addition-elimination pathways or metal-catalyzed processes.

Activating and Deactivating Effects in Aryl Halides

The reactivity of aryl halides is significantly influenced by the electronic effects of the halogen substituent on the aromatic ring. Halogens exert both inductive and resonance effects, which have opposing influences on the reactivity of the aromatic system.

Inductive Effects

Halogens are electronegative elements that withdraw electron density through the sigma bond framework (inductive effect):

• This inductive withdrawal makes the aromatic ring electron-deficient.

• The strength of this effect decreases with distance and follows the electronegativity trend: F > Cl > Br > I.

- The electron-withdrawing inductive effect deactivates the aromatic ring toward electrophilic substitution.

Resonance Effects

Halogens possess lone pairs of electrons that can participate in resonance with the aromatic ð-system:

- This resonance donation of electron density enriches the ortho and para positions of the aromatic ring.
- The strength of this effect depends on the effective overlap between the halogen's p-orbitals and the aromatic ð-system.
- The resonance effect activates the aromatic ring toward electrophilic substitution, particularly at the ortho and para positions.

Net Effect on Electrophilic Aromatic Substitution

The net effect of halogen substituents on electrophilic aromatic substitution is:

- Moderate Deactivation: The inductive withdrawal slightly outweighs the resonance donation, making halobenzenes less reactive than benzene toward electrophilic substitution.

- ortho/para Direction: Despite the overall deactivation, the resonance effect directs incoming electrophiles primarily to the ortho and para positions.

This combination of moderate deactivation and ortho/para direction places halogens in a unique category among aromatic substituents.

Applications of Aryl Halides

Aryl halides find extensive applications in various fields due to their versatile reactivity and the valuable products that can be derived from them.

Synthetic Intermediates

Aryl halides serve as crucial intermediates in organic synthesis:

1. Cross-Coupling Reactions:Aryl halides are essential substrates for numerous metal-catalyzed cross-coupling reactions, including:

- Suzuki-Miyaura coupling (with boronic acids)

- Heck reaction (with alkenes)
- Sonogashira coupling (with terminal alkynes)
- Stille coupling (with organostannanes)
- Negishi coupling (with organozinc compounds)
- Buchwald-Hartwig amination (with amines)

2. Grignard Reagent Formation:Aryl halides can be converted to aryl Grignard reagents, which are versatile nucleophiles for carbon-carbon bond formation.
3. Lithiation: Aryl halides can undergo halogen-lithium exchange to form aryllithium compounds, which are highlyreactive nucleophiles.

Industrial and Commercial Applications

1. Pharmaceuticals: Many pharmaceutical compounds contain aryl halide moieties or are synthesized using aryl halide intermediates.
2. Agrochemicals: Numerous pesticides, herbicides, and fungicides incorporate aryl halide structures.
3. Polymers: Chlorobenzene and its derivatives are used in the production of polymers like polychlorobiphenyls (PCBs) and polysulfones.
4. Solvents: Chlorobenzene serves as a solvent for various industrial processes, particularly those involving high-temperature reactions.
5. Flame Retardants: Brominated aryl compounds are widely used as flame retardants in various materials.

Environmental Considerations

Despite their utility, many aryl halides pose environmental concerns:

- Persistence: Many aryl halides, especially chlorinated and brominated compounds, are resistant to biodegradation.
- Bioaccumulation: Lipophilic aryl halides can accumulate in fatty tissues of organisms.
- Toxicity: Some aryl halides have been associated with various toxic effects, including endocrine disruption and carcinogenicity.

These concerns have led to increased regulation and the development of greener alternatives in many applications.

Analytical Methods for Aryl Halides

The identification and characterization of aryl halides involvevarious analytical techniques, which exploit their physical and chemical properties.

Spectroscopic Methods

1. Infrared (IR) Spectroscopy:

- C-Hal stretching vibrations: C-F (1400-1000 cm{ [1]), C-Cl (800-600 cm{ [1]), C-Br (600-500 cm{ [1]), C-I (500-400 cm{ [1])

- Characteristic aromatic C-H out-of-plane bending patterns that are affected by the halogen substitution patter

2. Nuclear Magnetic Resonance (NMR) Spectroscopy:

- ^{1}H-NMR: Halogen substituents cause deshielding of ortho protons due to their electronegativity
- ^{13}C-NMR: Carbon atoms bearing halogens show characteristic chemical shifts
- Coupling constants between protons in halogenated aromatic rings provide information about substitution patterns

3. Mass Spectrometry (MS):

- Distinctive isotope patterns due to the natural isotopic distribution of halogens (especially chlorine and bromine)
- Fragmentation patterns often involve the loss of halogen radicals

Chemical Tests

1. Beilstein Test: Copper wire is heated in a flame, dipped in the sample, and reheated. Agreen flame indicates the presence of halogen.
2. Silver Nitrate Test: After fusion with sodium metal, the sample is extracted with water and treated with silver nitrate. Formation of a silver halide precipitate confirms the presence of a halogen.

3. Reaction with Alcoholic KOH: Different classes of halogenated compounds show varying reactivity with alcoholic KOH, helping to distinguish between aryl, vinyl, and alkyl halides.

Structurally different from other compoundsAril halides compose an interesting group of compounds with specific structural characteristics and reactivity patterns. Aromatic halogenation and the Sandmeyer reaction The preparation methods mentioned above (aromatic halogenation and the Sandmeyer reaction) illustrate distinct strategies for attaching halogen atoms to aromatic rings, one of which has certain proficiencies/ limitations. The aryl halides are known to be resistant to nucleophilic substitution;

However the benzyne mechanism reveals how they can participate in such reactions given the right set of circumstances. This mechanism highlights both the versatility of aryl halides in organic synthesis as well as how reaction conditions can significantly influence the pathways of reactions. The relative reactivities of different classes of

halogenated compounds (aryl, vinyl and alkyl halides) can be understood by discussing carbon-halogen bond strengths.Aryl halides possess particularly strong carbon-halogen bonds, which benefit from their resonance interactions with the aromatic system,

resulting in their unique chemical properties, such as their resilience towards traditional nucleophilic substitution pathways and their broad applications in metal-catalyzed coupling reactions.

In the context of electrophilic aromatic substitution reactions, the dual electronic effects of halogen substituents on aromatic rings include the electron-withdrawing inductive effect combined with the electron-donating resonance effect, that adds complexity to the chemistry of aryl halides as substituents. The chemistry of aryl halides is of not only theoretical significance, but also wide applications in pharmaceutical synthesis, material science, and industrial chemistry. While synthetic methodologies improve, aryl halides are timeless and significance building blocks in the hands of the organic chemist, allowing viable assembly of complex molecular structures through selective carbon–carbon and carbon–heteroatom bond formation.

Check your Progress

1. Why are aryl halides less reactive toward nucleophilic substitution than alkyl halides?

…….
……
……..

2. How does the presence of electron-withdrawing groups on the aromatic ring affect the reactivity of aryl halides?

…….
……
….

2.7 Summary:

Aryl halides are aromatic compounds with halogen directly attached to benzene; the C–X bond has partial double bond character due to resonance, reducing nucleophilic reactivity; they undergo electrophilic substitution where halogen is deactivating but ortho/para-directing; they are more stable than alkyl halides; and they are important in the manufacture of dyes, drugs, pesticides, and polymers.

Q1. Which of the following is an aryl halide?

a) CH_3Cl b) C_2H_5Br c) C_6H_5Cl d) CH_2Cl_2

Answer: c) C_6H_5Cl

Q2. Reduced reactivity of aryl halides in nucleophilic substitution is due to:

a) High electronegativity of halogen b) Resonance giving partial double bond character

c) Weak C–X bond d) Instability of benzene ring

Answer: b) Resonance giving partial double bond character

Q3. In electrophilic substitution, halogen is:

a) Activating, ortho/para-directing b) Deactivating, ortho/para-directing

c) Deactivating, meta-directing d) Activating, meta-directing

Answer: b) Deactivating, ortho/para-directing

Q4. Which reaction is difficult for aryl halides compared to alkyl halides?

a) Nucleophilic substitution b) Electrophilic substitution

c) Nitration d) Sulfonation

Answer: a) Nucleophilic substitution

Q5. Aryl halides are industrially important in:

a) Refrigerants b) Dyes and drugs c) Fertilizers d) Fuels

Answer: b) Dyes and drugs

2.8 Exercise Question

Short Answer Type:

1. What is an aryl halide? Give one example.
2. Why is the C–Cl bond in chlorobenzene shorter than in CH_3Cl?
3. Why are aryl halides less reactive toward nucleophilic substitution?
4. Write the resonance structures of chlorobenzene.
5. Give two uses of aryl halides.

Long Answer Type:

1. Discuss the structure and reactivity of aryl halides with special reference to chlorobenzene.
2. Explain why aryl halides undergo electrophilic substitution more readily than nucleophilic substitution.
3. Describe the methods of preparation and reactions of chlorobenzene.
4. Compare the reactivity of alkyl halides and aryl halides toward nucleophilic substitution with reason

2.9 References and suggestive readings

1. Morrison, R. T., & Boyd, R. N. (2011). Organic Chemistry (6th ed.). Prentice Hall, 221 River Street, 2nd Floor, Hoboken, NJ 07030, USA. Florida Department of Education
2. Solomons, T. W. G., Fryhle, C. B., & Snyder, S. A. (2016). Organic Chemistry (12th ed.). Wiley India Pvt. Ltd., 4436/7, 2nd Floor, Ansari Road, Daryaganj, New Delhi, 110002, India. All India ITR+1
3. Carey, F. A., & Sundberg, R. J. (2007). Advanced Organic Chemistry: Part A: Structure and Mechanisms (5th ed.). Springer Nature, Europaplatz 3, 69115 Heidelberg, Germany.

Unit –3 Alcohols

Structure:

3.1 Introduction

Alcohols are organic compounds that contain one or more hydroxyl (–OH) groups attached to a saturated carbon atom. Their general formula is R–OH, where R represents an alkyl group. Depending on the number of hydroxyl groups present, alcohols are classified as monohydric, dihydric, or trihydric. Based on the nature of the carbon atom bonded to the –OH group, they are further classified as primary, secondary, and tertiary alcohols. In alcohol molecules, the oxygen atom of the –OH group is sp^3 hybridized and forms a polar covalent bond with hydrogen, which gives rise to hydrogen bonding. This hydrogen bonding is responsible for the relatively high boiling points and solubility of lower alcohols in water. Common methods of preparation of alcohols include hydration of alkenes, hydrolysis of alkyl halides, and reduction of aldehydes and ketones. Alcohols are colorless liquids or solids with characteristic odours; lower members like methanol and ethanol are completely miscible with water, while higher alcohols are less soluble. They are widely used as solvents, fuels, antiseptics, and in the manufacture of various chemicals. For example, ethanol is used in beverages, methanol as a fuel and antifreeze, and glycerol in cosmetics and pharmaceuticals.

3.2 Classification

Monohydric monohydric alcohols contain a single hydroxyl (-OH) group bonded to a saturated carbon atom. Their general formula is R-OH, where R is an alkyl group. These alcohols may then be classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms attached to the carbon atom which contains the hydroxyl group.

Nomenclature: Alcohols are named according to the IUPAC nomenclature by replacing the terminal "-e" (the final letter of the name of the alkane) with the suffix "-ol". Anumber prefix indicates the position of the hydroxyl group.

3.3 Preparation methods-

Hydration of Alkenes: Alkenes react with water in the presence of acids like H, SO,, or H*f* PO,, to form alcohols. This reaction follows Markovnikov's rule, where the hydroxyl group attaches to the more substituted carbon atom.

Hydrolysis of Alkyl Halides: Alkyl halides undergo nucleophilic substitution when treated with aqueous NaOH or KOH to yield alcohols. Reduction of **Carbonyl Compounds:** Aldehydes and ketones can be reduced to alcohols using reducing agents like LiAlH,, , NaBH,, , or through catalytic hydrogenation.

Grignard Reaction: Alcohols can be synthesized by treating carbonyl compounds with Grignard reagents (RMgX) followed by hydrolysis.

Reduction of Carboxylic Acids and Esters: These compounds can be reduced to primary alcohols using powerful reducing agents like LiAlH,, .

Oxymercuration-Demercuration: This two-step process involves treating an alkene with mercuric acetate in water, followed by reduction with NaBH,, , resulting in Markovnikov addition.

Hydroboration-Oxidation: This process involves the addition of borane to an alkene followed by oxidation with hydrogen peroxide, resulting in anti-Markovnikov addition.

3.4 Chemical Properties -

Reaction with Active Metals: Alcohols react with active metals like sodium and potassium to form alkoxides and hydrogen gas.

1. Reaction with Active Metals

$$2R\text{-}OH + 2Na \rightarrow 2R\text{-}ONa + H_2 \uparrow$$

Example:

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2 \uparrow$$

Reaction with Mineral Acids: Alcohols react with HX (X = Cl, Br, I) to form alkyl halides. The reactivity order is 3° > 2° > 1° due to the stability of the carbocation intermediate.

$$R\text{-}OH + HX \rightarrow R\text{-}X + H_2O \quad (X = Cl, Br, I)$$

Example:

$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$$

Reactivity order:

$$3^\circ > 2^\circ > 1^\circ$$

Dehydration: When heated with concentrated H, SO,, or H*f* PO,, , alcohols undergo dehydration to form alkenes. The ease of dehydration follows: 3° > 2°

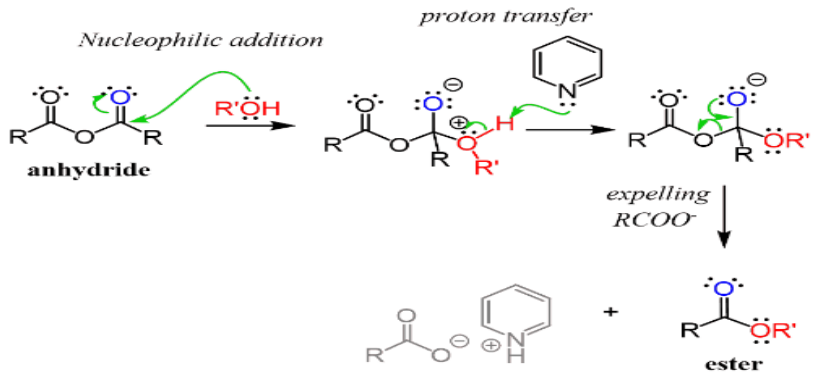
$$R\text{-}CH_2CH_2OH \xrightarrow[\text{conc. } H_2SO_4]{\text{heat}} R\text{-}CH{=}CH_2 + H_2O$$

Oxidation: Alcohols can be oxidized to form carbonyl compounds.

Esterification: Alcohols react with carboxylic acids in the presence of a catalyst (usually concentrated H, SO,,) to form esters.

$$R\text{-}OH + R'\text{-}COOH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} R'\text{-}COOR + H_2O$$

Reaction with Carboxylic AcidAnhydrides and Acid Chlorides: Alcohols react with these compounds to form esters



3.5 Physical Properties

Boiling Points: Alcohols have higher boiling points compared to alkanes of similar molecular weight due to hydrogen bonding. The boiling points increase with increasing molecular weight within a homologous series.

Solubility: Lower alcohols (C -C*f*) are completely miscible with water due to hydrogen bonding. As the carbon chain length increases, solubility in water decreases while solubility in organic solvents increases.

Density: Most alcohols have densities slightly less than water, except methanol.

Viscosity: Alcohols have higher viscosities compared to corresponding alkanes due to hydrogen bonding.Here are **two short questions** on **Alcohols**:

3.6 Applications of Alcohols

1. **As Fuels and Fuel Additives:**
   - Ethanol and methanol are used as clean-burning fuels or blended with petrol to form *gasohol* (used to reduce air pollution).
   - They provide high energy and are renewable biofuels.
2. **As Solvents:**
   - Alcohols, especially ethanol and methanol, are excellent solvents for many organic compounds such as resins, dyes, and essential oils.
   - They are used in perfumes, paints, and varnishes.
3. **In Pharmaceuticals and Medicine:**
   - Ethanol is used as an antiseptic and disinfectant in surgical spirit.
   - Glycerol is used in cough syrups, ointments, and as a soothing agent in creams and lotions.
4. **In Chemical Industry:**
   - Alcohols serve as important starting materials for the manufacture of aldehydes, ketones, esters, ethers, and carboxylic acids.
   - Methanol is used to produce formaldehyde and other organic chemicals.
5. **In Beverage Industry:**
   - Ethanol is the main component of alcoholic beverages such as beer, wine, and spirits.
6. **As Antifreeze:**
   - Methanol and ethylene glycol are used in automobile radiators to prevent freezing of water in cold climates.
7. **In Cosmetics and Personal Care:**
   - Glycerol and ethanol are used in lotions, creams, perfumes, and deodorants as moisturizers or carriers.
8. **In Explosives:**
   - Glycerol is used in the manufacture of nitroglycerin, which is an important component of dynamite.
9. **In Laboratory Uses:**
   - Alcohols are used as cleaning agents, sterilizers, and as solvents in organic synthesis and analytical chemistry.

Check your Progress

1. How are alcohols classified as primary, secondary, and tertiary based on their structure?

……
……
……
…

2.What happens when a primary alcohol is oxidized under mild and strong oxidizing conditions?

……
……

3.7 Summary

Alcohols are organic compounds containing the hydroxyl (–OH) functional group attached to a carbon atom. They are classified as primary, secondary, or tertiary based on the number of alkyl groups bonded to the carbon bearing –OH. Alcohols undergo oxidation, dehydration, and substitution reactions, making them important intermediates in organic synthesis.

○

3.8 Exercies Questions

Multiple Choice Questions (MCQs)

1. What type of reaction is Williamson's ether synthesis?

a) Electrophilic substitution

b) Nucleophilic substitution

c) Free radical reaction

d) Elimination reaction

2. The SN2 reaction is favored by:

a) Weak nucleophiles

b) Sterically hindered substrates

c) Polar aprotic solvents

d) Carbocation stability

3. What is the major product when chlorobenzene reacts with NaNH, in liquid ammonia?

a) Benzylamine

b) Phenol

c)Aniline

d) Benzyne

4. The oxidation of primary alcohols yields:

a) Ketones

b) Aldehydes

c) Esters

d) Ethers

5. Phenols exhibit higher acidity than alcohols due to:

a) Inductive effect

b) Resonance stabilization

c) Hyperconjugation

d) Steric hindrance

6. Which reagent is used in the Reimer-Tiemann reaction?

a) ZnCl,

b) Chloroform and NaOH

c) KMnO,,

d) PCl…

7. Which alcohol undergoes the fastest reaction in Lucas test?

a) Primary alcohol

b) Secondary alcohol

c) Tertiary alcohol

d) Dihydric alcohol

8. The Pinacol-Pinacolone rearrangement involves:

a) Dehydration of alcohol
b) Rearrangement of glycol
c) Formation of ester
d) None of the above

9. The most reactive compound in SN1 reaction is:

a) Methyl chloride
b) Benzyl chloride
c) Ethyl chloride
d) Vinyl chloride

10. The Fries rearrangement is used to prepare:

a) Ketones
b) Aldehydes
c) Hydroxy aryl ketones
d) Alcohols

Short Answer Questions

1. Define SN1 and SN2 reactions with examples.
2. What is the effect of solvent on SN2 reactions?
3. Explain the acidic nature of phenols compared to alcohols.
4. Write the mechanism of the Reimer-Tiemann reaction.
5. Why do tertiary alcohols react faster with Lucas reagent?
6. Differentiate between Williamson's ether synthesis and nucleophilic substitution.
7. What is the role of $NaNH_2$, in the Benzyne mechanism?
8. Explain the structure and bonding in phenoxide ion.
9. How does the presence of electron-withdrawing groups affect the acidity of phenols?
10. What are the key differences between electrophilic and nucleophilic substitution reactions?

Long Answer Questions

1. Explain in detail the SN1 and SN2 reaction mechanisms with suitable examples.

2. Describe the methods of preparation of alcohols and their physical and chemical properties.
3. Write a detailed note on the electrophilic substitution reactions of phenol.
4. Discuss the mechanisms of Fries rearrangement, Claisen rearrangement, and Reimer-Tiemann reaction.
5. Explain the concept of resonance stabilization in phenols and phenoxide ions.
6. Compare and contrast the acidic strength of alcohols and phenols with experimental evidence.
7. Describe the method of preparation and properties of dihydric and trihydric alcohols.
8. Explain the oxidation reactions of alcohols and their industrial importance.
9. Discuss the role of solvents in nucleophilic substitution reactions.
10. Explain the factors affecting the reactivity of alkyl and aryl halides in substitution reactions.

3.9 References and suggestive readings

1. Morrison, R. T., & Boyd, R. N. (2011). Organic Chemistry (6th ed.). Prentice Hall, 221 River Street, 2nd Floor, Hoboken, NJ 07030, USA. Florida Department of Education.
2. Carey, F. A., & Sundberg, R. J. (2007). Advanced Organic Chemistry: Part A: Structure and Mechanisms (5th ed.). Springer Nature, Europaplatz 3, 69115 Heidelberg, Germany.
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Structure

4.1 Introduction

Aldehydes and ketones are important classes of organic compounds that contain the carbonyl functional group (C=O). In aldehydes, the carbonyl carbon is bonded to at least one hydrogen atom and one alkyl or aryl group, whereas in ketones, it is bonded to two alkyl or aryl groups. The general formula of aldehydes is R–CHO and that of ketones is R–CO–R′. The carbonyl group is highly polar due to the difference in electronegativity between carbon and oxygen, making these compounds reactive towards various nucleophilic and oxidation–reduction reactions. Aldehydes and ketones are widely used in the chemical industry as solvents, intermediates, and precursors for the synthesis of alcohols, acids, and other important organic compounds. Common examples include formaldehyde (HCHO), acetaldehyde (CH_3CHO), and acetone (CH_3COCH_3).

4.2Objective

- Understand the nomenclature and structure of aldehydes, ketones, carboxylic acids, and their derivatives.
- Learn about the acidity of á-hydrogens and the concept of enolate formation.
- Study the preparation and reactions of aldehydes, ketones, and carboxylic acids.
- Explore important reactions like Cannizzaro, Perkin, and Wittig reactions.

4.3 Preparation methods The synthesis of aldehydes and ketones covers a wide variety of different approaches that can be classified depending on the type of transformation.

1. Oxidation of Alcohols:
Primary alcohols are oxidized to aldehydes, while secondary alcohols are oxidized to ketones. For example, ethanol when oxidized with acidified potassium dichromate gives acetaldehyde, and isopropyl alcohol gives acetone.

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$$

$$(CH_3)_2CHOH \xrightarrow{[O]} (CH_3)_2CO + H_2O$$

2. Dehydrogenation of Alcohols:
When vapours of primary or secondary alcohols are passed over heated copper at about 573 K, aldehydes and ketones are formed respectively.

$$CH_3CH_2OH \xrightarrow[573\ K]{Cu} CH_3CHO + H_2$$

$$(CH_3)_2CHOH \xrightarrow[573\ K]{Cu} (CH_3)_2CO + H_2$$

3. Ozonolysis of Alkenes:

Alkenes react with ozone followed by hydrolysis to give aldehydes or ketones depending on the structure of the alkene.

$$CH_2 = CH_2 \xrightarrow[H_2O]{O_3} 2HCHO$$

$$CH_3CH = CH_2 \xrightarrow[H_2O]{O_3} CH_3CHO + HCHO$$

5. From Acid Chlorides (Rosenmund Reduction):

Aldehydes can be prepared by the reduction of acid chlorides (acyl chlorides) with hydrogen in the presence of palladium catalyst poisoned with barium sulfate ($Pd/BaSO_4$).

$$RCOCl + H_2 \xrightarrow[BaSO_4]{Pd} RCHO + HCl$$

6. From Nitriles (Stephen's Reduction):

Nitriles are reduced with stannous chloride ($SnCl_2$) and hydrochloric acid to form imines, which on hydrolysis yield aldehydes.

$$RCN + 2H_2 \xrightarrow[H_2O]{SnCl_2/HCl} RCHO$$

7. Friedel–Crafts Acylation (for Ketones):

Aromatic ketones can be prepared by treating benzene with an acid chloride in the presence of anhydrous aluminum chloride ($AlCl_3$) catalyst.

