Bachelor of Science
(B.Sc.- PCM)

Chemical Energetics Equilibria & Functional Group Organic Chemistry-I
(DBSPCO201T24)

Self-Learning Material
(SEM II)

Jaipur National University
Centre for Distance and Online Education
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Jaipur National University

Course Code: DBSPCO201T24
Chemical Energetics, Equilibria &
Functional Group Organic Chemistry-I

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COURSE INTRODUCTION

This course explores the fundamentals of Chemical Energetics, focusing on the energy transformations during chemical reactions. The course is divided into 13 units and each unit is further divided into sub topics. It covers the First Law of Thermodynamics, which asserts that energy cannot be created or destroyed, only transformed. Students will learn to apply this principle to calculate energy changes in reactions, understand exothermic and endothermic processes, and analyze real-world applications such as industrial synthesis. The Second Law of Thermodynamics will be examined to understand entropy and spontaneity in reactions, with practical examples illustrating how energy dispersal drives chemical processes.

Chemical Equilibrium will delve into the state of dynamic balance in chemical reactions, where the rates of the forward and reverse reactions are equal.

Ionic Equilibrium I focuses on acid-base equilibria, covering the dissociation constants of acids and bases (Ka and Kb), and their implications for pH and buffer solutions. Ionic Equilibrium II will address solubility equilibria, exploring the solubility product constant (Ksp) and its application in predicting precipitate formation and solubility trends.

The course covers Benzene as a prototypical aromatic hydrocarbon, with an emphasis on its resonance structure and stability. Students will explore benzene's unique bonding characteristics, applications in synthesizing a wide array of chemical products, and its role in organic chemistry. The study of benzene will provide insights into aromaticity and reactivity patterns important for advanced chemical synthesis.

Alkyl Halides and Aryl Halides will be examined, focusing on their structure, reactivity, and applications. The course covers Alcohols, Phenols, and Ethers, focusing on their structural properties, reactivity, and synthesis.

The final part of the course will cover Aldehydes and Ketones, detailing their chemical properties, reactivity, and applications.

This comprehensive course provides an in-depth understanding of key chemical principles and their applications, equipping students with the knowledge necessary for advanced studies and practical applications in chemistry.

We hope you enjoy the course.

Course Outcomes:

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

1. Utilize the First and Second Laws of Thermodynamics to analyze and solve energy-related problems in chemical reactions and predict spontaneity based on entropy changes.
2. Determine equilibrium constants and apply Le Chatelier's Principle to predict and manipulate equilibrium positions in chemical processes.
3. Solve problems related to acid-base and solubility equilibria, including pH calculations, buffer solutions, and precipitation reactions.
4. Describe the structure, reactivity, and applications of benzene and other aromatic hydrocarbons.
5. Utilize alkyl and aryl halides in various organic reactions and syntheses.
6. Recognize and apply the chemical properties of alcohols, phenols, ethers, aldehydes, and ketones in synthetic and industrial context.

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Chapter: 1

Chemical Energetics

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Objectives:

- Understand the different types of systems in chemical energetics.

- Differentiate between extensive and intensive properties.

- Grasp the significance of state functions and path functions in thermodynamics.

- Comprehend various thermodynamic processes and their characteristics.

- Appreciate the importance of the Zeroth Law of Thermodynamics

1.1 Introduction

Chemical energetics is the study of energy changes that occur during chemical reactions and processes. Understanding these changes is crucial for predicting reaction outcomes, designing industrial processes, and optimizing energy usage. This chapter delves into the fundamental concepts of chemical energetics, including types of systems, properties, thermodynamic processes, and the Zeroth Law of Thermodynamics.

1.2 Types of System in Chemical Energetics

In chemical energetics, systems play a crucial role in understanding the energy changes associated with chemical reactions and processes. Systems are defined by their interactions with their surroundings, which can vary in terms of the exchange of matter and energy. Let's delve deeper into the types of systems with illustrative examples:

1.2.1 Isolated System

A system which does not exchange energy or matter with its surroundings is known as isolated system. This is a closedoff entity with no interaction beyond its boundaries. Examples of isolated systems include:

- Insulated Thermos Flask: A thermos flask with perfectly insulated walls that prevent the transfer of heat energy.

- Sealed Reaction Vessel: A container sealed to prevent the exchange of matter or energy with the environment, commonly used in laboratory experiments.