$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

4.4 Chemical properties: Aldehydes and ketones are characterized by the presence of the carbonyl group (C=O), which is highly polar. Because of this, they undergo various nucleophilic addition and oxidation–reduction reactions. The aldehydes are generally more reactive than ketones due to the presence of a hydrogen atom directly attached to the carbonyl carbon, making them easier to oxidize and more susceptible to attack by nucleophiles. The important chemical properties are as follows:

1. Nucleophilic Addition Reactions : The carbonyl carbon in aldehydes and ketones is electrophilic and readily attacked by nucleophiles.

(a) Addition of Hydrogen Cyanide (HCN): Aldehydes and ketones react with hydrogen cyanide in the presence of a base to form cyanohydrins.

$$RCHO + HCN \rightarrow RCH(OH)CN$$

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

(b) Addition of Sodium Bisulfite ($NaHSO_3$):

Aldehydes and ketones react with sodium bisulfite to form crystalline bisulfite addition compounds.

$$RCHO + NaHSO_3 \rightarrow RCH(OH)SO_3Na$$

(c) Addition of Alcohols (Formation of Hemiacetals and Acetals):

Aldehydes react with alcohols in the presence of dry HCl gas to form hemiacetals, which further react with alcohol to give acetals. Aldehydes are easily oxidized, whereas ketones resist oxidation.

$$RCHO + ROH \xrightarrow{H^+} RCH(OH)OR \xrightarrow{ROH} RCH(OR)_2 + H_2O$$

Ketones are oxidized only under strong conditions to give a mixture of acids with fewer carbon atoms.

3. Reduction Reactions Aldehydes and ketones can be reduced to alcohols by various reducing agents.

Reduction with $NaBH_4$ or $LiAlH_4$:

$$RCHO + [O] \rightarrow RCOOH$$

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

Aldehyde → Primary alcohol, Ketone → Secondary alcohol

4. Reaction with Ammonia Derivatives

Aldehydes and ketones react with compounds containing the $–NH_2$ group to form condensation products.

Examples:

- With hydroxylamine:

$$RCHO + NH_2OH \rightarrow RCH{=}NOH + H_2O$$

(Oxime)

- With hydrazine:

$$RCHO + NH_2NH_2 \rightarrow RCH{=}NNH_2 + H_2O$$

(Hydrazone)

- With phenylhydrazine:

$$RCHO + C_6H_5NHNH_2 \rightarrow RCH{=}NNHC_6H_5 + H_2O$$

5. **Aldol Condensation** (for Aldehydes and Ketones having α-Hydrogen) Two molecules of aldehyde or ketone containing α-hydrogen atoms combine in the presence of a base to form a β-hydroxy aldehyde (aldol) or β-hydroxy ketone, which on heating lose water to give an α,β-unsaturated compound.

$$2CH_3CHO \xrightarrow{NaOH} CH_3CH(OH)CH_2CHO \xrightarrow{heat} CH_3CH{=}CHCHO + H_2O$$

6. Cannizzaro Reaction Aldehydes which do not have α-hydrogen (like formaldehyde and benzaldehyde) undergo disproportionation in the presence of concentrated alkali to give an alcohol and a carboxylic acid.

$$2HCHO \xrightarrow{NaOH} CH_3OH + HCOONa$$

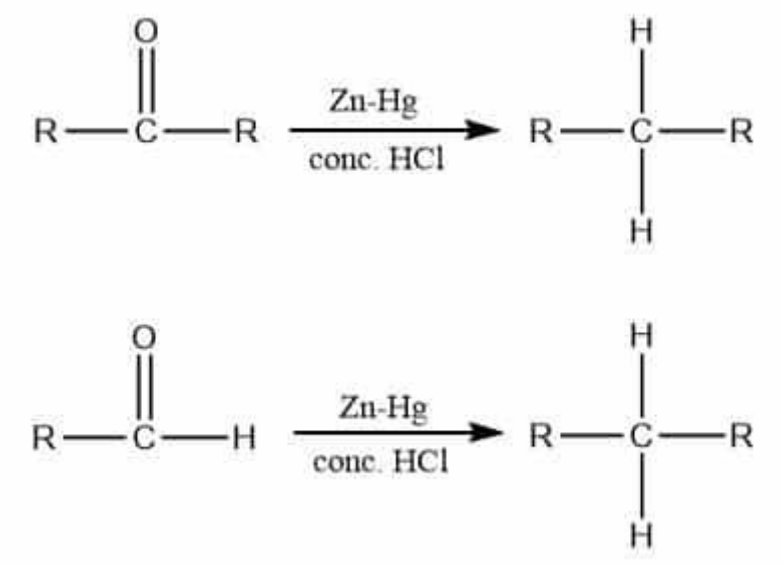
6. **Haloform Reaction:** Methyl ketones and compounds containing the –$COCH_3$ group react with halogens (Cl_2, Br_2, or I_2) in the presence of alkali to form haloform (CHX_3).

$$CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

Clemmensen Reduction

The Clemmensen reduction is a powerful method to convert carbonyl groups of aldehydes and ketones to methylene (CH,) groups in strongly acidic conditions. Originally described by Erik Christian Clemmensen in 1913, this transformation has become a useful method in organic synthesis, especially for the deoxygenation of base-sensitive carbonyl compounds. The Clemmensen reduction uses amalgamated zinc (zinc with mercuric chloride adsorbed onto it) in concentrated hydrochloric acid. The reaction is typically performed at high temperatures with extended reaction times, particularly for sterically highted substrates. 7 Although the exact pathways are still debated, the hypothesis is

formed on the basis of organozinc complexation at the metal surface followed by stepwise electron and proton transfers. This reduction is especially useful in a variety of scenarios. It is a very useful and selective reduction of aryl ketones and aldehydes to their corresponding complex alkylbenzenes which makes a rich source for aromatic compounds with defined substitution. This reaction has proven advantageous for substrates that would otherwise novelty undergo unwanted sidereactions in basic conditions; those prone to aldol condensations, concur. The Clemmensen reduction is also an important step in a number of natural product syntheses, as it allows the strategic removal of carbonyl functionalities.



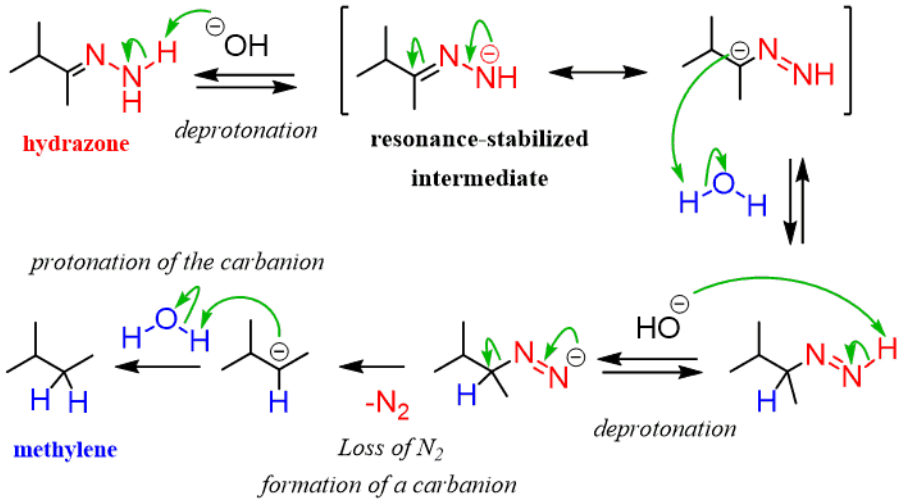
The efficiencyof the Clemmensen reduction is affected in several ways. The frequency of reactions is greatly influenced bythe surface area of the zinc amalgam in the reaction, as maximallygalked, freshly prepared and finely divided metal performs the best. The choice of solvent is critical, as the addition of cyclohaxane or diethyl ether typically helps to improve the solubility of substrate in the biphasic reaction system. We know that electronic factors present in the substrate can have very dramatic effects on the reactivity, leading to the generalization that electron-withdrawing groups tend to promote reductions (note the electron-deficient behavior of the cation transition state). Raffinose ether reduction and other variations of the Clemmensen reduction for certain synthetic problems have been reported. An alternative procedure for some sensitive substrates employs zinc dust with acetic anhydride in acetic acid. Ultrasound-assisted methods have made successful attempts to enhance reaction progress by improving mass transfer and the activation of the metal

surface. Continuous-flow methodologies allow for safer handling of the mercury-containing reagents while improving scalability.

Wolff-Kishner Reduction

The Wolff-Kishner reduction is a complementarymethod to the Clemmensen reduction for reduction of carbonyl compounds to (methylene) groups, but occurring under strongly basic instead of acidic conditions. This reaction, independently described by Nikolai Kishner in 1911 and Ludwig Wolff in 1912, is now a routine method in organic synthesis, particularly for substrates sensitive to acidic conditions. The Wolff- Kishner is conducted using hydrazine (often its hydrate) in high boiling basic solvent like ethylene glycol or diethylene glycol with potassium or sodium hydroxide as the base. The reaction occurs at elevated temperatures, typically above 180 °C, to encourage the removal of nitrogen gases.

The Mechanism of Wolff-Kishner Reduction



The reaction mechanism starts with the nucleophilic attack by hydrazine on the carbonyl group of the ketone or aldehyde leading to the formation of a hydrazone intermediate. Deprotonation of the terminal nitrogen of the hydrazone occurs under strongly basic conditions, resulting in a series of electron transfers that allows for loss of nitrogen gas to provide a carbanion. This carbanion abstracts a proton from the solvent or from other acid source resulting in the final reduced product.

The Wolff-Kishner reduction is especially useful in certain situations. It efficiently reduces aldehydes and ketones that are resistant to other reduction techniques, including sterically hindered carbonyl species. When applied to

substrates with acidic- or metal-hydride-sensitive functional groups, such as some heterocycles and acid- labile protecting groups, the reaction demonstrates utility. The Wolff-Kishner reduction is also important in total synthesis of various molecules where strategic deoxygenation of carbonyls is required in the context of complex molecular architectures. There are a few factors that determine the efficiencyof Wolff-Kishner reduction. The concentration of base can significantly affect reaction rates, with greater concentrations generally speeding up the process. Temperature control becomes critical: if the substrate is not heated adequately, the reaction may not go to completion, while if an excessive temperature is used, sensitive substrates may start to decompose. We have to take care about the water content of the reaction mixture because later stages of the mechanism can be obstructed by by-products. Numerous modifications have made the Wolff-Kishner reduction more practical, and provided it with a wider scope. In contrast, the Huang-Minlon modification makes the hydrazone at lower temperatures via a temperature-programmed process, heating for the reduction step, which improves yields in the scene of sensitive substrates. There are many variations of this reaction and one notable example is the Myers modification which instead of hydrazine uses trimethylsilyldiazomethane to generate the same carbonyl unit, which gives milder reaction conditions and better functional group compatibility. Microwave-assisted protocols have generally resulted in reaction times ranging from several minutes to a few hours at most without sacrificing good yields for most of the substrates.

Analysis and Synthetic Applications

The reactions reviewed here represent paradigm shifts in carbonyl chemistry, each with unique strengths and weaknesses with respect to addressing particular synthetic challenges. Knowledge of their relevant features allows organic chemists to make appropriate choices of methods for specific target molecules. The aldol, Perkin, and Knoevenagel reactions form carbon-carbon bonds via nucleophilic addition to carbonyl functionalities but differ in their respective nucleophilic coupling partners and reaction conditions. Enolates from carbonyl compounds are used in the aldol reaction, carbanions from acid anhydrides in the Perkin reaction, and active methylene compounds stabilized via electron-withdrawing groups in the Knoevenagel reaction. These differences translate into unique products in terms of structures and stereochemistry, therebyserving as complementary tools to construct carbon networks of different kinds. The Wittig and Mannich reactions contribute two unique functional groups during

carbon-carbon bond formation, thus broadening the synthetic arsenal. The Wittig reaction introduces carbon-carbon double bonds, with defined geometry, and the Mannich reaction adds amino substitutes when they are adjacent to the carbonyl moiety. Venture phosporation-reduction and anti-Wurtz reaction: The transformations are extremelyvaluable for obtaining complex molecular architectures, especially scaffolds encased with stereochemical moieties or heteroatom-embedded carbon centers. The carbony reductive methods—LeClemmensen and Wolff-Kishner reductions—represent complementary strategies to convert carbonyl groups to methylene units in either acidic or basic conditions, respectively. The choice among these methods typically hinges upon the sensitivity of the substrate to specific reaction environments and the presence of other functionality. The reduction of MPVs offers a milder approach for reducing carbonyls to alcohols while leaving other reactive functionalities intact.

Carbonyl chemistry offers a lot more than just simple additions, and the Baeyer- Villiger oxidation and the Cannizaro reaction are prominent examples of carbonyl's ability towards strategic oxidative transformations. Baeyer-Villiger oxidation adds oxygen next to carbonyls, transforming certain ketones into esters, and Cannizaro reactions disproportionate aldehydes into alcohols and carboxylic acids. This utility becomes especially important during functional group interconversions and oxidation state manipulations upon synthesis of complex molecules. Such elementary carbonyl transformations have been widely applied in natural product synthesis, pharmaceutical development and material chemistry. By forming carbon-carbon connections after adding functional groups strategically site-selectively and managing oxidation states, they empower the assembly of elaborate molecular edifices. Ongoing iterations of catalyst development, asymmetric modifications, and conditions optimizations also ensure their continued utility in modern organic synthesis.

4.5 Physical Properties

1. **State and Appearance:**
   Most low molecular weight aldehydes and ketones are **colorless liquids** with a characteristic pungent or pleasant smell.
   Formaldehyde is a gas at room temperature.
2. **Boiling Point:**
   Aldehydes and ketones generally have **higher boiling points than hydrocarbons** of similar molecular weight due to **dipole–**

dipole interactions between the polar carbonyl groups. However, their boiling points are **lower than alcohols** because they cannot form hydrogen bonds between themselves.

3. **Solubility:**
   - Lower aldehydes and ketones are **miscible with water** because they form hydrogen bonds with water molecules.
   - Solubility **decreases** with increasing molecular size or branching.
4. **Odor:**
   - Many aldehydes have **fruity or pungent odors** (e.g., formaldehyde, acetaldehyde).
   - Ketones also have **pleasant odors** and are often used in fragrances (e.g., acetone).

4.6 Applications of Aldehydes and Ketones

1. **Formaldehyde (HCHO):**
   - Used in **resins and plastics** (phenol–formaldehyde resin, urea–formaldehyde resin).
   - As a **disinfectant and preservative**.
   - In the manufacture of **textiles and dyes**.
2. **Acetaldehyde (CH_3CHO):**
   - Used in the production of **acetic acid, perfumes, and dyes**.
3. **Acetone (CH_3COCH_3):**
   - A common **solvent** in laboratories and industry (for paints, varnishes, and nail polish remover).
   - Used in **organic synthesis** as a reactant.
4. **Other Aldehydes and Ketones:**
   - Many are used as **flavoring agents and fragrances** in the food and cosmetic industry.
   - Serve as **intermediates** in the synthesis of pharmaceuticals, plastics, and agrochemicals

Check your Progress

1. What is the structural difference between an aldehyde and a ketone?

…..
……
…

2. How do aldehydes and ketones differ in their reactivity toward nucleophilic addition reactions?

…..
…….

4.7 Summary :- Aldehydes (–CHO) and ketones (C=O within chain) contain the carbonyl group; the C=O bond is polar, making them reactive. Aldehydes are more reactive than ketones due to less steric hindrance and +I effect. They undergo nucleophilic addition, oxidation (aldehydes → acids), and reduction (to alcohols). They also show special tests like Tollens' and Fehling's for aldehydes. They are widely used in perfumes, solvents, plastics, and pharmaceuticals.

4.8 Exercise Question

Q1. The functional group of aldehydes is:
a) –COOH b) –CHO c) –OH d) –CO–
Answer: b) –CHO

Q2. Which is more reactive towards nucleophilic addition?
a) Ketones b) Aldehydes c) Both equally d) Alcohols
Answer: b) Aldehydes

Q3. Which test is specific for aldehydes?
a) Tollens' test b) Lucas test c) Iodoform test d) Bromine water test
Answer: a) Tollens' test

Q4. Oxidation of a ketone generally gives:
a) Carboxylic acid b) Alcohol c) Another ketone d) No simple product
Answer: d) No simple product

Q5. Formaldehyde is widely used in making:
a) Refrigerants b) Perfumes and resins c) Fuels d) Fertilizers
Answer: b) Perfumes and resins

Short Answer Type Questions

1. Define aldehydes and ketones with examples.
2. Give the general formula of aldehydes and ketones.
3. What is the difference between an aldehyde and a ketone?
4. Write the IUPAC name of CH_3CH_2CHO and CH_3COCH_3.
5. Explain the structure and bonding of the carbonyl group.

6. State the difference in reactivity of aldehydes and ketones toward nucleophilic addition.
7. Write the reaction of aldehydes with Tollens' reagent.
8. Give one method for the preparation of aldehydes.
9. Give one method for the preparation of ketones.
10. What is the effect of electron-donating and electron-withdrawing groups on the carbonyl carbon?
11. Why are aldehydes generally more reactive than ketones toward nucleophilic addition?
12. Write the reaction of aldehydes with Fehling's solution.
13. Name a reagent used for the oxidation of alcohols to aldehydes.
14. Give an example of a molecule containing both aldehyde and ketone groups.
15. What happens when aldehydes react with $NaHSO_3$?

Long Answer Type Questions

1. Discuss the **structure, bonding, and reactivity** of the carbonyl group in aldehydes and ketones.
2. Describe the **methods of preparation of aldehydes and ketones** with equations.
3. Explain the **nucleophilic addition reactions** of aldehydes and ketones with examples.
4. Compare aldehydes and ketones in terms of **reactivity, physical properties, and chemical properties**.
5. Write the reactions of aldehydes and ketones with **hydrazine, hydroxylamine, and semicarbazide**.
6. Explain **oxidation reactions of aldehydes and ketones** and why ketones are generally resistant to mild oxidation.
7. Discuss **reactions of aldehydes and ketones with hydrogen cyanide** (cyanohydrin formation) with mechanism.
8. Explain the **Tollens' test, Fehling's test, and Benedict's test** for aldehydes, giving reactions and observations.
9. Write the **acetal and hemiacetal formation reactions** of aldehydes and ketones.
10. Describe the **Cannizzaro reaction** with conditions, mechanism, and examples.
11. Explain **aldol condensation** with mechanism and applications.
12. Discuss the industrial importance and applications of aldehydes and ketones.

4.9 References and suggestive readings

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Unit – 5 Carboxylic Acids

Structure

5.1 Introduction:

Carboxylic acids represent one of the most important classes of organic compounds, characterized by the presence of a carboxyl group (-COOH) attached to an alkyl or aryl group. These versatile compounds serve as precursors for numerous derivatives and playcrucial roles in biological systems, industrial processes, and organic synthesis.

Methods of Preparation: Carboxylic acids can be synthesized through various routes:

1. Oxidation of Primary Alcohols and Aldehydes: Primary alcohols and aldehydes can be oxidized to carboxylic acids using strong oxidizing agents like potassium permanganate (KMnO,,), potassium dichromate

2.Oxidation of Alkyl Benzenes: Side chains in alkyl benzenes can be oxidized to carboxyl groups using potassium permanganate or dichromate under reflux conditions, regardless of the alkyl chain length.

C† H… -CH, R + 3[O] '! C† H… -COOH + R-COOH

3.Hydrolysis of Nitriles: Nitriles undergo hydrolysis in the presence of acids or bases to form carboxylic acids. Acid hydrolysis yields the carboxylic acid directly, while base hydrolysis first forms a carboxylate salt that requires acidification.

R-CN + H, O + Hz '! R-COOH + NH,, z R-CN + 2NaOH + H, O '! R-COONa + NH*f* (followed by acidification)

4.Carbonation of Grignard Reagents: Grignard reagents react with carbon dioxide to form carboxylate salts, which upon acidification yield carboxylic acids.

RMgX + CO, '! RCOO{ MgXzRCOO{ MgXz + Hz '! RCOOH + Mg²z + X{

5.Hydrolysis of Esters: Esters undergo hydrolysis in acidic or basic conditions to form carboxylic acids. Base hydrolysis (saponification) requires subsequent acidification.

RCOOR' + H, O + Hz '! RCOOH + R'OH RCOOR' + NaOH '! RCOONa + R'OH (followed by acidification)

6.Oxidation of Alkenes: Vigorous oxidation of alkenes with potassium permanganate or ozone followed by oxidative workup cleaves the double bond, forming carboxylic acids.

RCH=CHR' + [O] '! RCOOH + R'COOH

7. From Alkyl Halides via Malonic Ester Synthesis: This multi-step process involves alkylation of diethyl malonate followed by hydrolysis and decarboxylation.

Chemical Properties : Carboxylic acids participate in various chemical transformations:

1.Salt Formation: Carboxylic acids react with bases to form carboxylate salts.

2.Esterification: Carboxylic acids react with alcohols in the presence of acid catalysts to form esters (Fischer esterification).

RCOOH + R'OH Ì! RCOOR' + H, O

3.Formation of Acid Chlorides: Treatment with thionyl chloride (SOCl,) or phosphorus pentachloride (PCl…) converts carboxylic acids to acid chlorides.

RCOOH + SOCl, '! RCOCl + SO, + HCl RCOOH + PCl… '! RCOCl + POCl*f* + HCl

4.Formation of Acid Anhydrides: Carboxylic acids react with dehydrating agents like P, O… or can be converted to acid anhydrides via acid chlorides.

2RCOOH + P, O… '! (RCO), O + H*f* PO,, RCOCl + RCOONa '! (RCO), O + NaCl

5.Formation of Amides: Carboxylic acids react with ammonia or amines, often via the acid chloride, to form amides.

6.Reduction: Carboxylic acids can be reduced to alcohols using lithium aluminum hydride (LiAlH,,) or borane (BH*f*).

RCOOH + LiAlH,, '! RCH, OH

7.Decarboxylation: Heating carboxylic acids with soda lime (NaOH + CaO) or certain catalysts leads to decarboxylation, producing hydrocarbons.

Hell-Volhard-Zelinsky (HVZ) Reaction: The Hell-Volhard-Zelinsky reaction is a method for á-halogenation of carboxylic acids. The reaction proceeds through the following steps:

1. **Lithium Aluminum Hydride (LiAlH,,):** This powerful reducing agent converts carboxylic acids to primaryalcohols through a two-electron reduction process. The reaction occurs via an aldehyde intermediate that is further reduced in situ.

2.Borane : This selective reducing agent also converts carboxylic acids to primary alcohols but with greater functional group tolerance.

3.Sodium Borohydride (NaBH,,): Unlike LiAlH,, ,NaBH,, alone is not strong enough to reduce carboxylic acids. However, when activated by iodine or when the acid is first converted to an acid chloride, reduction can proceed.

4.Catalytic Hydrogenation: Using hydrogen gas with catalysts like copper chromite or Raney nickel under high pressure and temperature, carboxylic acids can be reduced to alcohols or even alkanes depending on conditions.

RCOOH + H, /catalyst '! RCH, OH (moderate conditions) RCOOH + H, /catalyst '! RCH*f* (harsh conditions)

5. **Rosenmund Reduction:** This specialized method reduces acid chlorides to aldehydes using hydrogen gas and a poisoned palladium catalyst, allowing for a controlled partial reduction.

1. **Thermal Decarboxylation:** Simple aliphatic carboxylic acids typicallyrequire high temperatures (>200°C) for decarboxylation to occur. The mechanism involves breaking the C-C bond between the carboxyl group and the á- carbon: R-CH, -COOH + heat '! R-CH*f* + CO,

2. **Beta-Keto Acid Decarboxylation:** â-keto acids undergo facile decarboxylation at much lower temperatures due to the formation of a stable six-membered cyclic transition state. The process is driven by the formation of an enol intermediate that rapidly tautomerizes to the ketone:

R-CO-CH, -COOH '! R-CO-CH*f* + CO,

3. Alpha,Beta-Unsaturated Acid Decarboxylation: These acids decarboxylate relatively easily because the reaction forms a resonance-stabilized intermediate: R-CH=CH-COOH ’! R-CH=CH, + CO,

4. Malonic Acid Derivatives: Compounds with two carboxyl groups attached to the same carbon undergo decarboxylation readily through a cyclic transition state: R-CH(COOH), ’! R-CH, -COOH + CO,

5. Catalyzed Decarboxylation: Certain transition metals (Cu, Ag) or enzymes can facilitate decarboxylation by coordinating with the carboxyl group, weakening the C-C bond. The ease of decarboxylation follows this general trend: â-keto acids >á,â-unsaturated acids > á-amino acids > dicarboxylic acids > simple monocarboxylic acids

Dicarboxylic Acids: Methods of Formation Dicarboxylic acids contain two carboxyl groups and are important in various biological and industrial processes. Common methods of preparation include:

1. Oxidation of Cyclic Alkenes: Vigorous oxidation of cyclic alkenes with potassium permanganate or ozone cleaves the ring, forming dicarboxylic acids.

Cyclohexene + KMnO,, /Hz ’! HOOC-(CH,),, -COOH (adipic acid)

2.Oxidation of Diols: Primary diols can be oxidized to dicarboxylic acids using strong oxidizing agents like nitric acid or potassium permanganate.

HO-CH, -(CH,)n-CH, -OH + [O] ’! HOOC-(CH,)n-COOH

3.Oxidation of DicarbonylCompounds:Aldehydes with two carbonyl groups can be oxidized to form dicarboxylic acids.

OHC-(CH,)n-CHO + [O] ’! HOOC-(CH,)n-COOH

4.Hydrolysis of Dinitriles: Dinitriles undergo hydrolysis to form dicarboxylic acids.

5.Malonic Ester Synthesis: This method allows for the preparation of substituted malonic acids, which can be hydrolyzed to dicarboxylic acids.

6.Grignard Reaction with CO, : Di-Grignard reagents can react with carbon dioxide to form dicarboxylic acids after acidification.

7.Diels-Alder Reaction: Cyclic dienes can undergo Diels-Alder reactions with dienophiles, followed by oxidation to yield dicarboxylic acids.

Chemical Reactions of Dicarboxylic Acids

Dicarboxylic acids exhibit reactions similar to monocarboxylic acids but with some distinctive features:

1.Acid Strength: The first carboxyl group in dicarboxylic acids typically has a lower pKa than the second due to the electron-withdrawing effect of the adjacent carboxyl group. For example, in oxalic acid, pKa = 1.23 and pKa, = 4.19.

2.Salt Formation: Dicarboxylic acids can form either acid salts (with one carboxyl group neutralized) or normal salts (with both groups neutralized).

HOOC-(CH,)n-COOH + NaOH '! HOOC-(CH,)n-COONa + H, O HOOC-(CH,)n-COONa + NaOH '! NaOOC-(CH,)n-COONa + H, O

3.Esterification: Similar to monocarboxylic acids, dicarboxylic acids can undergo esterification to form diesters, or selective conditions can produce monoesters.

HOOC-(CH,)n-COOH + 2R'OH '! R'OOC-(CH,)n-COOR' + 2H, O

4.Formation of Acid Chlorides: Treatment with thionyl chloride converts both carboxyl groups to acid chlorides.

HOOC-(CH,)n-COOH + 2SOCl, '! ClOC-(CH,)n-COCl + 2SO, + 2HCl

5.Decarboxylation: Dicarboxylic acids undergo selective decarboxylation depending on their structure. á,ù-Dicarboxylic acids typicallylose one carboxyl group when heated.

HOOC-(CH,)n-COOH + heat '! CH*f*-(CH,)n-COOH + CO,

6.Reduction: Dicarboxylic acids can be reduced to diols with LiAlH,, or BH*f*

.Effects of Heat and Dehydrating Agents on Dicarboxylic Acids

2. Boiling Point: Higher than corresponding hydrocarbons due to dipole-dipole interactions but lower than corresponding carboxylic acids due to absence of hydrogen bonding.

3. Solubility: Insoluble in water due to hydrolysis but soluble in organic solvents like ethers, benzene, and chloroform.

4. Density: Generally greater than 1 g/cm³, denser than water.

5. Reactivity: Highly reactive and moisture-sensitive, undergo rapid hydrolysis when exposed to water.

Esters

1. Physical State: Lower members (up to C,,) are colorless liquids with pleasant, fruity odors; higher members are solids.
2. Boiling Point: Higher than corresponding alkanes due to dipole-dipole interactions but lower than corresponding carboxylic acids and alcohols due to absence of hydrogen bonding.
3. Solubility: Lower members are slightly soluble in water; solubility decreases with increasing carbon chain length. All esters are soluble in organic solvents.
4. Density: Generally less than 1 g/cm³, less dense than water.

5. Volatility: More volatile than corresponding carboxylic acids due to absence of hydrogen bonding.

Amides

1. Physical State: Lower members are colorless solids with high melting points; higher members are waxy solids.
2. Boiling Point and Melting Point: Much higher than corresponding esters and acid chlorides due to strong hydrogen bonding between amide molecules.
3. Solubility: Lower amides are soluble in water due to hydrogen bonding with water molecules; solubility decreases with increasing carbon chain length. All amides are soluble in polar organic solvents.

4. Dipole Moment: High dipole moment due to the polar C=O and C-N bonds.

5. Hydrogen Bonding: Primaryandsecondaryamides can form hydrogen bonds through their N-H groups, leading to higher melting and boiling points.

Urea

1. Physical State: White crystalline solid.
2. Melting Point: 132-135°C (decomposes).

3. Solubility: Highly soluble in water (about 1080 g/L at 20°C) due to extensive hydrogen bonding; moderately soluble in alcohols; insoluble in non-polar solvents.
4. Crystal Structure: Forms an extensive hydrogen-bonded network in its crystal structure.
5. Hygroscopic Nature: Absorbs moisture from the atmosphere.

Acid Anhydrides

1. Physical State: Lower members are colorless liquids with pungent odors; higher members are solids.
2. Boiling Point: Higher than corresponding esters but lower than corresponding carboxylic acids.
3. Solubility: Generally insoluble in water due to hydrolysis; soluble in organic solvents.
4. Reactivity: Reactive toward water and alcohols, but less reactive than acid chlorides.
5. Odor: Characteristic sharp, irritating odor, especially in lower members like acetic anhydride.

Relative Stability of Acyl Derivatives

The relative stability of carboxylic acid derivatives can be ranked based on the leaving group ability, resonance stabilization, and electronic effects. From least stable (most reactive) to most stable (least reactive):

1. Acid Chlorides (Least Stable):

- Chloride is an excellent leaving group due to its weak basicity.
- The C-Cl bond is polarized, making the carbonyl carbon highly electrophilic.
- No significant resonance stabilization from the chlorine atom.
- Highly susceptible to nucleophilic attack.

2. Acid Anhydrides:

- The carboxylate anion is a moderate leaving group.
- Some resonance stabilization exists but is insufficient to significantly reduce reactivity.

- The carbonyl carbon remains quite electrophilic.

3. Esters:

- Alkoxide is a poorer leaving group than chloride or carboxylate.
- The lone pairs on the alkoxy oxygen participate in resonance with the carbonyl group, stabilizing the ester.
- This resonance reduces the electrophilicity of the carbonyl carbon.

4. Amides (Most Stable):

- Amide ion is a very poor leaving group due to its high basicity.
- Extensive resonance stabilization occurs between the nitrogen lone pair and the carbonyl group.
- This strong resonance gives the C-N bond partial double bond character.
- The carbonyl carbon is significantly less electrophilic.
- Amides are the most stable of the carboxylic acid derivatives.

The relative reactivity toward nucleophilic acyl substitution follows the reverse order of stability: Acid Chlorides > Acid Anhydrides > Esters > Amides

This order of reactivity is reflected in the ease of hydrolysis, with acid chlorides hydrolyzing rapidly even at room temperature, while amides require strong acids or bases and heating for hydrolysis.

The stability order can also be explained using resonance structures. In amides, the nitrogen atom with its lone pair participates strongly in resonance with the carbonyl group, significantly stabilizing the molecule. In esters, similar resonance occurs with the alkoxy oxygen, but it's less effective than in amides. In acid anhydrides and acid chlorides, the resonance stabilization is much weaker or absent, making them more reactive.

The relative stability also correlates with carbonyl stretching frequencies in IR spectroscopy, with more reactive derivatives showing higher C=O stretching frequencies due to less resonance delocalization:

- Acid chlorides: ~1800 cm-1
- Acid anhydrides: ~1760 cm-^{1}

- Esters: ~1735 cm-1
- Amides: ~1650 cm-1

This trend in IR frequencies provides experimental evidence for the relative stability of these derivatives.

Check your Progress

1. What functional group is characteristic of carboxylic acids, and how does it influence their acidity?

……
……
…

2. How can carboxylic acids be prepared from primary alcohols or aldehydes?

……
……
…

5.7 Summary:

Carboxylic acids contain the –COOH functional group, with both carbonyl and hydroxyl groups attached to the same carbon. They are strongly polar, form hydrogen bonds, and have high boiling points. They are weak acids that partially ionize in water. They undergo reactions like esterification, reduction, decarboxylation, and substitution at the α-position. They are widely used in food preservatives, polymers, medicines, and solvents.

Carboxylic acids have systematic IUPAC names, with the base hydrocarbon name modified by replacing the terminal "e" with the "oic acid" suffix. As an illustration, CH*f* COOH is termed ethanoic acid (or acetic acid) and C† H… COOH is referred to as benzoic acid! Numbering of substituted acids begins from the carboxyl carbon, which is always given position 1. As a general nomenclature, lower carboxylic acids keep historical names based on where they were found in nature. Others are formic acid (from the Latin formica, which means ant), butyric acid (from the Latin butyrum, which means butter) and propionic acid (from the Greek protos pion, which means first fat). Dicarboxylic acid names end with "dioic acid"; examples are hexanedioic acid (adipic acid) and butanedioic acid (succinic acid) When necessary, especially for complex structures, the positions of the carboxyl groups are specified using numbers.

Structure The functional group of carboxylic acids is the carboxyl group, which is a carbonyl (C=O) directly attached to a hydroxyl (-OH) group. This

configuration leads to a quasi planar environment around the carboxyl carbon through sp^2 hybridization. The C=O bond has a partial double bond character with a bond length of <“1.20 Å; the C”O bond of the hydroxyl group has a length of <“1.34 Å. Dimers are widely formed in both solid and vapor phases of low molecular weight carboxylic acids due to the hydrogen bonding between two carboxyl groups. This dimerization has an important influence on their physical properties, such as boiling points and solubility trends. Carboxylic acids have resonance structures that show delocalization of electrons over the carboxyl group. This delocalization of electrons stabilizes the carboxylate anion that is formed through deprotonation and makes these compounds acidic.

Physical Properties

Carboxylic acids exhibit distinct physical characteristics influenced bytheir molecular structure and hydrogen-bonding capabilities:

1. State of Matter: Lower molecular weight carboxylic acids (C -C,,) are colorless liquids with pungent odors at room temperature. As the carbon chain length increases (C… -C‰), theybecome oily liquids with increasingly unpleasant odors. Higher members (C € and above) exist as waxy solids with minimal odor.

2. Boiling Points: Carboxylic acids have unusually high boiling points compared to alcohols and alkanes of similar molecular weights. This is attributed to the extensive hydrogen bonding that creates dimeric structures, effectively doubling their molecular mass. For instance, acetic acid (MW 60) boils at 118°C, while propanol (MW 60) boils at only 97°C.

3. Solubility: Lower carboxylic acids (up to C,,) demonstrate complete water solubility due to their ability to form hydrogen bonds with water molecules.As the hydrocarbon chain lengthens, water solubilitydecreases due to the increasing hydrophobic character.All carboxylic acids dissolve readily in less polar solvents like alcohols, ethers, and chloroform.

4. Density: Most carboxylic acids have densities slightly greater than water, with values typically between 1.0-1.1 g/cm^3 for the lower members of the series.

Acidity of Carboxylic Acids

Carboxylic acids are moderately strong acids with pKa values ranging from 3 to 5, making them significantly stronger than alcohols (pKa ~16-18) but weaker than mineral acids like HCl (pKa ~-7). Their acidic character arises from the ability to release a proton from the carboxyl group to form a resonance-stabilized carboxylate anion:

RCOOH Ì! RCOO{ + Hz

The acidity of carboxylic acids can be explained by:

1. Resonance Stabilization: The negative charge in the carboxylate ion is delocalized over two oxygen atoms through resonance, distributing the charge and stabilizing the anion.
2. Electronegativity: The electronegative oxygen atoms within the carboxyl group pull electron density away from the O-H bond, weakening it and facilitating proton donation.
3. Solvation Effects: The carboxylate ion forms strong hydrogen bonds with water molecules, further stabilizing the anion and drivingthe equilibrium toward dissociation.

Effect of Substituents on Acid Strength: The acidity of carboxylic acids is significantly influenced by substituents attached to the carbon chain:

Electron-Withdrawing Groups (EWG): Substituents like halogens (-F, - Cl, -Br), nitro (-NO,), and cyano (-CN) increase acid strength by inductively withdrawing electron density from the carboxyl group, stabilizing the carboxylate anion. This effect diminishes with distance from the carboxyl group. For example, trifluoroacetic acid (pKa 0.23) is much stronger than acetic acid (pKa 4.76).

Electron-Donating Groups (EDG): Groups like alkyl (-CH*f* , -C, H…) slightly decrease acidity**by**pushing electron density toward the carboxyl group through an inductive effect, destabilizing the carboxylate anion. This explains why formic acid (pKa 3.77) is stronger than acetic acid (pKa 4.76).

Resonance Effects: Aromatic rings can either increase or decrease acidity depending on the substituents. For instance, p-nitrobenzoic acid (pKa 3.44) is more acidic than benzoic acid (pKa 4.19) due to the electron-withdrawing nitro group, while p-methoxybenzoic acid (pKa 4.47) is less acidic due to the electron-donating methoxy group.

The relative acid strengths follow this general trend: CF*f* COOH > CCl*f* COOH > CHCl, COOH > CH, ClCOOH > CH*f* COOH

5.8 Excercises

Multiple Choice Questions (MCQs)

1.Which of the following is most reactive towards nucleophilic addition?

a) Acetone

b) Formaldehyde

c) Acetic acid

d) Benzophenone

2.Aldol condensation requires:

a) á-Hydrogen

b) Strong acid

c) Aromatic aldehyde

d) Dry ether

3.The Cannizzaro reaction is given by:

a) Formaldehyde

b) Acetone

c) Benzophenone

d) Acetic acid

4.The HVZ reaction is used for:

a) Halogenation of alkanes

b) Halogenation of carboxylic acids

c) Hydroxylation of alcohols

d) Oxidation of ketones

5.The reagent used in Clemmensen reduction is:

a) Zn/HCl

b) LiAlH,,

c) NaBH,,

d) KMnO,,

6.The product of Wolff-Kishner reduction of acetophenone is:

a) Benzyl alcohol

b) Ethanol

c) Toluene

d) Phenol

7.Keto-enol tautomerism is observed in:

a) Formaldehyde

b) Acetic acid

c) Acetoacetic ester

d) Methanol

8.The Baeyer-Villiger oxidation converts ketones into: a) Aldehydes
b) Carboxylic acids

c) Esters d) Alcohols
9. Which of the following acids is strongest?

a) Acetic acid

b) Chloroacetic acid

c) Formic acid

d) Propionic acid

10.Which reaction does NOT involve nucleophilic attack?

a) Aldol condensation

b) Perkin reaction

c) Cannizzaro reaction

d) Clemmensen reduction

Short Answer Questions

1. Explain the mechanism of Aldol condensation.
2. What is the effect of resonance on the acidity of carboxylic acids?
3. Describe the structure and reactivity of the carbonyl group.
4. How does the presence of á-hydrogen affect keto-enol tautomerism?

5. Write the mechanism of the Perkin reaction.
6. Explain the Clemmensen reduction and its applications.
7. What is the role of Tollen's reagent in aldehyde oxidation?
8. Differentiate between acid chlorides and acid anhydrides.
9. Describe the effect of electron-withdrawing groups on carboxylic acid strength.
10. What is the mechanism of decarboxylation of carboxylic acids?

Long Answer Questions

1. Explain the different methods of preparation of aldehydes and ketones.
2. Discuss the oxidation and reduction reactions of aldehydes and ketones.
3. Describe the mechanisms of the Cannizzaro reaction and Baeyer-Villiger oxidation.
4. Compare the acidity of carboxylic acids and phenols with examples.
5. Explain the formation of enolate ions and their role in condensation reactions.

5.9 Reference and suggestive readings

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BLOCK- 3

EQUILIBRIUM

Unit- 6 Chemical equilibria

Structure

6.1 Introduction:

Dynamic Nature of Equilibrium in Physical and Chemical Processes to achieve chemical equilibrium, rates of the forward and reverse reactions must become equal, and concentrations of the reactants and products no longer show a net change over time. This idea holds true for physical processes (such as the equilibrium between different phases of matter) as well as chemical reactions. In looking at equilibrium at the molecular level, one needs to realize that it is not a static condition where the reactions have ceased. Instead, it is a dynamic state where both forward and reverse processes continue to occur at an equilibrium rate. The fact that equilibrium can change with time is crucial to understanding how it reacts to external perturbations.

Suppose one considers the evaporation of water in a closed system:

Initially, molecules of liquid water enter the gas phase via evaporation. As more and more water molecules enter the gas phase, others start returning to their liquid state through the process of condensation. As time goes on, these rates become equal, leading to dynamic equilibrium. Even as individual molecules move back and forth between phases, the macroscopic conditions (pressure, concentration, and so on) are statistically frozen.Paved with turbulent roadsSo how’s this equilibrium breaking down in an exploding system? The same principle applies to chemical reactions. For a general reaction: aA + bB Ì! cC + At equilibrium, the rate at which Aand B form C and D equals the rate at which C and D revert to A and B. This balance creates a stable system despite ongoing molecular activity.

6.3 Law of Mass Action and Equilibrium Constants

The law of mass action, formulated by Cato Maximilian Guldberg and Peter Waage in 1864, provides a mathematical relationship between reactant and product concentrations at equilibrium. For the general reaction above, the equilibrium constantWhile K changes with temperature, it's important to note that it does not change with pressure or concentration changes. These factors affect the equilibrium position (the actual concentrations of reactants and products) but not the equilibrium constant itself. Changes in pressure particularly affect gas-phase reactions with unequal numbers of gaseous molecules on the reactant and product sides. However, these changes shift the equilibrium position within the constraint of the same equilibrium constant value at a given temperature. Similarly, adding or removing reactants or products shifts the equilibrium position as the system adjusts to maintain the same value of K, but doesn't change K itself. Factors Affecting Equilibrium - Le Chatelier's Principle Le Chatelier's principle, formulated by French chemist Henry Louis Le Chatelier in 1884, states that when a system at equilibrium is subjected to a change, the system will adjust to partially counteract the effect of the change and establish a new equilibrium. This principle helps predict how chemical equilibria respond to disturbances like changes in concentration, pressure, temperature, or the addition of catalysts:

1.Concentration Changes: When concentration of a reactant or product is altered, the equilibrium shifts to counteract this change.

- Increasing reactant concentration shifts equilibrium toward products
- Increasing product concentration shifts equilibrium toward reactants
- Removing a product shifts equilibrium toward products
- Removing a reactant shifts equilibrium toward reactants

2.Pressure Changes: Pressure changes affect gas-phase reactions with unequal numbers of gas molecules on each side.

- Increasing pressure favors the reaction direction that produces fewer gas molecules
- Decreasing pressure favors the reaction direction that produces more gas molecules
- For reactions with equal numbers of gas molecules on both sides, pressure changes have negligible effects

3.Temperature Changes: Temperature directlyaffects the equilibrium constant.

- For exothermic reactions (ÄH < 0), increasing temperature shifts equilibrium toward reactants

- For endothermic reactions (ÄH > 0), increasing temperature shifts equilibrium toward products
- This can be understood as the system “absorbing” some of the added heat in endothermic reactions or releasing heat to compensate for cooling in exothermic reactions

4. Catalysts: Catalysts increase the rates of both forward and reverse reactions equally, without changing the equilibrium position or equilibrium constant. They help the system reach equilibrium faster but don’t affect the final concentrations.

5. Addition of Inert Gases: Adding an inert gas at constant volume doesn’t affect equilibrium. However, adding an inert gas at constant pressure (which increases total volume) effectively decreases the partial pressures of reactants and products, potentially shifting gas-phase equilibria.

6.5 Quantitative Applications of Equilibrium Constants Equilibrium constants allow us to calculate equilibrium concentrations from initial conditions, predict the direction of reactions, and determine the extent of reaction completion.

For instance, the reaction quotient Q, which has the same form as K but uses non- equilibrium concentrations, helps predict reaction direction:

- Q < K: Reaction proceeds toward products
- Q > K: Reaction proceeds toward reactants
- Q = K: System is at equilibrium

The position of equilibrium can also be expressed using the extent of reaction (î) or percent conversion, which indicates how far a reaction has progressed toward completion.

Industrial Applications and Optimizations

Understanding equilibrium principles is crucial for industrial process optimization. The Haber-Bosch process for ammonia synthesis (N, + 3H, Ì! 2NH*f*) illustrates this well:

- The reaction is exothermic, so lower temperatures favor product formation (higher K)
- The reaction reduces the number of gas molecules, so higher pressures favor product formation
- However, very low temperatures make the reaction too slow to be practical

• The industrial compromise uses moderate temperatures (400-450°C), high pressures (150-300 atm), and iron-based catalysts to achieve reasonable yields and reaction rates

In the same manner as how the Contact Process for sulfuric acid production and the Ostwald Process for nitric acid use equilibrium management to optimize efficiency and yield.

Understanding of complex systems, from industrial processes, and building blocks of the chemical industry, to biological reactions, acid-base chemistry, solubility, and electrochemical cells is based on concepts of chemicalequilibrium. Dynamic equilibrium and Le Chatelier's principle are important for designing and controlling reactions in these many applications, both basic and applied.

6.4 Ionic Equilibria

Ionic equilibria form a fundamental aspect of chemical processes, governing the behavior of electrolytes in solution. These equilibria determine the extent to which compounds dissociate into ions, influencing properties like conductivity, acidity, and solubility. This chapter explores the principles of ionic equilibria, from basic acid-base ionization to complex buffer systems and their applications.