1.2.2 Closed System

A system which allows the exchange of energy with its surroundings but does not allow the transfer of matter is known as '**closed system'**. Energy can flow across the boundary.The mass of the system stays constant.Such closed systems include:

- Piston cylinder apparatus with rigid walls: The walls of the cylinder are impermeable to matter, but energy can be exchanged through them in the form of heat or work.
- Refrigerator: While matter (food items) can enter and leave the refrigerator, the system (refrigerator compartment) is considered closed as it exchanges energy with the surroundings to maintain a low temperature.

1.2.3 Open System

A system which permits the exchange of both matter and energy with its surroundings is known as open system. These systems are more common in natural processes and industrial applications. Examples of open systems include:

- Living Organisms: Organisms exchange matter (food intake, waste expulsion) and energy (metabolic processes) with their environment.
- Chemical Reactors: Industrial reactors where reactants are continuously fed and products are continuously removed, allowing for the exchange of both matter and energy with the surroundings.

1.3 Extensive & Intensive Properties

The properties which depend on the amount of matter present are the '**Extensive properties**', such as mass and volume. **Intensive properties** remain constant regardless of the quantity of the substance, such as temperature and density.

State Function and Path Function

A property that depend only on the current state of the system not on how it reached that state is known as state function. Examples include internal energy, enthalpy, and entropy. In contrast, a path function depends on the path taken to reach a particular state, such as work and heat.

1.4 Thermodynamic ProcessA thermodynamic process describes the transformation of a thermodynamic system from one state to another. These processes are characterized by changes in the system's properties like temperature, pressure, volume and energy.

Understanding thermodynamic processes is essential in various fields including engineering, chemistry, and physics. Let's delve into the details of some common thermodynamic processes:

1.4.1 Isothermal Process:

Definition: Process that occurs at a constant temperature is the isothermal process.

Characteristics: The internal energy change (ΔU) is zero since temperature remains constant. Heat energy input (Q) is balanced by work done (W) on the system.

Example: Expansion or compression of an ideal gas in a perfectly conducting cylinder at constant temperature.

1.4.2 Isobaric Process:

Definition: An isobaric process is one that occurs at a constant pressure.

Characteristics: The volume change (ΔV) is directly proportional to the temperature change (ΔT).Work done (W) is calculated as the product of pressure and volume change ($W = P\Delta V$).

Example: Heating water in an open container where the atmospheric pressure remains constant.

1.4.3 Isochoric Process:

Definition: Process that occurs at constant volume is known as isochoric process, which are also identified as an isovolumetric or isometric process.

Characteristics: No work is done as volume remains constant, ($W = 0$). All heat energy input (Q) results in an increase in internal energy (ΔU).

Example: Heating a closed container where the volume cannot change.

1.4.4 Adiabatic Process:

Definition: A process which occurs without the transfer of heat between the system and its surroundings ($Q = 0$) is called as adiabatic process.

Characteristics: Energy exchange occurs only in the form of work (W) done on or by the system.

Temperature changes significantly due to the absence of heat exchange.

Example: Rapid compression or expansion of a gas in a perfectly insulated container.

1.4.5 Reversible Process:

Definition: process that can be reversed without causing any change in the system or its surroundings is called as reversible process.

Characteristics: Occurs slowly, with infinitesimal changes at each step.

No entropy change for the system and surroundings combined ($\Delta S\_total = 0$).

Example: Slow expansion or compression of a gas where the pressure difference between the system and surroundings is infinitesimal.

1.4.6 Irreversible Process:

Definition: An irreversible process is one that cannot be reversed without affecting the system and its surroundings.

Characteristics: Occurs rapidly or spontaneously, leading to an increase in entropy

($\Delta S_{tot} > 0$).

Examples include sudden expansion, mixing of two substances or frictional processes.

1.5 The 'Zeroth Law' of Thermodynamics

In accordance with the '**Zeroth Law'**, two systems are considered to be in thermal equilibrium with each other if they are in thermal equilibrium with a third system. This law sets up the concept of temperature and allows for the construction of reliable thermometers. This Law plays a crucial role in ensuring accuracy, reliability and efficiency.

Imagine a world without the Zeroth Law: thermometers would be unreliable, temperature control systems would be erratic and scientific measurements would lack a fundamental reference point. It's truly remarkable how this seemingly straight forward principle enables us to navigate the complexities of thermal dynamics with confidence and precision.

Moreover, the Zeroth Law embodies a fundamental principle of nature: the tendency of systems to seek equilibrium. Whether it's the balance of heat between two objects or the harmony of temperatures within a complex system, the law reminds us of the underlying order and symmetry that govern the universe.