Ionization of Acids and Bases

Ionization refers to the process by which a neutral molecule splits into charged ions when dissolved in a suitable solvent, typically water. This phenomenon is particularly important for acids and bases. Acids are substances that donate protons (Hz) when dissolved in water. For example, hydrochloric acid ionizes as follows: HCl(aq) '! Hz (aq) + Cl{ (aq)

Bases are substances that accept protons or donate hydroxide ions (OH{). For example, sodium hydroxide ionizes as: NaOH(aq) '! Naz (aq) + OH{ (aq)

The Brønsted-Lowry theory defines acids as proton donors and bases as proton acceptors. According to this theory, acid-base reactions involve the transfer of protons from an acid to a base. When an acid donates a proton, it forms its conjugate base, and when a base accepts a proton, it forms its conjugate acid.

For example, in the ionization of acetic acid in water: CH*f* COOH(aq) + H, O(l) Ì! CH*f* COO{ (aq) + H*f* Oz (aq)

Here, CH*f* COOH acts as an acid by donating a proton to water, which acts as a base. After the proton transfer, CH*f* COO{ becomes the conjugate base of the acid, and H*f* Oz becomes the conjugate acid of the base.

Strong and Weak Electrolytes Electrolytes are substances that, when dissolved in water, produce a solution capable of conducting electricity due to the presence of ions. They can be classified as strong or weak based on their degree of ionization. Strong Electrolytes undergo complete or nearly complete ionization in solution. The concentration of undissociated molecules is negligible compared to the concentration of ions. Examples include:

- Strong acids: HCl, HBr, HI, HNO*f* , H, SO,, , HClO,,
- Strong bases: NaOH, KOH, Ca(OH), , Ba(OH),
- Most soluble salts: NaCl, KNO*f* , MgCl,

For instance, when sodium chloride dissolves in water, it completelydissociates: NaCl(s) '! Naz (aq) + Cl{ (aq)

Solutions of strong electrolytes conduct electricity effectively due to the high concentration of mobile ions.

Weak Electrolytes onlypartiallyionize in solution, establishing an equilibrium between the undissociated molecules and their constituent ions. Examples include:

- Weak acids: CH*f* COOH (acetic acid), HCOOH (formic acid), H, CO*f* (carbonic acid)
- Weak bases: NH*f* (ammonia), CH*f* NH, (methylamine)

For example, acetic acid establishes the following equilibrium: CH*f* COOH(aq) Ì! CH*f* COO{ (aq) + Hz (aq)

Solutions of weak electrolytes conduct electricity less effectivelythan strong electrolytes due to the lower concentration of ions.

Non-electrolytes do not produce ions when dissolved in water and therefore do not conduct electricity. Examples include glucose, sucrose, alcohol, and most **organic compounds.**

Degree of Ionization

The degree of ionization (á) quantifies the extent to which an electrolyte dissociates into ions. It is defined as the fraction of the total electrolyte that has ionized:

á = Number of molecules ionized / Total number of molecules dissolved

Alternatively, it can be expressed in terms of concentrations:

á = Concentration of ionized molecules / Initial concentration of electrolyte

For strong electrolytes, á H" 1 (or 100%), indicating complete ionization. For weak electrolytes, á < 1, typically ranging from 0.01 to 0.1 (1% to 10%), depending on the specific electrolyte and its concentration.

The degree of ionization depends on several factors:

1. Nature of the electrolyte: Stronger acids and bases have higher degrees of ionization.
2. Concentration of the solution: The degree of ionization generally decreases with increasing concentration due to the common ion effect and increased ionic interactions.
3. Temperature: Higher temperatures typically increase the degree of ionization.
4. Presence of common ions: The addition of a common ion decreases the degree of ionization of a weak electrolyte.

For a weak acid HA with initial concentration C€ , the degree of ionization can be related to the acid dissociation constant (K) by the expression:

á = "(K /C€) (when á is small, typically < 0.05)

This relationship indicates that the degree of ionization decreases with increasing concentration, which is known as the dilution law.

Ionization Constant and Ionic Product of Water Ionization Constant

The ionization constant (also called the dissociation constant) quantifies the extent of ionization of a weak electrolyte at equilibrium. For a weak acid HA that dissociates according to the equation:

HA(aq) Ì! Hz (aq) + A{ (aq)

The acid dissociation constant (K) is defined as:

K = [Hz][A{]/[HA]

Where [Hz], [A{], and [HA] represent the molar concentrations of hydrogen ions, anions, and undissociated acid at equilibrium, respectively.

Similarly, for a weak base B that ionizes according to:

B(aq) + H, O(l) Ì! BHz (aq) + OH{ (aq)

The base dissociation constant (K') is defined as:

K' = [BHz][OH{]/[B]

The magnitude of these constants provides insight into the strength of the acid or base. Larger values of K or K‘ indicate stronger acids or bases, respectively.

Ionic Product of Water

Pure water undergoes self-ionization (autoionization) to a small extent:

H, O(l) + H, O(l) Ì! H*f* Oz (aq) + OH{ (aq)

Often simplified as:

H, O(l) Ì! Hz (aq) + OH{ (aq)

At equilibrium, the product of the concentrations of hydrogen and hydroxide ions is constant at a given temperature. This constant is known as the ionic product of water (K!”):
K!” = [Hz][OH{]

At 25°C, K!” = 1.0 × 10{ ¹t mol²/L².

In pure water at 25°C, [Hz] = [OH{] = 1.0 × 10{ w mol/L, indicating a neutral solution. In acidic solutions, [Hz] > 10{ w mol/L and [OH{] < 10{ w mol/L. In basic solutions, [Hz] < 10{ w mol/L and [OH{] > 10{ w mol/L.
The value of K!” increases with temperature because the ionization of water is an endothermic process. For example, at 100°C, K!” H” 1.0 × 10{ ¹² mol²/L².
Ionization of Weak Acids and Bases Weak Acids
Weak acids partially ionize in aqueous solutions, establishing an equilibrium between the undissociated acid and its ions. Consider a generic weak acid HA:
HA(aq) + H, O(l) Ì! H*f* Oz (aq) + A{ (aq)

The acid dissociation constant (K) for this equilibrium is: K = [H*f* Oz][A{]/[HA]
For simplicity, H*f* Oz is often written as Hz , and the equilibrium becomes:

HA(aq) Ì! Hz (aq) + A{ (aq) K = [Hz][A{]/[HA]

If the initial concentration of the acid is C€ and the degree of ionization is á, then at equilibrium:

- [HA] = C€ (1-á)
- [Hz] = [A{] = C€ á

Substituting these values into the expression for K :

K = (C€ á)(C€ á)/(C€ (1-á)) = C€ á²/(1-á)

For weak acids where á << 1, the expression simplifies to: K H" C€ á² á H" "(K /C€)

This relationship indicates that the degree of ionization decreases with increasing concentration, which is known as Ostwald's dilution law.

Examples of weak acids and their dissociation constants at 25°C:

- Acetic acid (CH*f* COOH): K = 1.8 × 10{ u
- Formic acid (HCOOH): K = 1.8 × 10{ t
- Carbonic acid (H, CO*f*): K = 4.3 × 10{ w

Weak Bases : Weak bases also partially ionize in aqueous solutions. Consider a generic weak base B:

B(aq) + H, O(l) Ì! BHz (aq) + OH{ (aq) The base dissociation constant (K') for this equilibrium is: K' = [BHz][OH{]/[B]

Similar to weak acids, if the initial concentration of the base is C€ and the degree of ionization is á, then at equilibrium:

- [B] = C€ (1-á)
- [BHz] = [OH{] = C€ á

Substituting these values: K' = (C€ á)(C€ á)/(C€ (1-á)) = C€ á²/(1-á)

For weak bases where á << 1: K' H" C€ á² á H" "(K' /C€)

Examples of weak bases and their dissociation constants at 25°C:

- Ammonia (NH*f*): K' = 1.8 × 10{ u
- Methylamine (CH*f* NH,): K' = 4.4 × 10{ t
- Pyridine (C… H… N): K' = 1.7 × 10{ y

1. Strong Acids: For a strong acid with concentration C€ , assuming complete ionization: [Hz] = C€ pH = -log € (C€)
2. Strong Bases: For a strong base with concentration C€ , assuming complete ionization: [OH{] = C€ pOH = -log € (C€) pH = 14 - pOH = 14 + log
3. Weak Acids: For a weak acid HA with concentration C€ and dissociation constant K : [Hz] H" "(K × C€) (when á << 1) pH = -log € [Hz] = -log € ("(K × C€)) = -½log € (K × C€)

4. Weak Bases: For a weak base B with concentration C€ and dissociation constant K‘ : [OH{] H” “(K‘ × C€) (when á << 1) pOH = -log € [OH{] = -½log € (K‘ × C€) pH = 14 - pOH = 14 + ½log € (K‘ × C€)

The pHscale is extensivelyused in various fields, including chemistry, biology, medicine, agriculture, and environmental science, to monitor and control the acidity or basicity of solutions. Common Ion Effect and Solubility Product Common Ion Effect

The common ion effect refers to the suppression of the ionization of a weak electrolyte due to the presence of a common ion (an ion that is also produced by the ionization of the weak electrolyte). According to Le Chatelier’s principle, when a stress is applied to a system at equilibrium, the system adjusts to partially counteract the stress. In the context of ionic equilibria, adding a common ion shifts the equilibrium toward the undissociated form, reducing the degree of ionization.

For example, consider the ionization of acetic acid: CH*f* COOH(aq) Ì! CH*f* COO{ (aq) + Hz (aq)

If sodium acetate (CH*f* COONa), which dissociates to produce CH*f* COO{ ions, is added to an acetic acid solution, the equilibrium shifts to the left, decreasing the ionization of acetic acid and consequently decreasing the concentration of Hz ions, resulting in a higher pH.

Similarly, for a weak base like ammonia: NH*f* (aq) + H, O(l) Ì! NH,, z (aq) + OH{ (aq)

The addition of ammonium chloride (NH,, Cl), which provides NH,, z ions, shifts the equilibrium to the left, decreasing the concentration of OH{ ions and resulting in a lower pH.

Solubility Product

The solubility product (Ksp) is an equilibrium constant that describes the solubility of a sparingly soluble ionic compound. For a general salt A “ Ž B g”Ž that dissociates according to:

A “ Ž B g”Ž (s) Ì! xAz n(aq) + yB{ P”(aq) The solubility product is defined as:

Ksp = [Az n]ã[B{ P”]¸

Where [Az n] and [B{ P”] are the molar concentrations of the ions at equilibrium.

For example, for silver chloride: AgCl(s) Ì! Agz (aq) + Cl{ (aq) Ksp = [Agz][Cl{] For calcium phosphate: Ca*f* (PO„), (s) Ì! 3Ca²z (aq) + 2PO„ ³{ (aq) Ksp = [Ca²z
]³[PO„ ³{]²

The value of Ksp provides information about the solubility of the compound. Ahigher Ksp indicates greater solubility, while a lower Ksp indicates lower solubility.

Relationship between Solubility and Solubility Product

The molar solubility (S) of a salt is the number of moles of the salt that dissolve in one liter of solution to form a saturated solution. The relationship between the molar solubility and the solubility product depends on the stoichiometry of the salt.

For a salt A “ Ž B g”Ž :

- [Az n] = xS
- [B{ P”] = yS

Substituting into the Ksp expression: Ksp = (xS)ã(yS)¸ = x^x × y^y × S^(x+y) Rearranging to solve for S: S = [(Ksp)/(x^x × y^y)]^[1/(x+y)] For example, for silver chloride (AgCl): If S is the molar solubility, then [Agz] = [Cl{
] = S Ksp = [Agz][Cl{] = S × S = S² S = “Ksp

For calcium phosphate (Ca*f* (PO„),): [Ca²z] = 3S and [PO„ ³{] = 2S Ksp = [Ca²z
]³[PO„ ³{]² = (3S)³(2S)² = 108Su S = [(Ksp)/108]^(1/5)

Common Ion Effect on Solubility

The common ion effect also influences the solubility of ionic compounds. The presence of a common ion decreases the solubility of a sparingly soluble salt. For example, the solubility of silver chloride (AgCl) decreases in the presence of sodium chloride (NaCl) due to the common Cl{ ion. Similarly, the solubility

of calcium carbonate (CaCO*ƒ*) decreases in the presence of calcium chloride (CaCl,) due to the common Ca²z ion.

Mathematically, if a sparingly soluble salt A “ Ž B g”Ž is dissolved in a solution already containing one of its ions (e.g., Az n with a concentration [Az n]€), the molar solubility (S) can be calculated using the solubility product (Ksp): Ksp = [Az n]ã[B{ P”]¸ = ([Az n]€ + xS)ã(yS)¸

If [Az n]€ >> xS, the equation simplifies to: Ksp H” [Az n]€ ã(yS)¸ Solving for S: S H” [(Ksp)/([Az n]€ ã × y^y)]^(1/y)

Illustrative Examples Example 1: Calculating Solubility from Ksp Calculate the molar solubilityof calcium fluoride (CaF,) in water at 25°C, given that Ksp = 3.9 × 10{ ¹¹.

Solution: CaF, (s) Ì! Ca²z (aq) + 2F{ (aq)

Let S be the molar solubility of CaF, . At equilibrium: [Ca²z] = S [F{] = 2S

Ksp = [Ca²z][F{]² = S(2S)² = 4S³ 3.9 × 10{ ¹¹ = 4S³ S³ = (3.9 × 10{ ¹¹)/4 = 9.75 × 10{ ¹² S = “(9.75 × 10{ ¹²) = 2.13 × 10{ t mol/L

Example 2: Common Ion Effect on Solubility Calculate the molar solubility of calcium fluoride (CaF,) in a 0.10 M CaCl, solution at 25°C, given that Ksp = 3.9 × 10{ ¹¹.

Solution: In a 0.10 M CaCl, solution, [Ca²z]€ = 0.10 M (from CaCl,).

Let S be the molar solubility of CaF, in this solution. At equilibrium: [Ca²z] = 0.10 + S H” 0.10 (since S is expected to be very small) [F{] = 2S

Ksp = [Ca²z][F{]² = (0.10)(2S)² = 0.40S² 3.9 × 10{ ¹¹ = 0.40S² S² = (3.9 × 10{ ¹¹)/0.40 = 9.75 × 10{ ¹¹ S = “(9.75 × 10{ ¹¹) = 3.12 × 10{ v mol/L

Comparing the results from both examples, the molar solubility of CaF, decreases from 2.13 × 10{ t mol/L in pure water to 3.12 × 10{ v mol/L in 0.10 M CaCl, solution, demonstrating the common ion effect.

Salt Hydrolysis: Salt hydrolysis refers to the reaction of the cation or anion (or both) of a dissolved salt with water, resulting in a solution that is not neutral. The pH of a salt solution depends on the nature of the constituent ions.

Salts can be categorized into four types based on the nature of the acid and base from which they are derived:

1. Salts of strong acid and strong base (e.g., NaCl)
2. Salts of strong acid and weak base (e.g., NH,, Cl)

3. Salts of weak acid and strong base (e.g., CH*f* COONa)
4. Salts of weak acid and weak base (e.g., NH,, CH*f* COO)

Salts of strong acid and strong base do not undergo hydrolysis, and their solutions are neutral (pH = 7). The other types of salts undergo hydrolysis to varying extents, resulting in solutions that are either acidic or basic.

Hydrolysis of Salts of Strong Acid and Weak Base

When a salt derived from a strong acid and a weak base dissolves in water, the cation (the conjugate acid of the weak base) undergoes hydrolysis, while the anion (the conjugate base of the strong acid) does not.

Consider ammonium chloride (NH,, Cl), a salt of the strong acid HCl and the weak base NH*f* :

NH,, Cl(s) '! NH,, z (aq) + Cl{ (aq)

The ammonium ion undergoes hydrolysis: NH,, z (aq) + H, O(l) Ì! NH*f* (aq) + H*f* Oz (aq)

This reaction produces hydronium ions, making the solution acidic (pH < 7).

The hydrolysis constant (Kh) for this reaction is related to the dissociation constant of the weak base (K‘) and the ionic product of water

The degree ofhydrolysis (h) is defined as the fraction of salt that undergoes hydrolysis: h = Concentration of hydrolyzed salt / Initial concentration of salt

For a salt of a strong acid and a weak base with initial concentration C: h = “(Kh/C) (when h << 1)

The pH of the solution can be calculated as:

pH = -log € [Hz] = -log € (h × C) = -log € (“(Kh × C))

Calculation of Hydrolysis Constant and Degree of Hydrolysis for Salt of Strong Acid and Weak Base

Let’s consider a specific example: a 0.10 M solution of ammonium chloride (NH,, Cl) at 25°C, where K‘ for NH*f* is 1.8 × 10{ u .

Step 1: Calculate the hydrolysis constant (Kh). Kh = K!”/K‘ = 10{ ¹t /1.8 × 10{ u = 5.56 × 10{ ¹p

Step 2: Calculate the degree of hydrolysis (h). h = “(Kh/C) = “(5.56 × 10{ ¹p / 0.10) = “(5.56 × 10{ y) = 7.46 × 10{ u

This means that approximately 0.00746% of the NH,, z ions undergo hydrolysis.

Step 3: Calculate the pH of the solution. [Hz] = h × C = (7.46 × 10{ u)(0.10) = 7.46 × 10{ v mol/L pH = -log € [Hz] = -log € (7.46 × 10{ v) = 5.13

The solution is slightly acidic, as expected for a salt of a strong acid and a weak base.

Hydrolysis of Other Types of Salts

Salts of Weak Acid and Strong Base: The anion undergoes hydrolysis, producing hydroxide ions and making the solution basic (pH > 7).

For example, sodium acetate (CH*f* COONa): CH*f* COONa(s) ’! Naz (aq) + CH*f*COO{ (aq) The acetate ion undergoes hydrolysis: CH*f* COO{ (aq) + H, O(l) Ì! CH*f*COOH(aq) + OH{ (aq) The hydrolysis constant is: Kh = K!”/K (CH*f* COOH) = 10{ ¹t /1.8 × 10{ u =

5.56 × 10{ ¹p Salts of Weak Acid and Weak Base: Both the cation and anion undergo hydrolysis. The pH of the solution depends on the relative strengths of the acid and base.

For example, ammonium acetate (NH,, CH*f* COO): NH,, CH*f* COO(s) ’! NH,, z (aq) + CH*f* COO{ (aq)

Both ions undergo hydrolysis: NH,, z (aq) + H, O(l) Ì! NH*f* (aq) + H*f* Oz (aq) CH*f* COO{ (aq) + H, O(l) Ì! CH*f* COOH(aq) + OH{ (aq)

The pH of the solution depends on the relative values of K (acid) and K‘ (base)

- If K >K‘ , the solution is acidic (pH < 7).
- If K <K‘ ,the solution is basic (pH > 7).
- If K = K‘ , the solution is neutral (pH = 7).

Buffer Solutions: Introduction and Henderson-Hasselbalch Equations Buffer solutions play an important role as a chemical system that resist changes in pH upon the addition of small amounts of acid or base. Such solutions are important in numerous biological processes, lab exercises, and industrial applications where control over pH is needed for proper operation.

When a weak acid, and its conjugate base, or a weak base and its conjugate acid are present in appreciable and comparable concentrations, we have a buffer solution. Hence adding the buffer enables this combination to wipe out more

hydrogen hydroxide ions (OH-) or hydrogen ions (H+) strong, which step down the pH leaps. Buffer Composition and Function Some of the important factors that influence the effectiveness of a buffer include the relative concentrations of the buffer components and the correlation between the pH of the buffer and the pKa (or pKb) of the acidic (or basic) species involved in the system. Buffers function best when the pH is about one unit on either side of the pKa of the weak acid part.

pH = pKa + log [A"]/[HA] (2.2) When a small amount of strong acid is added to the buffer, conjugate base component of the buffer reacts with the added H+ ions to convert them to the weak acid form. In contrast, as you add a small amount of strong base, the weak acid component of the buffer gives up protons to neutralize the added OH- ions, resulting in water and converting some of the weak acid into its conjugate base form.

The Henderson-Hasselbalch Equation for Acidic Buffers

The Henderson-Hasselbalch equation, which defines the relationship between the pH of a buffer solution and the concentrations of the respective acidic and conjugate base components. For an acidic buffer that consists of a weak acid (HA) and it conjugate base (A-), the equation is:

pH = pKa + log([A-]/[HA]) Where:

- pH is the negative logarithm of the hydrogen ion concentration
- pKa is the negative logarithm of the acid dissociation constant
- [A-] is the molar concentration of the conjugate base
- [HA] is the molar concentration of the weak acid

This equation is derived from the acid dissociation equilibrium: HAÌ! H+ +A- The equilibrium constant for this reaction, Ka, is given by: Ka = [H+][A-]/[HA] Taking the negative logarithm of both sides: -log(Ka) = -log([H+]) - log([A-]/[HA]) Which rearranges to: pH = pKa + log([A-]/[HA])

The Henderson-Hasselbalch Equation for Basic Buffers

For a basic buffer composed of a weak base (B) and its conjugate acid (BH+), the Henderson-Hasselbalch equation takes a slightly different form:pOH = pKb + log([BH+]/[B]) Where:

- pOH is the negative logarithm of the hydroxide ion concentration

- pKb is the negative logarithm of the base dissociation constant
- [BH+] is the molar concentration of the conjugate acid
- [B] is the molar concentration of the weak base

Since pH + pOH = 14 (in aqueous solutions at 25°C), we can convert this to pH: pH = 14 - pKb - log([BH+]/[B])

Alternatively, using the relationship pKa + pKb = 14 for conjugate acid-base pairs, we can express the equation as:

pH = pKa - log([BH+]/[B])

This form of the equation is often more convenient, as it allows consistent use of pKa values for both acidic and basic buffers.

Buffer Capacity and Preparation The buffer capacity refers to the amount of acid or base a buffer can neutralize before significant pH changes occur. It is highest when the concentrations of the weak acid and its conjugate base are equal, which occurs when pH = pKa.

To prepare a buffer solution with a specific pH, the Henderson-Hasselbalch equation can be rearranged to determine the required ratio of conjugate base to acid:

[A-]/[HA] = 10^(pH - pKa)

Practical buffer preparation often involves:

1. Selecting an appropriate weak acid with a pKa near the desired pH
2. Calculating the required ratio of conjugate base to acid
3. Preparing solutions of the weak acid and its conjugate base, or
4. Preparing a solution of the weak acid and partially neutralizing it with a strong base to generate the conjugate base in situ

Check your Progress

1. What is meant by dynamic equilibrium in a chemical reaction?

…..
……

2. How does Le Chatelier’s principle predict the effect of changes in concentration, temperature, or pressure on equilibrium?

……
……
……

6.6 Summary

Ionic equilibrium is the dynamic balance between ions and undissociated molecules in a solution, and it is particularly important for weak acids, weak bases, salts, and sparingly soluble compounds. Weak acids and bases partially ionize in water, and their extent of ionization is described by the ionization constants K_a ,K_b. The fraction of molecules ionized is known as the degree of dissociation (α) and depends on concentration and ionic strength. Salts undergo hydrolysis depending on the nature of their ions. Acidic salts like ammonium chloride produce acidic solutions, basic salts like sodium cyanide produce basic solutions, and neutral salts like sodium chloride do not hydrolyze. Hydrolysis is determined by the interaction of cations and anions with water.

6.7 Exercises

1. Multiple Choice Questions (MCQs)

1. Which of the following salts produces a basic solution in water?
   a) NaCl
   b) NH_4Cl
   c) NaCN
   d) KBr
2. The pH of a 0.01 M HCl solution is:
   a) 1
   b) 2
   c) 3
   d) 4
3. In a solution of weak acid and its salt, the pH is determined by:
   a) Henderson-Hasselbalch equation
   b) Van't Hoff equation
   c) Nernst equation
   d) Arrhenius equation
4. Which of the following ions does not hydrolyze in water?
   a) NH_4^+
   b) NO_3^-
   c) F^-
   d) CH_3COO^-
5. The common ion effect leads to:
   a) Increase in solubility
   b) Decrease in solubility
   c) No change in solubility
   d) Precipitation of salt only

2. Short Answer Questions (SAQs)

1. Define ionic equilibrium and give one example.
2. Explain the concept of hydrolysis of salts with one example.
3. What is the effect of dilution on the pH of a weak acid?
4. Write the expression for the solubility product (K_{sp}) of CaF_2 and explain its significance.
5. Using the Henderson-Hasselbalch equation, calculate the pH of a solution containing 0.1 M CH_3COOH and 0.1 M CH_3COONa ($pK_a = 4.76$).