1.5.1 Applications:

1. **Temperature Control:**

    The Zeroth Law is fundamental for temperature control in various applications, including heating and cooling processes in HVAC systems, industrial processes, and environmental control systems.

2. **Thermal Analysis:**

   In scientific research and engineering, the Zeroth Law is used for thermal analysis, including the determination of thermal properties of materials and the characterization of thermal processes.

3. **Quality Control:**

   It is employed in quality control processes to ensure that systems and materials are maintained at desired temperatures and that temperature sensitive processes are performed accurately.

Summary

Chemical energetics explores energy changes in chemical systems. Systems can be categorized into isolated, closed, and open systems. Properties can be classified as extensive or intensive, depending on their dependency on the amount of substance. State functions are independent of the path taken, while path functions depend on the path. Various thermodynamic processes, such as isothermal and adiabatic processes, describe changes in system variables. Finally, the Zeroth Law establishes the concept of temperature and thermal equilibrium. Understanding these concepts forms the basis for further exploration in chemical energetics and thermodynamics.

Keywords:

- **Chemical Energetics:** The study of energy changes that occur during chemical reactions and processes.
- **Systems:** Portions of the universe under investigation, categorized as isolated, closed, or open based on their interaction with surroundings.
- **Extensive Properties:** These are depends on the quantity of substance present, such as Mass and Volume.
- **Intensive Properties:** That remains constant regardless of the quantity of substance, such as temperature and density.
- **Thermodynamic Processes:** Transformations of a thermodynamic system from one state to another, characterized by changes in temperature, pressure, volume, and energy.

- **Zeroth Law of Thermodynamics:** Two systems are in thermal equilibrium if both are in equilibrium with a third system

MCQs

1. The example of an extensive property?

A) Temperature   B) Volume   C) Density   D) Specific Heat

Answer: B

2. Which type of thermodynamic process occurs at constant pressure?

A) Isothermal   B) Isobaric   C) Isochoric   D) Adiabatic

Answer: B

3. Which law of thermodynamics establishes the conception of temperature?

A) First Law   B) Second Law   C) Third Law   D) Zeroth Law

Answer: D

4. **Which property is a state function in thermodynamics?**

A) Work   B) Heat   C) Enthalpy   D) Heat Capacity

Answer: C

5. **What type of system allows the exchange of together energy and matter with its surroundings?**

A) Isolated   B) Closed   C) Open   D) Insulated

Answer: C

Short Answer Questions:

1. Define and differentiate between extensive and intensive properties.
2. Explain the Zeroth Law of Thermodynamics and its significance in temperature measurement.
3. Describe the characteristics of an isothermal process and provide an example.
4. What is a state function in thermodynamics? Give an example.
5. Briefly discuss the types of systems in thermodynamics and provide an example of each

Chapter: 2
First Law of Thermodynamics

Objectives:

- Understand the First Law of Thermodynamics and its application in energy conservation.

- Explore the concept of enthalpy and its significance in thermodynamics.

- Analyze the relationship between specific heat capacities Cp and Cv.

- Comprehend the concept of work in the context of thermodynamics.

- Examine the Joule-Thomson effect and its implications on real-world processes.

2.1 Introduction

Thermodynamics, a cornerstone of physical chemistry, provides a profound understanding of energy and its transformations in chemical systems. At its core lies the First Law, a fundamental principle that governs the conservation of energy and forms the basis of chemical thermodynamics.

2.2 The First Law of Thermodynamics

The 'First Law of Thermodynamics' asserts that energy can neither be created nor destroyed; it can only change its forms. In the context of chemistry, this principle underpins all energy-related processes, from chemical reactions to phase transitions and beyond. Chemical reactions involve the conversion of reactants into products, accompanied by changes in energy. The First Law allows chemists to quantify these energy changes, distinguishing between exothermic reactions, which liberate energy to the surroundings, and endothermic reactions, which take up energy from the surroundings.

Law of Thermodynamics manifests in chemical processes:

1. **Combustion Reactions:** Combustion reactions, such as the burning of fuels like methane (CH_4) or propane (C_3H_8), exemplify the First Law in action. These reactions release heat energy (q) to the surroundings, manifesting as an increase in temperature. The energy released during combustion is a result of the conversion of chemical potential energy stored in fuel molecules.

2. **Endothermic Reactions:** Endothermic reactions, such as the dissolution of ammonium nitrate (NH_4NO_3) in water, absorb heat energy (q) from the surroundings. As a result, the surroundings experience a decrease in temperature. The energy

absorbed is utilized to break bonds in the reactant molecules, overcoming the intermolecular forces holding them together.

3. **Phase Transitions:** Phase transitions, such as the melting of ice $H_2O(s) \rightarrow H_2O(l)$, exemplify the First Law as well. During melting, heat energy (q) is absorbed by the solid ice to overcome the intermolecular forces, transitioning it into the liquid phase. Similarly, during freezing, heat energy is released to the surroundings as the liquid water solidifies into ice.

4. **Reaction Enthalpies:** The enthalpy change (ΔH) associated with chemical reactions provides a quantitative measure of the heat energy exchanged at constant pressure. For an exothermic reaction, ΔH is negative, indicating that heat is released to the surroundings. Conversely, for an endothermic reaction, ΔH is positive, indicating that heat is absorbed from the surroundings.

5. **Calorimetry:** Calorimetry experiments, where heat changes in chemical reactions are measured, rely on the principles of the First Law. By monitoring temperature changes in a calorimeter, the heat absorbed or released during a reaction can be determined, allowing for the calculation of reaction enthalpies (ΔH).

2.3 Enthalpy:

The entire energy of a thermodynamic system is expressed in terms of Enthalpy. It includes the energy needed to take pressure and volume variations into consideration in addition to internal energy. Changes in enthalpy (ΔH) provide insights into the heat absorbed or released during chemical reactions, facilitating their quantitative analysis.

2.3.1 Effects of Temperature on Enthalpy:

Temperature plays a pivotal role in determining the enthalpy of a substance. As temperature increases, the kinetic energy of molecules rises, leading to changes in their vibrational, rotational, and translational energies. Consequently, the enthalpy of the substance may increase or decrease, depending on the specific process and molecular interactions involved.

2.4 Cp−Cv Relation: Understanding Specific Heat Capacities

The specific heat capacities at constant pressure (Cp) and constant volume (Cv) are essential parameters in thermodynamics. The Cp−Cv relation describes the difference between these two specific heat capacities and provides valuable insights into a substance's thermodynamic behavior.

2.4.1 Theoretical Foundation of the Cp−Cv Relation:

The Cp−Cv relation stems from the principles of thermodynamics and statistical mechanics. It relates the changes in internal energy (ΔU) and enthalpy (ΔH) to changes in temperature (ΔT) at constant pressure and volume, respectively, providing a fundamental understanding of heat transfer mechanisms

2.4.2 Practical Implications of the Cp−Cv Relation:

The Cp−Cv relation finds wide-ranging applications in various fields, including chemistry, physics, and engineering. It aids in the calculation of thermodynamic properties, such as enthalpy changes and heat capacities, facilitating the design and optimization of processes and systems.

2.4.3 Experimental Determination of Cp and Cv:

Experimental techniques, such as calorimetry and differential scanning calorimetry (DSC), are commonly employed to measure specific heat capacities (Cp and Cv). These measurements provide valuable data for validating theoretical models and understanding the thermodynamic behavior of materials under different conditions.

2.4.4 Temperature Dependence of Cp and Cv:

The specific heat capacities (Cp and Cv) of substances often exhibit temperature dependence. This phenomenon arises due to changes in molecular vibrations, rotations, and electronic transitions with temperature. Understanding these temperature-dependent behaviors is crucial for accurately predicting heat transfer processes and designing thermal systems.

2.5 Work

Work, a fundamental concept in thermodynamics, represents the transfer of energy between systems through mechanical means. It plays a crucial role in various thermodynamic processes, including compression, expansion, and mixing.

2.5.1 Types of Work:

Thermodynamics recognizes several forms of work, each associated with specific processes and energy transformations. These include:

- Expansion Work: Work done by a system as it expands against an external pressure.

- Compression Work: Work done on a system as it is compressed against an external pressure.
- Shaft Work: Work done by or on a system through rotating machinery, such as turbines and compressors.
- Electrical Work: Work associated with the flow of electric current in electrical systems.

2.5.2 Mathematical Representation of Work:

In thermodynamics, work (W) is quantified using mathematical expressions tailored to the specific type of work being considered. For example:

- $W = -P \cdot \Delta V$ for expansion or compression work, where P is the pressure and ΔV is the change in volume.
- $W = \int_{V_1}^{V_2} P_{ext} \cdot dV$ for reversible processes, where P_{ext} is the external pressure and dV is an infinitesimal change in volume.