3. Long Answer Questions (LAQs)

1. Derive the Henderson-Hasselbalch equation for a buffer solution and explain the factors affecting buffer capacity.
2. Derive the relationship between the degree of dissociation (α), ionic strength, and Ka of a weak acid in aqueous solution.
3. Discuss the hydrolysis of salts in detail. Classify salts according to their acidic, basic, and neutral nature, and give examples.
4. Derive the expression for pH of a solution of a weak acid and its salt (buffer solution) using the common ion effect.
5. Explain the solubility product concept. Derive the expression for the solubility of a sparingly soluble salt in the presence of a common ion and illustrate with an example.

6.8 References and Suggested readings

1. **Atkins, P., & de Paula, J. (2010). Physical Chemistry (9th ed.). Oxford University Press, Great Clarendon Street, Oxford, OX2 6DP, UK.**
2. **Castellan, G. W. (1983). Physical Chemistry (3rd ed.). Addison-Wesley, 75 Arlington Street, Boston, MA, USA.**
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Unit -7 Phase Equilibrium

Structure

7.1 Introduction

Phase equilibrium refers to the state in which two or more phases of a substance coexist in equilibrium with each other, with no net change in the amounts of the phases over time. A phase is defined as a homogeneous part of a system that is physically distinct and mechanically separable. Common examples include the coexistence of solid and liquid in melting/freezing, liquid and vapor in boiling/condensation, or multiple immiscible liquids in contact. Phase equilibrium is governed by the conditions of temperature and pressure, and it is characterized by the equality of chemical potential of a substance in all coexisting phases. The study of phase equilibrium involves understanding how pressure, temperature, and composition affect the stability and coexistence of phases. Key concepts include vapor pressure, boiling point, freezing point, and solubility, which can be predicted and explained using thermodynamic principles. Phase equilibria are classified into one-component systems, like water, which exhibit liquid-vapor-solid equilibrium, and multi-component systems, such as solutions, alloys, or gas mixtures, which involve interactions between different substances.

7.2 Objective:

To understand the concept of phase, component, and degree of freedom in a system.

To learn and apply the Gibbs phase rule to predict the number of independent variables in a system.

To analyze phase diagrams for one-component and multi-component systems.

To understand the effect of temperature, pressure, and composition on the stability and coexistence of phases.

Phase Equilibrium Gibbs Phase Rule, Phases, Components, and Degrees of Freedom The freedom degree is the number of independent intensive variables (like, temperature, pressure and composition) which could be changed, without disturbing the equilibrium state of the system. To characterize the state of a system, we need to specify these variables. The number 2 in the Gibbs Phase Rule equation corresponds to the two most common external parameters of phase equilibria: temperature and pressure. Neutron pipes are made of transparent, homogeneous material so that Neutron phase equilibrium is a crucial rule in trying to penetrate different matter. Before getting into phase equilibrium, we need to understand the Gibbs Phase Rule.

The Gibbs Phase Rule relates the number of degrees of freedom (F) in a system at equilibrium to the number of components (C) and the number of phases (P) It is the basis of the analysis of phase equilibria in systems of this type. Let us tease out the individual terms in this equation:A phase is a physically separate, homogeneous body of matter in which all physical and chemical properties are the same throughout the system. Known examples may involve solid, liquid and gas phases, although a system may consist of multiple solid phases with different crystal arrangements or multiple liquid phases that do not mix. A component is a chemically independent part of a system. The minimum number of independent chemical species required to define the composition of all phases in the system is the number of components. For uncomplicated systems, this often corresponds to the number of unique chemical substances, but for systems with chemical reactions or constraints, it may be lesser number of components.

Application of Phase Rule to One-Component Systems Water System The water system is a classic example of a one-component system (C = 1) that exhibits rich phase behavior. Applying the Gibbs Phase Rule:

$F = 1 - P + 2 = 3 - P$

For this system, the maximum number of phases that can coexist in equilibrium is three (when F = 0), which occurs at the triple point where solid, liquid, and

vapor phases coexist at a specific temperature (0.01°C) and pressure (611.73 Pa). The phase diagram of water displays several noteworthy features:

1. Triple point: Where ice, liquid water, and water vapor coexist (F = 0)
2. Critical point: Where the distinction between liquid and vapor phases disappears (T = 374°C, P = 218 atm)
3. Sublimation curve: Direct transition between solid and vapor phases
4. Melting curve: Transition between solid and liquid phases
5. Vapour pressure curve: Transition between liquid and vapor phasesA unique characteristic of the water system is the negative slope of the solid-liquid equilibrium line, indicating that ice melts under pressure. This unusual property arises because water expands upon freezing, unlike most substances. Along any phase boundary (where two phases coexist), F = 1, meaning only one variable (either temperature or pressure) can be independently varied while maintaining equilibrium between the two phases. Sulfur System: The sulfur system presents a more complex one-component system due to sulfur's allotropy (existence in different solid forms). The main phases in the sulfur system include:

1. Rhombic sulfur (Sá): Stable below 95.5°C
2. Monoclinic sulfur (Sâ): Stable between 95.5°C and 119°C
3. Liquid sulfur: Exists above melting points of solid phases
4. Sulfur vapor: Gaseous phase

Applying the Gibbs Phase Rule to the sulfur system:

Similar to water, the maximum number of phases that can coexist at equilibrium is three, which occurs at transition points.

The phase diagram of sulfur features:

1. Triple points: Where three phases coexist (F = 0)

- Rhombic sulfur, monoclinic sulfur, and vapor
- Rhombic sulfur, monoclinic sulfur, and liquid sulfur
- Monoclinic sulfur, liquid sulfur, and vapor

2. Phase boundaries: Where two phases coexist (F = 1)

- Rhombic-monoclinic transition line
- Solid-liquid transition lines
- Solid-vapor and liquid-vapor transition lines

The existence of multiple solid phases makes the sulfur system a rich example for studying phase transformations in single-component systems.

Reduced Phase Rule: In certain situations, we may wish to analyze phase equilibria at constant pressure or constant temperature, leading to the Reduced Phase Rule: For constant pressure: F' = C - P + 1 For constant temperature: F' = C - P + 1 Where F' represents the reduced degrees of freedom. This simplification is particularly useful when working with phase diagrams that are commonly constructed at either constant pressure or constant temperature.

For example, in a one-component system at constant pressure: F' = 1 - P + 1 = 2 – P This implies that a maximum of two phases can coexist at equilibrium under isobaric conditions.

7.4 Application of Phase Rule to Two-Component Systems

Two-component systems (C = 2) introduce compositional variables, making their phase diagrams more complex and typicallyrequiring three-dimensional representation. However, by fixing one variable (usually pressure), we can analyze these systems using two-dimensional phase diagrams.

Applying the Gibbs Phase Rule to a two-component system: F = 2 - P + 2 = 4 - P

At constant pressure, the reduced phase rule gives: F' = 2 - P + 1 = 3 - P

Lead-Silver (Pb-Ag) System :The lead-silver system is a classic example of a two-component system with limited solid solubility and a eutectic point. Key features of this system include:

1. Liquid phase: Homogeneous mixture of molten Pb and Ag
2. Solid phases: Almost pure Pb and Ag with limited solid solubility
3. Eutectic point: Where the liquid phase solidifies directly into a mixture of two solid phases. At constant pressure, applying the reduced phase rule: F' = 2 - P + 1 = 3 - P The phase diagram consists of several regions:

1. Single-phase regions (F' = 2):

- Liquid solution (L): Requires specifying both temperature and composition
- Solid solution rich in Ag (á): Limited solubility of Pb in Ag
- Solid solution rich in Pb (â): Limited solubility of Ag in Pb

7.5Application of phase rule to two component systems: Pb-Ag system.

- L + á: Liquid in equilibrium with solid á phase
- L + â: Liquid in equilibrium with solid â phase
- á + â: Two solid phases in equilibrium

3. Three-phase point (F' = 0):

• Eutectic point: Where L, á, and â phases coexist at a specific temperature (303°C) and composition (2.6 wt% Ag)

The eutectic composition represents the lowest melting point in the system. The phase diagram guides understanding how the Pb-Ag system behaves during cooling or heating:

• Above the liquidus line: Only liquid phase exists

• Between liquidus and solidus: Two phases coexist (liquid + solid)=

• Below the solidus: Only solid phases exist

For any overall composition, the lever rule can be applied to determine the relative amounts of phases present in two-phase regions.

7.6Congruent Ferric chloride system.

Ferric Chloride System (Congruent Melting) The ferric chloride-water system (FeCl*ƒ* -H, O) exhibits congruent melting behavior, which occurs when a solid compound melts to form a liquid of the same composition. This system features several solid hydrates of ferric chloride with different water content.

Applying the reduced phase rule at constant pressure: F’ = 2 - P + 1 = 3 - P The phase diagram of the FeCl*ƒ* -H, O system includes:

1. Single-phase regions (F’ = 2):

• Liquid solution: Homogeneous mixture of FeCl*ƒ* and H, O

• Solid phases: Various hydrates like FeCl*ƒ* •6H, O, FeCl*ƒ* •4H, O, FeCl*ƒ* •2.5H, O, etc.

2. Two-phase regions (F’ = 1):

• Liquid in equilibrium with a solid phase

3. Three-phase points (F’ = 0):

• Eutectic points: Where liquid and two solid phases coexist

• Peritectic points: Where a solid phase decomposes upon heating to form a different solid phase and liquid

A key feature of this system is the congruent melting point of the FeCl*ƒ* •6H, O hydrate at around 37°C. At this point, the hydrate melts to form a liquid of identical composition without decomposition.

The phase diagram for this system displays multiple thermal arrest points corresponding to eutectic and peritectic transformations. These transitions are critical in understanding the behavior of the system during processes like crystallization, dissolution, and hydration/dehydration.

Practical Significance of Phase Equilibria: Understanding phase equilibria has numerous practical applications:

1. Materials processing: Controlling phase transformations during heat treatment, casting, and solidification
2. Separation processes: Designing distillation, extraction, and crystallization operations
3. Alloy design: Developing materials with desired microstructure and properties
4. Geological processes: Understanding mineral formation and metamorphism
5. Chemical reactions: Optimizing reaction conditions for desired products The Gibbs Phase Rule provides a powerful framework for analyzing and predicting the behavior of systems under various conditions, making it an essential tool in thermodynamics, materials science, and chemical engineering.

By systematically applying the phase rule to increasingly complex systems—from one-component systems like water and sulfur to two-component systems like Pb-Ag and FeCl*f* -H, O—we gain insights into the fundamental principles governing phase transformations and equilibria in matter.

Check your Progress

1. What conditions must be satisfied for a system to be in phase equilibrium?

…….
…….

2. How does temperature and pressure affect the phase equilibrium of a pure substance?

…. ……
……

7.7 Summary

Phase equilibrium refers to the state in which multiple phases of a substance—such as solid, liquid, and gas—coexist in balance without any net change over time. At equilibrium, the rates of phase transitions (like evaporation and condensation) are equal. It is governed by temperature, pressure, and composition, and represented by phase diagrams showing the conditions under which each phase is stable.

7.8 Exercise Questions

Multiple Choice Questions (MCQs)

1. The equilibrium constant for a reaction is affected by:

a) Temperature

b) Catalyst

c) Pressure

d) Both (a) and (c)

2. Le Chatelier's principle states that:

a) Equilibrium shifts to oppose changes

b) Reaction rate remains constant

c) Equilibrium favors reactants

d) Temperature has no effect

3. A weak acid has:

a) Low pKa value

b) High degree of ionization

c) Strong conjugate base

d) Partial dissociation in water

4. The common ion effect is observed in

a) Buffered solutions

b) Solutions of weak acids and their salts

c) Neutral solutions

d) None of the above

5. The solubility of a salt decreases if:

a) The temperature is increased

b) A common ion is added

c) Pressure is increased

d) pH is increased

6. Henderson-Hasselbalch equation is used to calculate:

a) Solubility

b) pH of buffer solutions

c) Gibbs free energy

d) Equilibrium constant

7. Which is NOT an example of a one-component system?

a) Water system

b) Sulfur system

c) Pb-Ag system

d) CO, system

8. The number of phases in a water system at 0°C and 1 atm pressure is:

a) 1

b) 2

c) 3

d) 4

9. In the Pb-Ag system, the phase rule applies to:

a) A pure substance

b) Abinary system

c) A ternary system

d) Anon-equilibrium system

10. The solubility product is applicable for:

a) All electrolytes

b) Strong electrolytes

c) Sparingly soluble salts

d) None of the above

Short Answer Questions

1. Define the law of mass action and its significance in equilibrium.
2. Explain the effect of temperature on equilibrium constants.
3. What is Le Chatelier's principle? Give an example.
4. Define pH and write the Henderson-Hasselbalch equation.
5. What is the common ion effect? How does it affect solubility?
6. Explain the significance of solubility product in precipitation reactions.
7. Differentiate between strong and weak electrolytes with examples.
8. How does the phase rule apply to the water system?
9. What is the reduced phase rule?
10. Describe the concept of salt hydrolysis and its effect on solution pH.

Long Answer Questions

1. Derive the expression for the equilibrium constant and explain its significance.

2. Explain Le Chatelier's principle with industrial examples.

3. Discuss the concept of ionic equilibrium and the dissociation of weak acids and bases.
4. Explain the common ion effect and its applications in chemical equilibrium.

5. Describe the solubility product and its significance in qualitative analysis.

6. Derive the Henderson-Hasselbalch equation and explain its applications.

7. Explain the Gibbs phase rule and its applications in one- and two-component systems.
8. Describe the phase diagram of the Pb-Ag system and its industrial importance.

9. Discuss the importance of buffer solutions in biological and industrial applications.
10. Explain how the solubility of a salt is affected by temperature, pressure, and pH.

7.9 References and suggestive readings

1. Atkins, P., & de Paula, J. (2010). Physical Chemistry (9th ed.). Oxford University Press, Great Clarendon Street, Oxford, OX2 6DP, UK.
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BLOCK-4
PHOTOCHEMISTRYAND LIQUID-LIQUID MIXTURES

Unit -8 Photochemistry

Structure

8.1 Introduction

Radiation with Matter: Depending on the nature of the interaction, electromagnetic radiation may either pass through matter, be absorbed by matter, be reflected by matter, scatter off matter, or a combination of these processes. Key processes involved are absorption, reflection, refraction, scattering, and transmission. Absorption is the most important of these for photochemistry. Molecules absorb indeed photons of the right amount of energy and the electrons go from their ground states to excited states. Photo-excitation is also very selective, as this energy absorption takes place only at particular wavelengths, which correspond to the difference in energy between the electronic states of the molecule. The energy absorbed in the absorption events can then be released into the environment via different pathways, for example through photochemical processes (the energy is used to break/form chemical bonds) or photophysical processes (the energy is released in the form of radiation through fluorescence and phosphorescence).

Since the energy state of molecules are quantized molecules can exist in discrete energy levels. When radiation interacts with matter, only photons of energy precisely equal to the energy difference between these quantised states can be absorbed. This principle is responsible for the selectivity of photochemical reactions and, therefore, for the differing reactions by different molecules to different wavelengths of light. Absorption of UV-Vis irradiation, which excites organic molecules, resides in the electronic energy levels range; hence of immediate interest, whilst infrared radiation induces vibrational transitions and microwave radiation-excites rotational transitions.

8.2 Objective

- Understand the interaction of radiation with matter.
- Differentiate between thermal and photochemical reactions.
- Learn the laws governing the absorption of light
- Study the Jablonski diagram, quantum yield,

8.3 Reactions based on thermal and photochemical mechanisms

At high temperatures, the kinetic energy transfer between colliding molecules induces thermal reactions. The energy gets split among all the available vibrational modes of the molecule according to the Boltzmann distribution. Consequently, thermal reactions typically take place along the minimum energy reaction coordinate of the ground state potential energy surface, yielding the most thermodynamically stable products. Unlike these nonradiative processes, photochemical reactions begin with the absorption of photons which results in the electronic excitation of molecules to higher energy states. This electronic excitation is not random, and localized, the way that thermal processes spread energy out in a soup. Excited states function the same wayafter photochemical reactions, with different electronic configurations, and different potential energy surfaces with respect to the ground state. It thus allows for reaction pathways that are otherwise unattainable under thermal reactions, leading to the formation of thermodynamically disfavored products. Photochemical reactions are also possible at low temperatures because instead of thermal energy, the activation in photoreactions is provided by light energy.

Afurther important difference is in reaction selectivity. For example, thermal reactions follow the Woodward-Hoffmann rules for pericyclic reactions, but photochemical reactions typically show reverse stereoselectivity because of the differing orbital symmetry requirements of a singlet state versus a triplet state. This transition is responsible for the photochemical utility of certain thermally forbidden cycloaddition reactions that become photochemically available. Because of the high degree of specificity of photochemical reactions with respect to the range of light used, it is possible to control pathways to the formation of products by performing the reactions at the right wavelengths of light, making photochemical methods extremely useful in organic synthesis especially in the preparation of structures that may be otherwise difficult to access using standard thermal methods.

8.4 Principles of the Absorption of Light

Several universal laws govern the way that matter absorbs light. The most well-known of these is the Beer-Lambert Law which relates the amount of light

absorbed by a sample to its properties. It says that the absorbance (A) is directly proportional to the concentration (c) of the absorbing species and the pathlength (l) of the sample: A = åcl, where å is the molar absorption coefficient (or molar absorptivity), which is specific to each substance at a specific wavelength. Beer's Law is used to quantitatively relate concentrations of absorbing species determined via spectrophotometric methods.

The Grotthuss-Draper Law (also called the First Law of Photochemistry) states that a compound must absorb light in order for a photochemical reaction to take place. This is expressed in the principle that only absorbed but not incident photons can trigger a photochemical process. Complementing this is the Stark-Einstein Law, or Second Law of Photochemistry, which states that for each photon of light absorbed

bya chemical system, only one molecule gets activated for later reaction. This creates one-to-one correspondence between the absorbed photons and the activated molecules, even though, depending on competing deactivation pathways, the final chemical event might be different. Moreover light absorption obeys quantum mechanical selection rules. The transition probability between electronic states is mediated bythe overlap of their vibrational wavefunctions (Franck-Condon principle), as well as by spin conservation (spin selection rules). These determine the allowed and forbidden transitions, which affect the degree of intensity observed in absorption spectra. Knowledge of these laws is foundational for interpreting spectroscopic data as well as being able to design efficient photochemical processes.

8.5 Laws of Photochemistry

Photochemistry is a discipline governed by a few fundamental laws that apply to the interaction of light with matter and subsequent transformations. The making of a new rule and a Grotthuss-Draper Law in photochemistry comes from the early 19thcentury. Only the light absorbed by a molecule can produce photochemical change. This is a basic principle because it asserts that only when light is absorbed by the system will a photochemical reaction be processed rather than when just arrive at system. The absorption process depends on the wavelength, which is given by the molecular species (determined by the electronic structure). The Stark-Einstein Law (also called the Second Law of Photochemistry or the Photochemical Equivalence Law) gives this quantitative link. It says, for every quanta of radiation absorbed by a chemical system, onlya single molecule is permitted activation for follow-up reaction. 11, 12 More specifically, it means that one mole of a substance

undergoing photochemical reaction absorbs one einstein(6.022×10^{23} photons) of radiation. This law defined the primary quantum yield as theoretically no greater than unity; however, secondary processes may result in apparent deviation. The Bunsen-Roscoe Law of Reciprocity states that the photochemical effect is proportionate to the total energy dose, no matter how that dose is administered. So, the same photochemical principle should work when exposing a system to a strong light (high intensity) for a short period of time, in comparison of low intensity light for a proportionally longer period of time, given that the total delivered energy in both cases is the same. This law, however, is limited and fails to hold true under very high or low intensities or when other processes compete at different rates. It states that for luminescence, the quantum yield is generally independent of the excitation wavelength (Kasha-Vavilov Rule). This implies that regardless of the excited state which was initially populated, there is normally a rapid internal conversion to the lowest excited state of the same multiplicity before emission. Hence, fluorescence normally takes place from S , the lowest excited singlet state (T , lowest triplet state), regardless of where the initial excitation is.

8.6 The Jablonski Diagram Showing Different Processes: This visualizes the electronic states of molecules as well as transitions between them; it is called a Jablonski diagram. It is a basic tool to understand photophysical and photochemical processes. In the diagram, energy levels are represented as horizontal lines, often with the ground singlet state (S€) at the bottom, then the next higher singlet states (S , S, , etc.) and the lower triplet states (T , T, , etc.). There are also several vibrational levels that the electronic states can be in, shown as thinner lines within each electronic state. Most molecules upon absorption of a photon arepromoted from S€ to one of the vibrational levels of S a process that takes place on the femtosecond time scale. After this first excitation, there are multiple routes to dissipate the energy. Vibrational relaxation (VR) describes the process by which the molecule undergoes a rapid cascade from higher to lower vibrational levels of a given electronic state with excess energy released into the surrounding medium as heat. And this happens in the span of picoseconds. 9. Internal conversion (IC) is a radiationless transition between electronic states of the same spin multiplicity, i.e. from higher to lower energy states (e.g. S, to S). This process is also very fast taking place in the range of picoseconds to nanoseconds.

In other words, fluorescence is a radiative transition from the lowest vibrational level of S to the ground state (S€) with emission of a photon. This

fluorescence is generally emitted on the nanosecond timescale and at longer wavelengths/lower energy than absorption, due to the loss of energy from vibrational relaxation i.e., Stokes shift. Intersystem crossing (ISC) is a non-radiative path from an excited state (e.g. S) to a different lower state (e.g. T) of different spin multiplicity. This spin-forbidden process is typically slower than internal conversion, but can be facilitated by the presence of heavy atoms or paramagnetic species. It is worth noting that phosphorescence is a radiative transition from T to S€ , which is spin-forbidden and therefore occurs significantly slower than fluorescence, across timescales from microseconds to seconds at low temperatures and longer. Triplet states have a longer lifetime; therefore, they are of particular importance for photochemistry because they allow sufficient time for chemical reactions to happen. The Jablonski diagram also provides information regarding non-radiative decayfrom T to S€ and photochemical

pathways that maybranch off of excited states, thereby providing a complete overview of excited state dynamics.

Quantum Yield

Quantum yield (Ö) is a key parameter in photochemistry quantifying the efficiency of a photochemical process. The quantum yield is defined as the ratio of the number of individual molecules that undergo a specific photochemical reaction to the number of photons absorbed by the system. Quantum yield, for a photochemical reaction that yields a given product, is given by: Ö = Number of molecules reacted or products formed / Number of photons absorbed.

This is a dimensionless ratio that directly quantifies the efficiency of light energy absorption into chemical change. A quantum yield of 1.0 corresponds to total efficiency, where every absorbed photon causes one molecule to react. Quantum yields less than 1.0 denote that counteracting deactivation processes are extracting energy from the photochemical reaction pathway we want most, whereas values greater than 1.0 inform us of chain reactions or secondary thermal processes that are amplifying the initial photochemical step. Depending on reactant molecular types, reaction environment (temperature, pressure, solvent) and type of incoming radiation, quantum yield is a function. Different photochemical processes from the same excited state will usually compete with each other (19), and thus their individual quantum yields will sum to the total quantum yield determined for deactivation of that state. In the absence of photochemical reactions, the sum of the quantum yields for the primary photophysical processes (e.g., fluorescence, phosphorescence, intersystem

crossing) will equal unity. Quantum yield is an important indicator of the potential and efficiency of photochemical processes in applications, from synthetic organic chemistry to solar energy conversion. This enables researchers to optimize both reaction conditions and photosensitizer to design more efficient photochemical systems. In addition, the determination of quantum yields offers fundamental information on reaction mechanisms and competition between the different deactivation processes of excited states.

Quantitative Study of Reaction Quantum Yields

Accurate estimation of quantum yield is crucial for unraveling photochemical reaction mechanisms and designingefficient photochemical systems. Thereare several methods for doing this, each with their own specific use cases and limitations. The most basic method is measuring how many photons are absorbed and what photochemical change was generated. The actinometric methods are broadlyapplicable in measuring quantum yields. Chemical actinometers (e.g., potassium ferrioxalate, uranyl oxalate, 2,2'-dimethoxybenzoin) are defined quantum yield systems that should be used as references. Byplacing the same excitation source on the sample and the actinometer

(in the same conditions) and using the response of the actinometer, the photon flux can be calculated. Subsequently, the quantum yield of the sample reaction is determined by comparing the extent of reaction in the sample to the evolution of the actinometer, correcting for differences in absorption.Alternatively, one canuse specialized equipment such as quantum yield determination systems that combine light sources, monochromators, sample chambers, and detection systems. These configurations closely regulate the irradiation conditions and measure the incident light intensity(using calibrated photodiodes) and the sample’s absorption, and progress of reaction directly. Moreover, time-resolved spectroscopy is able to provide detailed information about the lifetimes and concentrations of such transient species, which together can be used to determine the quantum yields for complex photochemical processes.

For fluorescence quantum yields, standard methods relying on an appropriate standard of known quantum yield are widely adopted. The sample and the standard are prepared at equal absorbance at the excitation wavelength, and their fluorescence emission spectra are measured under the same conditions. The fluorescence quantum yield of the sample relative to that of the standard

can be determined by comparing the integrated emission intensities while correcting for the differences in absorption and refractive indices of the solvents. R, where \Phi is the quantum efficiencies evaluated for the observed photochemical reaction method, which examine the calorimetric heat (phonons/photons or other) released relative to the energy of the incident photons. This is particularly valuable for systems in which shaking off traditional analytical methods is hard. Regardless of the spectroscopic method chosen for measuring quantum yield, accurate quantum yield determination requires a close attention to experimental conditions including monochromatic light sources, uniform irradiation, accurate measurement actinometry, and secondary thermal reactions that may occur after the primary photochemical step.

Low and High Quantum Yields

A photochemical reaction's quantum yield can range widely from system to system and conditions to conditions, taking values far below unity, to values well in excess of

100. This understanding of the low or high quantum yields sheds light on the reaction mechanisms and allows designing of more efficient reaction photochemical processes. Low quantum yields (Ö 1) represent that the number of produced molecules is higher than apparent photons absorbed by the reaction system, which also would imply the existence of chain reactions or secondary processes. In these scenarios, chain reactions occur when the first photochemical step produces chemically reactive intermediates (radicals), causing the photonic energy to propagate through multiple thermal reaction cycles until termination. As an example, quantum yields on the order of several thousand are possible for the photodissociative chlorination of methane, where each photochemically generated chlorine radical initiates a cascade of consecutive propagation steps. Photosensitization processes wherein excited sensitizer molecules transfer energy to substrate molecules that subsequently undergo chemical reaction can also produce apparent quantum yields greater than unity so long as the sensitizer is regenerated and available for multiple energy transfer events.

Quantum yield is a phenomenon that is critically dependent on experimental conditions. Temperature impacts the rates of competing processes and the stability of reactive intermediates. The solvent characteristics play a critical role in stabilizing excited states and reactive intermediates, and concentration effects can either promote or inhibit intermolecular interactions. Especially critical is

the wavelength of excitation, which sets the initial excited state and its energy content. Insights into these factors not only account for measured quantum yields, but also inform design strategies to optimize photochemical reactions for target applications, spanning organic synthesis, solar energy conversion systems, etc.

Grid-Gated X-ray Source Based on Quantum Yield Principles

Quantum yield control has opened most significant innovations in numerous fields of science and technology. Inspired by nature, which has evolved complex light-harvesting complexes with near-unityquantum yield energytransfer inphotosynthetic systems, artificial photosynthetic systems for solar energy conversion has been developed. Biomimetic systems take advantage of arrayed chromophores and energy funneling to accomplish well-characterized functions such as efficient light harvesting and charge separation, which are important for solar cells and photocatalytic systems. Because of the role of quantum yield on efficacy, quantum yield design is of paramount importance in the design of PDT agents for cancer. Photosensitizers designed for PDT should have sufficient quantum yields for intersystem crossing, allow populations for reactive triplet states to be > 10% as these react with molecular oxygen to form cytotoxic singlet oxygen. Porphyrins and phthalocyanines were subsequently optimized for this purpose, and structural improvements to enhance the efficiency of intersystem crossing and thus therapeutic action were made. In materials science, the principles governing quantum yield underpin the development of efficacious OLED (organic light-emitting diodes) and luminescent materials. Phosphorescent compounds with internal quantum efficiencies approaching 100% have been realized through strategies to limit non–radiative decay pathways and augment radiative transitions. This has been accomplished by incorporation of heavy atoms for enhanced intersystem crossing and through placing rigidities in the molecular structure to block the vibrational modes contributing to the non-radiative decay.

Another major application area is photoinitiators for polymerization processes. They are intended to maximize quantum yields of radical or cationic species produced via irradiation for effective chain initiation in photopolymerization reactions in the fields of 3D printing, coatings, and adhesives. Bimolecular reactions between an excited photosensitizer and a co-initiator can also improve quantum yields through optimized processes of electron or hydrogen transfer (Type II photoinitiators). Compounds with high quantum yields (QY) for well

defined photochemical transformations undergoes the molecular switches and the photochromic materials. Irradiation induces reversible conformational transitions in molecules such as azobenzenes, diarylethenes, and spiropyrans with quantum yields varying significantly depending on the specific structure. These compounds serve as the foundation for optical data storage, smart materials, and molecular machines that react to light stimuli. The principles of quantum yield also underpin newer technologies such as upconversion processes, where triplet- triplet annihilation or lanthanide-based systems convert several lower-energy photons into a single higher-energyphoton.Although heavilycompromised bypoor efficiencies in earlier years, new advancements in relevant molecular design and nanomaterials have drastically increased upconversion quantum yields to create paths toward solar cells, bioimaging and photocatalysis utilizing low energyterrestrial light sources. Heterocycles in Photochemistry: Environmental and Practical Considerations

While application of photochemical principles to address environmental problems has gained ground during the last few decades, they achieved particular momentum in the water treatment sector. Advanced oxidation processes (AOPs) utilize photochemical methods to produced highly active hydroxyl radicals for degradation of organic micropollutants. Akey parameter is the quantum yield for hydroxyl radical production, as this governs the efficiencyof these reactions. In this sense, photocatalytic systems — generally employing semiconductors such as titanium dioxide — are now working in order to achieve the highest possible quantum yields for converting pollutants under solar irradiation, thus providing a sustainable solution in water purification. Atmospheric photochemistry controls a wide variety of processes important to the environment of our home planet from Ozone layer dynamics to smog formation. The rates of these processes and hence their environmental impact are strongly dependent on both quantum yields of key reactions like the photolysis of nitrogen dioxide or volatile organic compounds. These quantum yields are crucial for accurate atmospheric modelling and predicting the impacts of anthropogenic emissions on air pollution and climate change. In home/factory photochemistry, down- or up-scaling is another issue to be considered in the quantum yield optimization. Light penetration is reduced in large reaction volumes, and thus specialized reactor designs such as falling film reactors, spinning disc reactors, or microflow systems that highlight surface-to-

volume ratios are required for efficiency. Furthermore, for industrial photochemical processes to be economicallyviable, it is critical toensurehighquantum yields andefficient light utilization, leading to innovations in light sources, efficient reactors, and catalysts.

Visible light photoredox catalysis has provided groundbreakingways to conduct difficult transformations in synthetic organic chemistryunder mild conditions. Catalysts include transition metal complexes and organic dyes that can achieve high quantum yields for photoinduced electron transfer and carry out single-electron transfer processes to enable many types of reactions. The migration of these methodologies to the photocatalytic family relyon understanding and controlling quantum yields of crucial steps in the catalytic cycle, such as excitation, electron transfer or catalyst regeneration. Photochemical stability is of key importance in many applications ranging from pharmaceuticals to sunlight-exposed materials. Some compounds that shown high quantum yields for photodegradation, possess a shorter shelf life and cannot be use at outdoors. Hence, stabilization strategies such as the addition of UV absorbers, quenchers or physical barriers are applied to suppress undesired photochemical reactions. Accelerated photostability testing, wherein the quantum yields of new compounds are correlated under exaggerated conditions to their likely real-world

performance, has since become standard practice in pharmaceutical, coating and plastics industries. Such practical considerations underscore the importance of quantum yield as not just a theoretical quantity, but a parameter with significant consequences for technological applications and environmental phenomena. Shrinking uncertainty about controlling quantum yields, while also finding novel ways to take advantage of light energy with ever-increasing economy and specificity, will augur even further progress in photochemistry.

Photochemical Reactions Examples

Photochemical Reactions, which are an interesting intersection between light energy and chemical conversion providing electromagnetic radiation as the catalyzing force for molecular transformation. In contrast to thermal reactions which extract energy from heat, photochemical approaches instead make use of the energy of photons to promote electrons to their respective higher energy states, allowing access to pathways that maybeotherwise unavailable. Within

these, the relativelyunexplored photochemical domain, a vast array of reactions critical to natural processes and industrial application.

Photochemical Decomposition of Hydrogen Iodide

A classic case of the simplest photolytic process is the photochemical decomposition of hydrogen iodide (HI). Under UV light (less than 300 nm), hydrogen iodide absorbs photons resulting in homolytic bond cleavage to produce hydrogen and iodine atoms. This primary photochemical process is expressed as:

HI + hí '! H• + I•

After this first photodissociation, the highlyreactive radical species engage in secondary reactions. Iodine atoms can dimerize, producing molecular iodine (I,), and hydrogen atoms can combine molecular hydrogen (H,). The general reaction might be summed up like this:

2HI + hí '! H, + I,

The reaction goes through a chain mechanism includes initiation, propagation, and termination steps. The quantum yield (the number of molecules that rea absorbed) for this reaction may be greater than unity, sometimes in the hundreds under the best reaction conditions. The high quantum yield means one photon can initiate the decomposition of many HI molecules via the chain reaction.

The rate of this decomposition depends on several factors, such as light intensity, wavelength, and temperature, as well as the concentration of hydrogen iodide. Experimental studies of this reaction have thus yielded useful information on reaction kinetics, quantum yields, and radical intermediates, and have made this an important model system in photochemistry.

Photosynthesis of HBr from H, and Br,

The photochemical synthesis of hydrogen bromide from hydrogen and bromine represents another significant chain reaction initiated by light. When a mixture of hydrogen and bromine gases is exposed to visible light (particularly blue-violet light with wavelengths between 400-500 nm), a reaction occurs leading to the formation of hydrogen bromide: The mechanism of this photochemical process involves several distinct steps. Initially, bromine molecules absorb photons and undergo photodissociation to generate bromine atoms:

These bromine radicals then react with hydrogen molecules in a propagation

The hydrogen atoms produced in this step continue the chain reaction by interacting with bromine molecules:

The cycle continues as the newlyformed bromine atom participates in further reactions with hydrogen molecules. The chain is eventually terminated when radicals combine:

The photochemical synthesis showed a few interesting features. This involves chain reactions with rate-of-termination that is second-order, consistent with binaryencounter

recombination of two chain radical species, and a square-root dependence of the reaction rate on the intensity of light. Moreover, the quantum yield for this reaction can be extremely high (10t –10v under idealized conditions), which results in the generation of thousands or even millions of HBr molecules from the absorption of a single photon via an autocatalytically-propagated chain reaction3,4.

Oxygen can intercept hydrogen atoms and halt the chain reaction. In a similar vein, nitric oxide canmop up bromine atoms, which also prevents the reaction from occurring. The influence of the flow or no flow state on the reaction demonstrates the use inhibition effect as a probe of the reaction mechanism and radical intermediate behavior.

Photosynthesis of HCl from H, and Cl, The photochemical synthesis of hydrogen chloride from hydrogen and chlorine gases proceeds through a mechanism similar to the HBr synthesis but exhibits some distinctive characteristics. When a mixture of hydrogen and chlorine is exposed to ultraviolet light or even strong visible light, a rapid and sometimes explosive reaction occurs:

H, + Cl, + hí ’! 2HCl

The mechanism begins with the photodissociation of chlorine molecules: Cl, + hí ’! 2Cl•

The resulting chlorine radicals react with hydrogen molecules: Cl• + H, ’! HCl + H•

The hydrogen atoms then react with chlorine molecules to continue the chain: H• + Cl, ’! HCl + Cl•

This chain propagationcontinues until termination occurs through radical recombination: H• + Cl• ’! HCl Cl• + Cl• ’! Cl,

The photochemical HCl synthesis is much more violent than the analogous HBr synthesis, which is even reported to proceed with an explosive force given a high enough light intensity. This increased reactivity is due to the more reactive nature of Cl• radicals compared to Br• radicals and the lower activation energy . propagation steps. Under ideal conditions, the quantum yield for the HCl synthesis may be as high as 10v , reflecting a highlyefficient chain mechanism. The sensitivity of this reaction to light makes it a colourful example of photochemistry, which was also used famously in photographic experiments and demonstrations very early on. As for the HBr synthesis, the HCl photochemical process is suppressed by a number of species capable of trapping free radicals, such as molecular oxygen, nitric oxide, and certain organic compounds. Such inhibitory effects have been well studied to understand the reaction mechanism and the behavior of the respective radical intermediates involved7,8.

Photosensitization and Quenching

Photosensitization is a complex photochemical process in which a molecule (the photosensitizer) absorbs light energy and transfers it to a second molecule, driving reactions that the second molecule would be unable to perform directly. This process effectively bypasses the need to directly excite the reactive species, enabling photochemical transformations at wavelengths not absorbable by the reactant itself.

A photosensitization process usually involves the following steps:

Sensitiser (S) absorbs a photon to become electronically excited: S + hí ’! S*
Excited sensitizer transfers energy to reactive molecule (R): S* + R ’! S + R*
The rousing reactive multi-atom undergoes a tempo-chemistry transformation: R* ’! Products

FRET occurs via dipole-dipole coupling, while Dexter electron transfer involves electron exchange between donor and acceptor. The efficiency of sensitization is influenced bymanyfactors: lifetime of the excited state, distanceand orientation between the molecules, and spectral overlap between the emission of the sensitizer and the absorption of the acceptor. Photosensitization is used in many natural and synthetic systems.An example being photodynamic therapywhere, for example, photosensitizers like porphyrins or phthalocyanines are supplied to the tissue of interest and then activate/ react to the correct wavelength of light producing reactive oxygen

species (mainly singlet oxygen) which damage the components of the cell resulting in cell death. This has been beneficial in the management of some cancers and some skin diseases.

Conversely, photochemical quenching occurs when an excited molecule transfers its energy to another molecule (the quencher), resulting in deactivation without chemical change. In this process:

1. The molecule (M) absorbs a photon: M + hí '! M*
2. The excited molecule encounters a quencher (Q): M* + Q '! M + Q* or M* + Q '! M + Q

Quenching can be caused by a few different mechanisms, for example, by collisional quenching (i.e. when 2 molecules make contact, allowing energy to be released), static quenching (which occurs when a non-fluorescent complex is formed between the fluorophore and quencher), and resonance energy transfer (where energy transfer occurs without physical contact). Oxygen is a well-known quencher of both fluorescence and phosphorescence, allowing for oxygen-sensitive measurements with careful analysis of photoluminescence behavior. In the natural photosynthetic systems, quenching processes are also important for regulating energy flow and photodamage in high light.

The balance of photosensitization with quenching processes controls the efficiency of many photochemical systems and has given rise to strategies to regulate and optimize photochemistry for a variety of applications.

Photosensitized Reactions

Photosensitized reactions encompass a diverse array of chemical transformations facilitated by photosensitizers. These reactions can be broadly categorized based on the nature of the energy transfer and the subsequent chemical processes. One significant class of photosensitized reactions involves the generation of singlet oxygen (^1O,). When certain photosensitizers like methylene blue, rose bengal, or tetraphenylporphyrin absorb light, they can transfer energy to ground-state triplet oxygen (^3O,), converting it to the highlyreactive singlet state:

Sens + hí '! Sens* Sens* + ^3O, '! Sens + ^1O,

Singlet oxygen is an active participant in a number of reactions such as [4+2] cyclo- additions with dienes (endoperoxides), [2+2] cyclo-additions with alkenes (dioxetanes), and ene-type reactions where the alkene has allylic hydrogens. These transformations find applications in organic synthesis for

preparing complex oxygenated compounds and in photodynamic therapy for inducing cytotoxic effects in targeted cells.

Another major class of photosensitized reactions are those that involve electron transfer processes. During these reactions, the excited state photosensitizer either transfers an electron to or receives an electron from a second molecule, forming radical ions that can participate in further reactions:

Sens + hí '! Sens* Sens* + D '! Sens•z + D•{ (reductive quenching) Sens* + A '! Sens•{ +A•z (oxidative quenching)

These photoinduced electron transfer (PET) processes are fundamental to artificial photosynthesis, photocatalysis, and photoredox catalysis. For example, transition metal complexes such as [Ru(bpy)*ƒ*]²z and [Ir(ppy)*ƒ*] can be used as photoredox catalysts which mediate otherwise challenging transformations that would typically require extreme conditions or toxic reagents. These catalysts have transformed organic synthesis by enabling bond formation in milder conditions and with enhanced selectivity.

Another prominent class of reactions is photosensitized isomerization. For example, the triplet sensitization of trans-stilbene can facilitate its isomerization to the cis form19.

Sens + hí '! Sens* (singlet state) Sens* '! Sens* (triplet state via intersystem crossing) Sens* (triplet) + trans-stilbene '! Sens + trans-stilbene* (triplet) trans-stilbene* (triplet) '! cis-stilbene

This approach to isomerization often offers advantages over direct photolysis, including the ability to use longer wavelengths of light and achieving different selectivity patterns.

Photosensitized cycloadditions constitute yet another important category. For instance, the [2+2] cycloaddition of enones can be efficiently promoted by triplet sensitizers like benzophenone:

Sens + hí '! Sens* Sens* + enone '! Sens + enone* (triplet) enone* (triplet) + alkene '! cyclobutane derivative

These reactions have found extensive applications in the synthesis of natural products and pharmaceuticals, offering access to structural motifs that would be challenging to construct through ground-state chemistry.

The versatility of photosensitized reactions extends to numerous other transformations, including hydrogen atom abstractions, fragmentation reactions,

and rearrangements. The ability to select appropriate sensitizers and reaction conditions allows chemists to access diverse chemical pathways and achieve transformations with high efficiency and selectivity.

Photosynthesis: Nature's Masterpiece of Photochemistry

While the term "photosynthesis" has been used earlier to describe the light-induced synthesis of hydrogen halides, it is perhaps most prominently associated with the biological process occurring in plants, algae, and certain bacteria. Biological photosynthesis represents nature's most sophisticated and consequential photochemical process, converting light energy into chemical energy that sustains virtually all life on Earth.

The overall reaction of oxygenic photosynthesis can be summarized as: 6CO, + 6H, O + light energy '! C† H , O† + 6O,

This deceptively simple equation encompasses a remarkable series of photochemical and dark reactions occurring across thylakoid membranes and the stroma of chloroplasts. The process begins with the absorption of photons by chlorophyll and accessory pigments within protein complexes known as photosystems. The absorbed energy excites electrons to higher energy states, initiating electron transport chains that ultimately drive the synthesis of ATP and NADPH.

Chlorophyll molecules serve as the primary photosensitizers in this system, absorbing predominantlyblueand red light whilereflecting green wavelengths. Whena chlorophyll molecule absorbs a photon, an electron is promoted to an excited state:

This excited configuration triggers a cascade of electron transfers along the thylakoid membrane, establishing a proton gradient that powers ATP synthesis by a process called chemiosmosis. The electron transport chain, at the same time, reduces NADPz to NADPH, which will then be utilized as reducing agent in the following carbon fixation reactions.

Tone: Very formal and technical, academic style

The photochemical phase generates ATP and NADPH, which in the dark reactions (a.k.a. Calvin-Benson cycle, light-independent reaction) will re-reduction carbon dioxide into carbohydrates. While not directly light-driven, these reactions are related to the photochemical processes and are the final chemical process enabled by the absorbed light energy. Number of references on biomimetic approaches to artificial photosynthesis and their highlights,

inspired by the efficiency and sophistication of photosynthesis to har46%0 In the past several decades, numerous biomimetic approaches to the development of artificial photosynthesis have been carried out to take advantage of solar energy for fuel and other substances. Many of these systems are inspired by both biological photosynthesis and conventional photochemistry to find efficient ways to harvest light, separate charge, and convert simple substrates into energy-rich molecules12–15.

Check your Progress

1. What happens when a molecule absorbs a photon of light in a photochemical reaction?

……
……

2. How does the Grotthuss–Draper law explain the initiation of photochemical processes?

……
……
……

8.7 Summary:

Photochemistry deals with chemical reactions initiated by absorption of light energy. Molecules absorb photons and get excited from ground to higher electronic states. The Grotthuss–Draper law states only absorbed light can cause a reaction, while the Stark–Einstein law states one photon activates one molecule. Excited molecules may undergo photophysical processes (fluorescence, phosphorescence) or photochemical reactions (isomerization, dissociation, oxidation). Applications include photosynthesis, photography, solar cells, and photodynamic therapy.

8.8 Exercise Questions

Self assessments exercise -

Q1. Photochemistry is the study of:
a) Heat reactions b) Light-induced reactions c) Nuclear reactions d) Enzymatic reactions
Answer: b) Light-induced reactions

Q2. According to Grotthuss–Draper law:
a) Every photon causes reaction b) Only absorbed light produces reaction

c) Emitted light produces reaction d) Intensity has no effect
Answer: b) Only absorbed light produces reaction

Q3. Stark–Einstein law states:
a) One photon excites one atom b) One photon excites one molecule
c) Many photons excite one molecule d) Photons are not absorbed
Answer: b) One photon excites one molecule

Q4. Which is a photophysical process?
a) Oxidation b) Isomerization c) Fluorescence d) Photolysis
Answer: c) Fluorescence

Q5. Which natural process is photochemical?
a) Combustion b) Photosynthesis c) Fermentation d) Neutralization
Answer: b) Photosynthesis

Short Questions

1. Define photochemical reactions and give one example.
2. State **Grotthuss-Draper law** and its significance.
3. State **Stark-Einstein law (law of photochemical equivalence)**.
4. What is meant by **quantum yield** in a photochemical reaction?
5. Give two examples of **photochemical reactions in gases**.
6. Give two examples of **photochemical reactions in solutions**.

Long Questions – Photochemical Reactions

1. Explain the **laws of photochemistry**. Discuss the **Grotthuss-Draper law** and **Stark-Einstein law** with examples.
2. Derive the expression for **quantum yield** and discuss factors affecting it in photochemical reactions.
3. Discuss the **mechanism of photochemical reactions in gases**, such as the **photodissociation of Cl_2** or **photochemical formation of ozone**.
4. Explain the difference between **primary and secondary photochemical processes**, giving suitable examples for each.
5. Describe the **applications of photochemical reactions** in industry, such as **photosynthesis, photopolymerization, and manufacture of vitamin D**.

8.8 References and Suggetsed Readings

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Unit -9. Applications of Photochemical Reactions

9.1 Introduction

The principles and processes of photochemistry find application across numerous fields, from industrial manufacturing to medicine and environmental remediation.

9.2 Objective

To understand how light energy can initiate and drive chemical reactions.

To explore industrial and biological applications of photochemical processes.

To study the role of photochemistry in areas such as photosynthesis, polymerization, and environmental chemistry.

9.3 Industrial Applications: Photochemical methods are advantageous for industrial applications as they allow for mild reaction conditions, spatial and temporal control, and unique reaction pathways. Examples of large-scale photochemical synthesis include the chlorination of hydrocarbons, the manufacture of caprolactam (a nylon precursor) by the photorearrangement of cyclohexanone oxime, and the production of vitamin D by the UV irradiation of 7-dehydrocholesterol. Photopolymerization (or light-initiated chain reaction) has transformed a wide range of industries byoffering rapid curing of coatings, adhesives, and dental materials. Irradiation of photoinitiators such as benzophenone derivatives or á-hydroxyketones forms reactive species that initiate the polymerization of acrylates, methacrylates, and other functional monomers. Check out this link to read the full article on Ion Beam Induced Polymers with DBT:These processes allow for the following advantages: they

are solvent-free, cure quickly and can achieve spatial control by selective irradiation.

9.4 Environmental Applications: Photochemical phenomena are important to both natural and engineered environments. In recent years, the purification of air and water based on the photodegradation of pollutants by AOPs has received attention as one of the effective approaches[7–9]. These processes generally include photochemically stimulated production of highly reactive hydroxyl radicals (•OH):

These hydroxyl radicals, in turn, can oxidize organic contaminants, eventuallybreaking them down to carbon dioxide, water and benign inorganic ions. Titanium dioxide- (TiO_2-) and other semiconductor-based photocatalytic systems have demonstrated potential for the treatment of a wide variety of contaminants, including pharmaceutical products, pesticides, and industrial chemicals. The photochemical production of smog is an example of an environmentallyunfriendlyapplication of photochemistry. In urban areas, nitrogen oxides and volatile organic compounds react photo chemically in the presence of sunlight to form ozone, peroxyacetyl nitrate (PAN), and other secondary pollutants. Analyzing these photochemical processes is fundamental to create optimal air quality strategies.

Applications in Medicine and Biology: Photochemical principles govern a variety of medical applications, particularly photodynamic therapy (PDT). PDT involves the administration of photosensitizers (e.g., porphyrins or chlorins) to a patient, which selectively accumulate in target tissues. Afterward, irradiation with light of the appropriate wavelength induces the production of reactive oxygen species, particularly singlet oxygen, which causes cytotoxicity in a localized area. This has shown efficacy in treating a range of cancers, certain dermatological diseases, and age-related macular degeneration. Photochemistry is also important to vision, in which the photoisomerization of 11-cis-retinal to all-trans- retinal in rhodopsin activates the signaling cascade that ultimately leads to visual perception. Triggerable by a single photon, this remarkably efficient photochemical process has served as a prized model system for understanding ultrafast photochemical reactions in biological systems. Crosslinking techniques include photochemical crosslinking in applications in corneal crosslinking (e.g., corneal collagen crosslinking for keratoconus treatment) and in photodynamic antimicrobial therapyto treat infections. These applications illustrate the precision and selectivitythat photochemical approaches can provide in medical settings.

This has led to new avenues being explored for technological breakthroughs, through photochemistry developments in recent years. Chromogenic materials, changing color upon irradiation with light of different wavelengths in a reversible fashion, have been useful in applications in smart windows, optical data storage and adaptive eyeglasses. More specifically, these materials have integrated photoswitchable moieties (e.g., azobenzenes, spiropyrans, or diarylethenes) that exhibit reversible photochemical transformations. Photoresponsive polymers/hydrogels are light-activated materials that can be applied in drug deliverysystems, artificial muscles, and soft robotics. Introducing photoswitchable groups in polymeric networks allows researchers to create materials that will expand, contract or change their permeability in response to irradiation. One of the most ambitious applications of photochemistryis artificial photosynthesis, which aims to create a process that closely mimics the fundamental elements of natural photosynthesis for solar energyconversion and storage. These systems generally consist of light harvesting, charge separation, and catalytic transformation of substrates, like water or carbon dioxide, to form energy-dense products, like hydrogen or carbon- based fuels.

Understanding the theory behind photochemical reactions: The need to rely on both quantum mechanics and kinetics to interpret photochemical reactions. When a molecule absorbs a photon it transitions from its ground electronic state to an excited state as permitted by the selection rules imposed by quantum mechanics. The energyof the incoming photon must be equal to the energy difference between these states, given by the Planck-Einstein relation: where h is Planck's constant, í is the frequency, c is the speed of light, and ë is the wavelength.The excited molecule can subsequently undergo various processes, including:

1. Photochemical reaction: The excited molecule transforms into a different chemical species
2. Radiative decay: The molecule returns to the ground state with the emission of a photon (fluorescence or phosphorescence)
3. Non-radiative decay: The energydissipates as heat through internal conversion or intersystem crossing
4. Energy transfer: The excitation energy transfers to another molecule through various mechanisms

The quantum yield of the photochemical reaction, which is defined as the number of reactant molecules converted for every photon absorbed, can be

understood as a competition between these processes. The quantum yield can only approach unity for primaryphotochemical steps (those directlyarising from electronic excitation); it cannot exceed unity unless chain reactions or some other secondary process is taking place. Stark-Einstein law (first law of photochemistry) states that a photochemical reaction will occur only if light is absorbed by the system. The Grotthuss-Draper only the light absorbed by the system can produce a photochemical alteration (the second Law of Photochemistry).

9.5 The efficiency of a photochemical process

The efficiency of a photochemical process depends on various factors, including:

1. The absorption cross-section of the molecule at the irradiation wavelength
2. The lifetime of the excited state
3. The rate constants for the various competing processes
4. Environmental factors such as temperature, solvent properties, and the presence of quenchers or sensitizers

Today, theoretical approaches to photochemistryfrequentlyuse computational methods to compute potential energysurfaces of both ground and excited states, predict reaction pathways, and simulate the dynamics of photochemical reactions. While conducted on relative small scales, TD-DFT (or time-dependent density functional theory) and multiconfigurational methods such as CASSCF (Complete Active Space Self- Consistent Field) have been particularly useful for excited states and photochemical reaction mechanisms.

Experimental Techniques in Photochemistry

Photoscientists can utilize specialized experimental methods to initiate, investigate, and characterize photochemical reactions. Ranging from conventional lamps (mercury, xenon) to lasers, light sources emit the photons necessary to excite these reactions. Wavelength selection is possible through theuse of monochromators orfilters, permitting wavelength-dependent studies that can illuminate mechanistic features and facilitate conditions optimization. Actinometryis an important method for measuring the photon flux in photochemical processes, through which yield measurements are made and comparative studies can be carried out. Areliable way to quantify the light

intensity is by the use of a chemical actinometer such as ferrioxalate, which undergoes a well- characterized photoreduction with known quantum yield.

Time-resolved spectroscopic techniques have revolutionized thestudyof photochemical processes by allowing observation of short-lived intermediates and tracking reaction dynamics on timescales ranging from femtoseconds to seconds. These techniques include:

1. Transient absorption spectroscopy: Monitoringchanges inabsorption following excitation with a pump pulse
2. Time-resolved fluorescence: Tracking emission decayprofiles to reveal excited- state dynamics

3. Flash photolysis: Using intense light pulses to generate high concentrations of intermediates for detection

4. Pump-probe techniques: Exciting the sample with one pulse and probing with another after a controlled delay

Computational methods complement experimental approaches by providing insights into electronic structures, transition states, and reaction pathways. These methods have become increasingly sophisticated, allowing simulation of excited-state dynamics and prediction of photochemical reaction outcomes.

Future Directions in Photochemistry

The field of photochemistrycontinues toevolve, driven byadvancesin both fundamental understanding and practical applications. Several emerging areas promise to shape the future landscape of photochemical research:

1. Visible light photocatalysis: Developing catalysts that operate with visible light rather than UV radiation, enhancing energy efficiency and allowing solar- driven processes
2. Flow photochemistry: Implementing continuous-flow systems for photochemical transformations, offeringadvantages in scale-up, reproducibility, and process intensification
3. Photoredox catalysis: Expanding the repertoire of radical-based transformations enabled by photoredox catalysts, providing access to novel chemical space for pharmaceutical and materials synthesis

4. Artificial photosynthesis:Advancing systems for solar energy conversion and storage, potentially addressing global energy challenges through sustainable fuel production

5. Two-photon and multiphoton processes: Exploring reactions triggered by the simultaneous or sequential absorption of multiple photons, enabling three- dimensional spatial control and access to high-energy intermediates using lower-energy photon To enhance viscosity effects, we anticipate new approaches in combining photochemistry with other emerging fields, like microfluidics, nanotechnology, and machine learning, resulting in opportunities for cutting-edge approaches for fundamental studies and industrial applications. Microfluidic systems afford fine-tuning of reaction conditions and are able to provide improved light penetration, whilst nanostructured materials canact as photocatalysts withtunable properties. While the field has previously relied heavily on empirical data, returning the favor, machine learning methods are now enabling predictions of photochemical reaction outcomes and the optimization of reaction conditions, acting as a discovery accelerator in this complex area.

Photochemical reactions represent a whole class of reactions which share a basic commonality in being induced by light as the energy source for chemical change. These goes from the commutative photodissociation of hydrogen iodide to the complex machineryof biological photosynthesis, and illustrate how fundamental is the interaction of electromagnetic radiation and molecular behavior. Ferbinteanu and Zyrian (2012)— examples (again); photochemical decomposition of hydrogen iodide; photoinitiated ice-like vibrational polaron: vibrational polaron formation in photoexcited hydrogen halide or related systems; kinetics; microscopy photosensitization quenching in hydrogen halides—whispering gallery modes. These reactions function via radical chain mechanisms energy transfer electrons transferas well as the simple cleavage of chemical bonds, all of which allow new pathways for chemical conversion. Photochemistryhas applications in a wide range of fields, including (but not limited to) industrial synthesis, environmental remediation, medicine, and new technologies. Concurrently, advancements in computational methods and experimental probes that enable increasinglydetailed studies of photochemical processes over multiple timescales continue to enrich the theoretical landscape of the field. With continued advancements in the field, emerging catalysts, reaction mechanisms, and potential applications continue to be developed,

leading to greater efficiency and selectivity and more sustainable routes to chemical synthesis and energy conversion.

Check your Progress

1. How are photochemical reactions utilized in the purification of air and water?

……
……
…

2. What role do photochemical reactions play in the degradation of environmental pollutants?

.

……
……

9.6 Summary: Photochemical reactions are applied in **photosynthesis**, where plants convert CO_2 and H_2O into glucose using sunlight; in **photography**, where light causes chemical changes in silver halides on films; in **polymerization**, where UV light initiates reactions to form plastics; in **photodynamic therapy**,

9.7 Exercise Questions

Multiple Choice Questions

1. Which of the following is an example of a photochemical reaction?

A) Combustion of methane

B) Photosynthesis

C) Neutralization of acid and base

D) Electrolysis of water

Answer: B) Photosynthesis

2. In photographic films, the light-sensitive compound is:

A) Silver chloride

B) Silver nitrate

C) Silver bromide

D) Silver sulfate

Answer: C) Silver bromide

3. The Grotthuss–Draper law states that:

A) Only light that is absorbed can cause a reaction

B) Light intensity determines product yield

C) Every photon produces one molecule

D) Light has no effect on reaction rate

Answer: A) Only light that is absorbed can cause a reaction

4. Photochemical smog is mainly caused by reactions involving:

A) Nitrogen oxides and hydrocarbons

B) Carbon dioxide and oxygen

C) Sulfur dioxide and ozone

D) Water vapor and ammonia

Answer: A) Nitrogen oxides and hydrocarbons

5. Which type of radiation is generally responsible for initiating photochemical reactions?

A) Infrared

B) Ultraviolet

C) Microwave

D) X-ray

Answer: B) Ultraviolet

Short Questions

1. What is the primary requirement for a photochemical reaction to occur?
2. Qantum yield in photochemical reactions.
3. How is light energy converted into chemical energy during photosynthesis?
4. Name two industrial applications of photochemical reactions.
5. Why are photochemical reactions often more selective than thermal reactions?

5 Long Questions

1. Explain the mechanism of photosynthesis as a photochemical process.
2. Describe the photochemical reactions involved in photographic film development.
3. Discuss the principles of the Grotthuss–Draper and Stark–Einstein laws and their importance in photochemistry.
4. Explain how photochemical reactions contribute to the formation of photochemical smog.
5. Discuss various industrial and environmental applications of photochemical reactions with suitable examples.

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Unit 10 Liquid-Liquid mixtures

Structure

10.1 Introduction

Liquid-liquid blends are at the heart of many commercial processes and natural occurrences. Mixtures of liquids behave ideally if the two liquids experience from the additive molecular interactions, but generally, the behavior can be very non-ideal in case liquits interact differently. Ideal liquid mixtures are theoretical concept mixtures of fluids whose intermolecular attractors are alike, the same as those that exist between molecules of leading types. In a perfect mixture of two liquids, the interaction of molecure Awith molecule B is equal to the average of an A-A interaction and a B-B interaction. This means that when different molecules meet, there is no energy cost or energy benefit compared to the pure components. This is captured in the expression for the enthalpyof mixing (ÄH_mix), which equals zero for ideal mixtures. The default assumption of ideal liquid mixtures is that the molecules of each of the components have similar size, shape, and chemical nature.As this similarity, there is an even scattering of the molecules around them, i.e., no clustering is preferred. Typical representatives for mixture of chemically close components (for example, benzene and toluene, n- hexane and n-heptane) behave closely to ideal behavior.

10.2 Objective

Ideal liquid mixtures have several important properties. First, the volume of an ideal mixture is the sum of the volumes of its pure components (no volume change on mixing). Secondly, there is no heat exchange when mixing (ÄH_mix = 0). Third, the entropychange for an ideal mixture, evaluated using statistical mechanical models, for perfect random mixing. The notion of ideality is a useful benchmark to assess from, and quantify real mixing behavior against. Ideal mixing behavior serves as a baseline for comparison and allows chemists and engineers to detect and characterize non- ideal interactions in actual systems.

10.3 Classification

Raoult's Law of Ideal Solutions

Raoult's law constitutes one of the fundamental principles governing the behavior of ideal liquid mixtures. Formulated by French chemist François-Marie Raoult in the late 19th century, this law describes the relationship between the vapor pressure of components in a mixture and their mole fractions in the liquid phase. According to Raoult's law, for an ideal solution, the partial vapor pressure of each component equals the vapor pressure of the pure component multiplied by its mole fraction in the liquid mixture. Mathematically, this relationship is expressed as:

$P_i = P_i° \times x_i$ Where:

- P_i represents the partial vapor pressure of component i in the mixture
- $P_i°$ is the vapor pressure of pure component i at the same temperature
- x_i denotes the mole fraction of component i in the liquid phase

For a binary mixture of components A and B, the total vapor pressure follows the additive relationship:

$P_{total} = P_A + P_B = P_A° \times x_A + P_B° \times x_B$

According to the thermodynamic definition of an ideal solution, the chemical potential of each component is a linear function of the logarithm of its mole fraction, givingrise to Raoult's law. This relationship is true where all molecules within the solution experience identical intermolecular forces regardless of whether they are like or unlike molecules. Raoult's law can predict various colligative properties of solutions. By extending to all composition of a binary mixture, it made the vapor-liquid equilibrium diagrams on temperature function of liquid and vapor composition. Such plots (conventionally known as Pxy diagrams) are of paramount importance in designing separation processes like distillation. There are several experimental

approaches to such validation of Raoult‘s law for a liquid mixture. This most direct approach requires measuring the vapor pressure of the mixture at different compositions and comparing it with calculated values. How these deviations from Raoult’s law allow determining the molecular nature and strength of interaction in the mixture is a subject of various works.

However, we can say that in practice, Raoult’s law announced above is indeed a simplification of what actually happens in a solution, and it provides incredibly good approximations for a mixture of components that have similar chemistryand similar sizes. Ethanol and propanol, and benzene and toluene are examples of adjacent members of a homologous series from which mixtures often behave as practically ideal mixtures specifically obeying Raoult’s law. Ideal mixture models like Raoult’s law are generally just the beginning for a more sophisticated physical model due to non-ideality. The extent to which a real solution differs from Raoult’s law is informative about the molecular interactions within and the structure of the mixture.

10.4 Deviations from Raoult’s Law:

Although Raoult’s law is a very good approximation for ideal liquid mixtures, most real systems show some degree of non-ideality. Such deviations occur only because the intermolecular forces between unlike molecules are different from the intermolecular forces between like molecules. Positive deviations are a result of the intermolecular attractions between the unlike molecules (A-B interactions) being weaker than the intermolecular attractions present between the like molecules (A- A and B-B interactions). In these situations, molecules leave for the vapor phase more easily than suggested by Raoult’s law, thus increasing vapor pressures. Typical examples are mixtures of polar and a non-polar the aromatic compounds such as ethanol–benzene in which the hydrogen bonding of ethanol network is broken by the insertion of benzene molecules. Negative deviations arise when unlike molecules attract each other more strongly than like ones. These more substantial A-B interactions make it less likely that molecules will enter the vapor phase, giving them lower vapor pressures than predicted by Raoult’s law. For example, chloroform and acetone is a common example, as the strong hydrogen bonds form between the hydrogen of chloroform and oxygen of acetone creating stronger intermolecular attractions.

Typically, the width of these deviations is related to the enthalpyof mixing. Positive deviations are usually associated with endothermic mixing processes (ÄH_mix > 0), and negative deviations are more often associated with

exothermic mixing (ÄH_mix < 0). Positive deviations can be huge and lead to phase separation, exhibiting partial miscibility or complete immiscibilityof liquids.

To quantify these deviations, chemists use activity coefficients (ã)=, which adjust Raoult's law to account for non-ideal behavior.:

ã_i is defined as the activity coefficient of component i, which indicates deviation from ideal behavior. For perfect solutions ã_i = 1; values > 1 denote positive and values < 1 negative deviations.

Thermodynamic models, includingthe Margules equations, Wilson model, NRTL(Non- Random Two-Liquid) model, and UNIQUAC (Universal Quasi-Chemical) equation, are thus developed to evaluate activity coefficients as a function of the molecular characteristics and interaction parameters of components. Such models are integral to most aspects of the design and optimization of industry separation processes.

Understanding deviations from Raoult's law has useful applications across many domains, such as pharmaceutical formulation, petrochemical processing, and modeling the environmental fate of chemicals. These deviations in their nature and magnitude provide the basis for molecular guiding principles that aids in the design of superior mixing, separation, and purification strategies.

10.5 Henry's Law and Its Applications

Henry's law, formulated by English chemist William Henry in 1803, describes the solubility of gases in liquids. While Raoult's law typically applies to the more concentrated component in a mixture, Henry's law governs the behavior of dilute components, particularly gases dissolved in liquids. According to Henry's law, at a constant temperature, the amount of a gas dissolved in a liquid is directly proportional to the partial pressure of that gas in equilibrium with the liquid. Mathematically, this relationship is expressed as:

P_i = k_H × x_i Where:

- P_i is the partial pressure of the gas above the solution
- x_i represents the mole fraction of the gas in the liquid phase
- k_H denotes the Henry's law constant, which is specific to the gas-solvent pair and temperature

For an ideal gas, the chemical potential relates to partial pressure through the logarithmic relationship:

ì_gas = ì_gas° + RT ln(P/P°)

In the liquid phase, for sufficiently dilute solutions, the chemical potential of the solute varies logarithmicallywith its mole fraction:

ì_solute = ì_solute° + RT ln(x). At equilibrium, these chemical potentials must be equal, leading to the relationship: ln(P/P°) = ln(x) + constant

This exponential form transforms into the linear relationship described by Henry's law when considering infinitely dilute solutions, where the constant term incorporates the Henry's law constant.

The theoretical basis of Henry's law connects to the fundamental principles of statistical thermodynamics. The linear relationship between concentration and pressure at infinite dilution reflects the statistical independence of solute molecules in the solution, where each molecule behaves independently without significant interaction with other solute molecules.

Modified Forms of Henry's Law

In practice, various modified forms of Henry's law are used depending on the application and the concentration units preferred. These include concentration-based forms (using molarity instead of mole fraction), mass-based forms (using mass fraction or parts per million), and dimensionless forms (using ratios of concentrations in different phases).

The concentration-based form expresses Henry's law as:

P_i = K_H × C_i

Where C_i represents the molar concentration of the solute in solution and K_H has units of pressure divided by concentration.

The dimensionless form, particularly useful in environmental applications, defines Henry's law in terms of the ratio of gas concentration in air to its concentration in water:

K_H' = C_air / C_water

This dimensionless constant facilitates the calculation of equilibrium partitioning of chemicals between environmental compartments and proves especially valuable in fate modeling of pollutants.

10.6 Limitations of Henry's Law:

Henry's law gives a unique relation between the molecules in the gas and the molecules in solution, and it is an incredibly useful discussion of gas-liquid equilibria, but there are several important caveats. The first limitation is that it onlyapplies to dilute solutions where solute-solute interactions can be ignored. At greater concentrations, these interactions lead to larger deviations. Second,

the law assumes that the gas and solution phases behave ideally. In non-ideal gas systems the behavior is described using the Real (non-ideal) equation of states which accounts for the deviation of gases from ideal behavior at high pressure and real (non-ideal) solutions can have positive or negative heat of dilutions (real solution behavior). Corrections are required then for the deviations from ideality via fugacityfor gas-phase systems and activity coefficients for solution-phase systems.

Third, the law presupposes that gas solubilization is purely physical, not chemically reacting with the solvent. In cases where an equilibrium between reactants and products establishes, like with dissolved carbon dioxide in water that forms carbonic acid, more complex relationships apply.

Lastly, Henry's law constants are highly dependent on temperature, usually following the van 't Hoff relation:

d(ln k_H)/d(1/T) = ÄH_soln/R

Where ÄH_soln represents the enthalpy of solution. This relationship allows the calculation of k_H at different temperatures when the enthalpy of solution is known.

Practical Applications of Henry's Law The principles of Henry's law find application in numerous practical scenarios beyond those alreadymentioned. In analytical chemistry, techniques such as headspace analysis rely on Henry's law used to calculate the concentration of volatile compounds in liquid samples based on vapor concentration above the solution. Henry's law involves Gas solubility in the crude oil which helps leading gas showing a gas solubility structure in crude oil which guides in the designing of different separation processes in petroleum industryand modelingof released gas from crude oil or other hydrocarbons. In reservoir engineering, the law is a major factor in determining the behavior of gases dissolved in formation fluids.

Groundwater environmental remediation technologies like air stripping of volatile organic compounds, which utilizes these principles of Henry's law. The effectiveness of these processes is governed by the Henry's law constants of the target contaminants. In carbonated beverages, carbonation processes depend on Henry's law to model and control the levels of CO2 in products. The signature "fizz" of carbonated drinks comes from dissolved carbon dioxide escaping as pressure is reduced by opening the container. Henry's law behaviors are also observed in biological systems. This is because the transport of respiratory gases in blood obeys modified versions of Henry's law, which describe gas

dissolution in solution, and the oxygen-binding characteristics of hemoglobin adds layers of complexity to the simple dissolution process.

Solution thermodynamics — which uses Michel ratio / solvent / solute ratio equations

— is defined by the concepts of ideal mixtures such as Raoult's law and Henry's law, the foundation of their association by liquid-liquid and vapor-liquid systems. Although these principles describe idealized conditions, theyserve as helpful benchmarks against which actual mixture behaviors can be evaluated and quantified. However, the vapor- liquid equilibrium behavior of ideal solutions is described by Raoult's law over the entire composition range (especially those of the major component of the mixture). Henry's law goes hand in hand here, describing the behavior of dilute fractions, most notably the dissolved gases. Collectively, these laws facilitate the prediction of key mixture properties and provide guidance to the design of many industrial processes, environmental models, and scientific studies. Knowing when these laws follow, and when real systems vary from them, gives an essential knowledge of molecular connection and blending conduct. Ridley's second sense of emergence leads naturally to practical applications across disciplines as diverse as chemical engineering, environmental science, pharmaceuticals, geology and medicine. Whether it is how bubbles of gas form in carbonated drinks, or how we design and optimize distillation columns; whether it is about modeling chemical reactions in the environment, or designing a medical gas delivery system, the interrelationship between the various variables governing the behavior of liquid mixtures are the concepts provided by these laws, which continue to be the foundation upon which any theoretical understanding and innovation are built.

Nernst Distribution Law, Limitations and Applications

The Nernst distribution law (also called the partition law or distribution law) states that the ratio of the concentrations of a solute in two immiscible solvents (when the solvent is in contact with the two immiscible phases) is constant as long as the temperature is constant. This law, proposed by German chemist Walter Nernst in the late nineteenth century, serves as a cornerstone for many relevant chemical separation techniques. If two immiscible liquids contain the solute, which is distributed between both phases until equilibrium arouses. The concentrations of the solute in the two phases will achieve a constant ratio at a

given temperature and regardless of the total amount of solute at equilibrium. This constant ratio is termed the partition coefficient or distribution coefficient.
Mathematically, Nernst distribution law can be expressed as: K = C /C,
Where:

- K is the partition coefficient
- C is the concentration of the solute in the first solvent
- C, is the concentration of the solute in the second solvent

The partition coefficient K is a constant determining characteristic for the specific solute and the specific pair of solvents for specific temperatures. It measures the relative solubility of the solute in both solvents. Above a value of K more solute will go to solvent 1 than to solvent 2. It is worth noting that this law is only strictly applicable if the molecular identity of the solute is identical between the two solvents. Changes in dissolved species due to association or dissociation of the solute in either solvent violate the simple form of the law, which must, therefore, be corrected for molecular changes.
The Nernst distribution law has much importance in physical chemistry and is implemented in various ways such as:
The distribution law has a thermodynamic origin that gives it its physical significance. At equilibrium the chemical potential of the solute must be equal between the two phases. It is this equality of chemical potential that results in the constant ratios of concentrations.
From the molecular viewpoint, once a solute is added to a two-phase system, the molecules exchange between the phases indefinitely.At equilibrium, molecules leaving the phase at a rate vr equals molecules entering the phase from the other phase at a rate vl. And this dynamic equilibrium leads to constant concentration ratio.
The value of the distribution coefficient depends on several factors:

1. The nature of the solute and solvents
2. Temperature
3. Pressure (though pressure effects are typically small for liquid systems)
4. The presence of other solutes that might affect solubility

While we won't delve into the mathematical derivation, it's worth noting that the Nernst distribution law can be derived from fundamental thermodynamic principles. At equilibrium, the chemical potential of the solute must be the same

in both phases. This equalityof chemical potentials leads directly to the constant ratio of concentrations expressed in the distribution law.

Limitations of Nernst Distribution Law

Despite its wide applicability, Nernst distribution law has several limitations that restrict its use in certain systems:

1. Association of the Solute: If the solute molecules associate to form dimers, trimers, or higher aggregates in one of the solvents, the simple form of the law breaks down. For example, benzoic acid tends to dimerize in non-polar solvents like benzene due to hydrogen bonding between carboxyl groups, while it remains predominantly monomeric in water.

When association occurs, the effective concentration in that phase is reduced, altering the expected distribution ratio. If a solute with normal formula S exists as S, in phase 2, then the modified distribution law becomes:

K’ = C /”C, where C, refers to the total concentration of the solute expressed as monomers.

2. Dissociation of the Solute: If the solute undergoes dissociation (ionization) in one of the phases, the simple distribution coefficient no longer applies. For example, a weak acid like acetic acid may remain largely un-ionized in an organic solvent but partially dissociate in water.

For a weak acid HA that dissociates in phase 2 to form Hz and A{ , the modified distribution law becomes:

K’ = C /(C, + Cf)

where C, is the concentration of un-ionized solute and Cf is the concentration of ionized solute in phase 2.

3. Chemical Reactions: If the solute undergoes a chemical reaction with either solvent, the simple distribution law cannot be applied. The concentrations would need to account for both the original solute and its reaction products.

4. Concentration Dependence: The law assumes that the partition coefficient is independent of concentration. However, at high concentrations, deviations

can occur due to non-ideal behavior, molecular interactions, and changes in the properties of the solutions.

5. Temperature Effects: The partition coefficient is temperature-dependent. Changes in temperature can affect the solubility of the solute in both phases differently, leading to variations in the value of K. The distribution law does not explicitly account for these temperature effects.

6. Influence of Additional Solutes: The presence of other solutes can affect the distribution coefficient byaltering the solvent properties or through specific interactions with the solute of interest.

7. Non-Ideal Solutions: The law assumes ideal behavior of the solute in both phases. In real systems, especially at higher concentrations, deviations from ideality can lead to variations in the distribution coefficient.

8. Limited to Dilute Solutions: Nernst distribution law is strictly valid only for dilute solutions where the activity coefficient approaches unity. At higher concentrations, activity coefficients must be considered instead of simple concentrations.

Check your Progress

1. What factors determine whether two liquids are miscible or immiscible?

…….
……

2. How does temperature affect the mutual solubility of liquids in a mixture?

…….
……..

10.7 Summary : Liquid–liquid mixtures are combinations of two or more liquids that may be miscible or immiscible. Miscible liquids (e.g., ethanol and water) mix completely in all proportions due to strong intermolecular interactions. Immiscible liquids (e.g., oil and water) separate into layers because of weak interactions between them. Partially miscible liquids (e.g., phenol and water) mix only up to a certain limit and show critical solution temperature. Such mixtures are important in separations, solvent extraction, and chemical processes.

10.8 Exericise Question

Multiple Choice Questions (MCQs)

1. When two liquids mix in all proportions, they are called:
   a) Immiscible liquids
   b) Partially miscible liquids
   c) Completely miscible liquids
   d) Colloids
   Answer: c) Completely miscible liquids
2. The phenomenon of separation of a homogeneous mixture into two layers on heating is called:
   a) Distillation
   b) Miscibility
   c) Critical solution temperature
   d) Extraction
   Answer: c) Critical solution temperature
3. Which of the following pairs is **partially miscible**?
   a) Ethanol and water
   b) Phenol and water
   c) Benzene and toluene
   d) Acetone and water
   Answer: b) Phenol and water
4. The **upper critical solution temperature (UCST)** for the phenol-water system is approximately:
   a) 33°C
   b) 66°C
   c) 150°C
   d) 374°C
   Answer: b) 66°C
5. The temperature above which two partially miscible liquids become completely miscible is called:
   a) Freezing point
   b) Boiling point
   c) Critical solution temperature
   d) Eutectic temperature
   Answer: c) Critical solution temperature

Short Questions

1. Define liquid–liquid mixture and give examples.
2. What are completely miscible and partially miscible liquids?
3. Explain the term critical solution temperature (CST).
4. What is the difference between upper and lower CST?
5. Give one example each of systems showing UCST and LCST.
6. What happens when phenol–water mixture is heated above its CST?
7. How does the addition of impurities affect CST?
8. Write two applications of liquid–liquid mixtures in industry.
9. What is the conjugate solution curve?
10. Explain why phenol and water are partially miscible.

Long Questions

1. Explain in detail the types of liquid–liquid mixtures with examples.
2. Discuss the concept of critical solution temperature and describe upper and lower CST with suitable diagrams.
3. Describe the phenol–water system and explain how temperature affects their miscibility.
4. Explain trimethylamine–water and nicotine–water systems showing both UCST and LCST behavior.
5. Discuss the thermodynamic principles governing miscibility of liquids.

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Unit -11Applications of Nernst Distribution Law

Structure

11.1 Introduction

The Nernst Distribution Law, also known as the Partition Law, is an important principle in physical chemistry that explains how a solute distributes itself between two immiscible solvents at equilibrium. It was proposed by Walther Nernst and states that when a solute dissolves in two immiscible liquids that are in contact with each other, the ratio of its concentrations in the two phases remains constant at a given temperature, provided the solute exists in the same molecular form in both solvents. This law forms the theoretical basis for solvent extraction, purification, and separation techniques used in analytical and industrial chemistry. It also helps in understanding various phenomena such as drug distribution in biological systems and the determination of equilibrium constants in heterogeneous systems.

11.2 Objective-

1. To understand the principle of distribution of a solute between two immiscible solvents and the factors affecting the distribution constant.
2. To apply the Nernst Distribution Law in practical processes such as solvent extraction, purification, and quantitative analysis of compounds.

11.3 Applications -

Nernst distribution law finds extensive applications in various fields of chemistry and related sciences:

1. Solvent Extraction One of the most important applications is in solvent extraction, a technique widely used for the separation and purification

of compounds. The process involves transferring a solute from one liquid phase to another based on differences in solubility.

In industrial chemistry, solvent extraction is employed for:

- Purification of pharmaceutical compounds
- Recovery of metals from aqueous solutions
- Separation of aromatics from petroleum fractions
- Extraction of essential oils from plant materials
- Purification of antibiotics

The efficiency of an extraction process can be calculated using the distribution coefficient. Multiple extractions with smaller volumes of solvent are often more efficient than a single extraction with a larger volume, as predicted by the distribution law.

2.Analytical Chemistry: In analytical chemistry, liquid-liquid extraction based on Nernst distribution law is used for:

- Preconcentration of analytes
- Matrix simplification
- Interference removal
- Sample preparation prior to chromatographic or spectroscopic analysis

The distribution law helps in optimizing extraction conditions and predicting extraction efficiencies.

3.Pharmaceutical Industry

The pharmaceutical industryextensively uses the principles of Nernst distribution law for:

- Drug purification
- Determination of lipophilicity of drug molecules
- Predicting drug absorption and distribution in the body
- Development of sustained-release formulations

The partition coefficient between anol and water (log P) is a critical parameter in drug development, indicating a drug's ability to cross biological membranes.

4.Environmental Chemistry: In environmental science, distribution law helps in understanding:

- Fate and transport of pollutants in environmental compartments
- Bioaccumulation of contaminants in aquatic organisms
- Soil-water partitioning of pesticides and other contaminants
- Design of remediation strategies for contaminated sites

4. The theoretical foundation of various chromatographic techniques lies in Nernst distribution law. In chromatography, the stationary and mobile phases represent the two immiscible phases between which solutes distribute themselves. The retention behavior of compounds in chromatographic columns can be explained based on their distribution coefficients. Types of chromatography based on distribution principles include:

- Liquid-liquid chromatography
- Gas-liquid chromatography
- High-performance liquid chromatography (HPLC)
- Thin-layer chromatography (TLC)

6.Study of Association and Dissociation Phenomena

The deviations from the simple form of Nernst distribution law provide valuable information about molecular association and dissociation processes. By studying how the apparent distribution coefficient varies with concentration, researchers can determine: Association constants for dimerization or higher-order aggregation

- Dissociation constants for weak acids and bases
- Self-association behavior of amphiphilic molecules

7. Hydrometallurgy

In hydrometallurgy, solvent extraction based on distribution principles is used for:

- Selective recovery of valuable metals from leach solutions
- Purification of metal concentrates
- Separation of rare earth elements
- Recovery of uranium and other nuclear materials

8. Food Industry The food industryapplies distribution principles for:

- Extraction of flavors and colorants
- Removal of caffeine from coffee (decaffeination)
- Purification of food additives
- Oil refining processes

9. **Biological Systems and Pharmacokinetics**

The distribution of drugs and xenobiotics between different bodycompartments follows principles similar to Nernst distribution law. Pharmacokinetic parameters such as:

- Blood-brain barrier penetration
- Placental transfer
- Milk-plasma ratio
- Tissue distribution

can be related to the partition coefficients of compounds between aqueous and lipid phases.

Case Studies Showing Application of Nernst Distribution Law Case Study 1: Association - Benzoic Acid in Benzene and Water

Benzoic acid provides a classic example of how association affects distribution behavior. When distributed between benzene and water, benzoic acid exists Predominantlyas monomers in water but dimerizes in benzene due to hydrogen bonding between carboxyl groups. If C represents the concentration in benzene and C, the concentration in water, the simple Nernst distribution law would predict a constant ratio C /C, . However, experimental measurements show that this ratio varies with concentration.

The modified distribution coefficient accounting for dimerization is: K’ = C /”C,

where C represents the total concentration in benzene (expressed as monomers) and C, is the concentration in water.

This modification results in a more constant value of K’ across different concentrations, confirming the dimerization of benzoic acid in benzene.

Case Study 2: Dissociation - Distribution of Weak Acids

Consider a weak acid HA distributing between an organic solvent (like chloroform) and water. In the organic phase, the acid remains un-ionized, while in the aqueous phase, it partially dissociates according to:

HA Ì! Hz + A{

If we denote the concentration in the organic phase as C and the total analytical concentration in the aqueous phase as C, , the simple distribution law would predict C /C, to be constant. However, because of dissociation in the aqueous phase, this ratio varies with pH.

The total concentration in the aqueous phase is the sum of the un-ionized acid [HA] and the ionized form [A{]:

C, = [HA] + [A{]

The true distribution coefficient applies only to the un-ionized form: K = C /[HA]

From the dissociation equilibrium, we can calculate [HA] in terms of C, , pH, and the acid dissociation constant .

This leads to the pH-dependent apparent distribution coefficient: K' = C /C, = K/(1 + Ka/[Hz])

This equation explains why the extraction efficiency of weak acids from aqueous solutions increases at lower pH values, where dissociation is suppressed.

Case Study 3: Industrial Application - Copper ExtractionIn hydrometallurgy, copper is often extracted from acidic leach solutions using organic extractants like LIX reagents (chelating agents) dissolved in kerosene. The extraction equilibrium can be represented as:

Cu²z (aq) + 2HR(org) Ì! CuR, (org) + 2Hz (aq)

where HR represents the extractant and CuR, is the copper-extractant complex. The distribution of copper between the aqueous and organic phases depends on:

- pH of the aqueous phase
- Concentration of the extractant
- Presence of other metal ions
- Temperature

By controlling these parameters, especially pH, selective extraction of copper can be achieved. The loaded organic phase is then stripped using strong acid to recover copper in a concentrated form.

This process clearly illustrates how the principles of Nernst distribution law, modified to account for chemical reactions, guide industrial separation processes.

11.4 Modern Extensions and Modifications of Nernst Distribution Law-

While the classical form of Nernst distribution law provides a solid foundation, modern approaches have extended and refined it to address its limitations:

1. Activity-Based Formulations: Instead of using concentrations, modern formulations often use activities to account for non-ideal behavior in

concentrated solutions:K = a /a,where a and a, are the activities of the solute in phases 1 and 2, respectively.

2. Temperature-Dependent Models: The van't Hoff equation relates the temperature dependence of the distribution coefficient to the enthalpy change associated with the transfer of solute between phases:

d(ln K)/d(1/T) = -ÄH°/Rwhere T is the absolute temperature, ÄH° is the standard enthalpy change, and R is the gas constant.

3. Computational Approaches: Modern computational chemistry methods, such as molecular dynamics simulations and quantum mechanical calculations, can predict partition coefficients based on molecular structures and solvent properties.

4. QSAR Models: Quantitative Structure-Activity Relationship (QSAR) models correlate distribution coefficients with molecular descriptors, allowing for the prediction of partition behavior for new compounds.

5. Multicomponent Systems: Extensions of the basic law have been developed to handle systems with multiple solutes that may interact with each other.

11.5 Experimental Determination of Distribution Coefficients

Several methods are employed to experimentally determine distribution coefficients:

1. Shake-Flask Method: The traditional approach involves equilibrating the solute between two phases in a separatory funnel, separating the phases, and analyzing the concentration in each phase using appropriate analytical techniques.

2. Slow-Stirring Method: This method minimizes the formation of emulsions and is particularly useful for highly hydrophobic compounds.

3. HPLC-Based Methods: High-performance liquid chromatography can be used to rapidly determine partition coefficients between an aqueous buffer and a stationary phase that mimics a specific solvent.

4. Potentiometric Methods: These methods are useful for ionizable compounds and provide information about both the partition coefficient and dissociation constants.

5. Filter-Probe Methods: These automated systems allow for rapid determination of partition coefficients for multiple compounds.

The Nernst distribution law describes thepartitioning of a solutebetween two immiscible phases and is a fundamental principle in physical chemistry.Although the law does not applydirectlyto systems containing data involving association, dissociation, or chemical reaction, it still offers an approximate theoretical background for many separation
processes and analytical methods. This law is widely applicable in many areas — pharmaceutical research, environmental science, industrial separations and analytical chemistry, to name but a few — and is often used to predict the partitioning of a test
compound between two phases based on its molecular structure. The distribution behavior of compounds between aqueous and non-aqueous phases is vital for the design of extraction processes, understanding environmental fate, drug delivery, and the development of analytical methods.

Multiproduct extensions, extensions to non-convex productions, imperfect batches, besides many modifications of the classical formulation soon removed most of the restrictions, making the distribution law also applicable to these types of systems but leaving the original more natural for non-multiproduct systems. With the continued development of analytical techniques and increasingly sophisticated computational approaches, the predictive power and utility of distribution-based phenomena will eventually lead to increased efficiency and selectivity of separation processes. Cases of association and dissociation, although they describe exceptions to the simple form of the law, are very informative from the point of view of molecular behavior and interaction in several solvent media. Byproperlymodifyingthe fundamental relationship to account for these phenomena, the distribution law becomes useful even in complex systems. As we move towards a more sustainable future, the Nernst distribution law remains a testament to the importance of efficient separation and purification techniques in resource recovery and environmental remediation.

Check your Progress

1. How does the Nernst Distribution Law help in the extraction and separation of organic compounds?

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2. What factors can cause deviations from the Nernst Distribution Law in practical applications?

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11.6 Summary

The Nernst Distribution Law explains how a solute distributes itself between two immiscible solvents at equilibrium. It is widely used to determine partition coefficients and study solute-solvent interactions. The law forms the basis of solvent extraction techniques used in separation and purification processes. It also helps in understanding drug distribution between aqueous and lipid phases in biological systems.

11.7 Exercise Question

Multiple Choice Questions (MCQs)

1. Which of the following is a photochemical reaction?

a) Oxidation of ammonia
b) Photosynthesis
c) Rusting of iron
d) Burning of methane

2. The Jablonski diagram explains:

a) Molecular motion
b) Thermal energy transfer
c) Excited state processes
d) None of the above

3. The quantum yield of a reaction is defined as:

a) Number of molecules decomposed per photon absorbed
b) Total energy of photons absorbed
c) Total energy emitted
d) None of the above

4. The laws of photochemistry were given by:

a) Einstein

b) Grotthus-Draper
c) Kirchhoff
d) Le Chatelier

5. Photosensitization refers to:

a) Absorption of light by a molecule
b) Energy transfer from one molecule to another
c) Heat energy conversion
d) None of the above

6. Raoult's law is applicable to:

a) Gaseous mixtures
b) Non-ideal solutions
c) Ideal solutions
d) None of the above

7. Henry's law states that:

a) The solubility of a gas is inversely proportional to pressure
b) The solubility of a gas is directly proportional to pressure
c) The solubility of a gas is independent of pressure
d) None of the above

8. Nernst distribution law applies to:

a) Gas-liquid systems
b) Solid-liquid mixtures
c) Two immiscible liquids
d) None of the above

9. The main limitation of Henry's law is:

a) It applies only to ideal gases
b) It is independent of temperature
c) It applies only to ionic substances
d) It is not affected by pressure

10. Photochemical decomposition of HI occurs by:

a) Thermal activation
b) Absorption of UV light
c)Reaction with water
d)None of the above

Short Answer Questions

1. Differentiate between photochemical and thermal reactions.

2. Explain the significance of the Jablonski diagram.

3. What is quantum yield? How is it determined?

4. Write the laws of photochemistry with examples.

5. Explain the concept of photosensitization and its applications.

6. State and explain Raoult's law.

7. Describe Henry's law and give its applications.

8. What are ideal and non-ideal solutions? Give examples.

9. Explain the Nernst distribution law and its limitations.

10. How does Raoult's law explain vapor pressure in liquid mixtures?

Long Answer Questions

1. Describe the interaction of radiation with matter and its consequences.

2. Explain the laws governing photochemical reactions with examples.

3. Discuss the Jablonski diagram and various photophysical processes.

4. What are the factors affecting quantum yield? Explain with examples.

5. Explain photochemical reactions with at least three examples.

6. Discuss the principles and applications of photosensitization and quenching.

7. Derive Raoult's law and explain its significance in ideal solutions.

8. Discuss the applications and limitations of Henry's law.

9. Derive the Nernst distribution law and explain its significance.

10. Compare and contrast ideal and non-ideal solutions based on Raoult's law.

11.7 References and suggestive readings

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GLOSSARY

1.Alkyl Halides: Organic compounds containing a halogen atom (F, Cl, Br, attached to an sp^3 hybridized carbon atom.

2. Aryl Halides: Compounds in which a halogen atom is directly bonded to an aromatic ring, such as chlorobenzene.

3. Nucleophilic Substitution: A reaction where a nucleophile replaces a leaving group (like a halide) on a carbon atom.

4. Elimination Reaction: A reaction in which two atoms or groups are removed from a molecule, forming a double bond.

5. Alcohols: Organic compounds containing a hydroxyl (–OH) group attached to a carbon atom; classified as primary, secondary, or tertiary.

6. Oxidation of Alcohols: Conversion of alcohols into aldehydes, ketones, or carboxylic acids depending on the oxidation conditions.

7. Aldehydes: Organic compounds with the functional group –CHO, where the carbonyl carbon is bonded to at least one hydrogen atom.

8. Ketones: Organic compounds containing a carbonyl group (C=O) bonded to two alkyl or aryl groups.

9. Nucleophilic Addition Reaction: A reaction in which a nucleophile adds to the electrophilic carbon of a carbonyl group.

10. Carboxylic Acids: Compounds containing the carboxyl (–COOH) group; known for their acidity and hydrogen bonding.

11. Acid Derivatives: Compounds derived from carboxylic acids such as esters, amides, anhydrides, and acid chlorides.

12. Esterification: Reaction between a carboxylic acid and an alcohol forming an ester and water.

13. Amide: A compound formed when a carboxylic acid reacts with ammonia or an amine, replacing the –OH with $–NH_2$.

14. Chemical Equilibrium: The dynamic state in a reversible reaction where the rates of forward and reverse reactions are equal.

15. Le Chatelier's Principle: States that if a system at equilibrium is disturbed, it shifts in a direction that minimizes the disturbance.

16. Equilibrium Constant (K): A numerical value expressing the ratio of concentrations of products to reactants at equilibrium.

17. Dynamic Equilibrium: A condition where reactions continue to occur, but there is no net change in concentration of reactants and products.

18. Reversible Reaction: A chemical reaction that can proceed in both forward and backward directions.

19. Miscibility: The ability of two liquids to mix in all proportions without separating into layers.

20. Partition Coefficient: The ratio of concentrations of a solute distributed between two immiscible solvents at equilibrium.

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