2.5.3 Work in Different Thermodynamic Processes:

Work manifests differently in various thermodynamic processes, depending on factors such as system constraints, pressure-volume relationships, and external conditions. For instance:

- Isothermal Processes: Work done during isothermal expansion or compression occurs at constant temperature.
- Adiabatic Processes: In adiabatic expansion or compression, no heat exchange occurs between the system and its surroundings, affecting the work done.

2.5.4 Significance of Work in Thermodynamics:

Work is integral to understanding and analyzing thermodynamic systems. It contributes to changes in internal energy, enthalpy, and overall system behavior. By quantifying work interactions, thermodynamics provides a comprehensive framework for studying energy transformations and optimizing system performance.

2.6 Introduction to the Joule-Thomson Effect:

The name of the 'Joule-Thomson effect' comes from James *Joule* and *William Thomson* (Lord Kelvin), illustrate the phenomenon of temperature change that occurs when a compressed gas is allowed to expand through a throttling valve or porous plug while being

insulated from its surroundings. The Joule-Thomson effect was first observed in the mid-19th century during experiments investigating the behavior of gases under pressure. James Joule and William Thomson independently discovered that certain gases exhibited unexpected temperature changes upon expansion, laying the groundwork for further study.

2.6.1 Mechanism and Explanation:

The Joule-Thomson effect arises due to the interplay between the attractive and repulsive forces between gas molecules. During expansion, the gas molecules experience a decrease in potential energy, leading to a corresponding decrease in kinetic energy and thus a decrease in temperature. Conversely, for certain gases, expansion may result in a temperature increase.

2.6.2 Factors Influencing the Joule-Thomson Coefficient:

The magnitude and direction of temperature change during the Joule-Thomson process are determined by several factors, including the nature of the gas, its initial temperature and pressure, and the Joule-Thomson coefficient (μ_{JT}).

2.6.3 Applications in Industrial Processes:

The Joule-Thomson effect finds widespread applications in various industrial processes, particularly in the liquefaction and refrigeration of gases. By carefully controlling the expansion of gases, engineers can achieve desired temperature changes, enabling the efficient production of liquefied gases for industrial and scientific purposes.

2.6.4 Limitations:

While the Joule-Thomson effect offers valuable insights and practical applications, it is not without limitations and challenges. For some gases, the temperature change may be minimal or negligible, limiting its applicability in certain scenarios. Additionally, the behavior of real gases may deviate from idealized models, posing challenges in predictive modeling and process design.

Summary

The First Law of Thermodynamics serves as the cornerstone principle in thermodynamics, asserting the conservation of energy. It asserts that energy can only be transformed from one form to another; it cannot be created or destroyed. Enthalpy, a key concept in thermodynamics, offers a convenient measure for studying energy changes in various

processes. Temperature plays a crucial role in thermodynamics, influencing the behavior of substances in different states. The specific heat capacities, Cp and Cv, describe the amount of heat energy required to change the temperature of a substance at constant pressure and volume, respectively. Work, in thermodynamic terms, represents the transfer of energy between systems through mechanical means. It can take various forms, including expansion work, compression work, and shaft work, each contributing to the overall energy balance of a system. The Joule-Thomson effect, named after James Joule and William Thomson (Lord Kelvin). This effect is particularly significant in refrigeration and liquefaction processes, where precise control over temperature changes is essential.

Keywords:

- **First Law of Thermodynamics:** Energy can change forms but cannot be created or destroyed.
- **Enthalpy:** Refers the total 'internal energy' of a system.
- **Specific Heat Capacities (Cp and Cv):** The quantity of heat energy required to raise the temperature by one degree Celsius of a unit mass at constant pressure and volume.
- **Work:** The transfer of energy from one system to another through mechanical means.
- **Joule-Thomson Effect:** The change in temperature of a gas when it expands without doing work and without heat exchange with the surroundings.

MCQs

1. First Law of Thermodynamics states?

   A) Energy can be created but not destroyed

   B) Energy can neither be created nor destroyed, only transformed

   C) Energy can be destroyed but not created

   D) Energy remains constant in an isolated system

   Answer: B

2. Enthalpy (ΔH) is a measure of:

   A) Internal energy only   B) Pressure only

   C) Volume only   D) Internal energy and pressure-volume work

   Answer: D

3. How does temperature affect the enthalpy of a substance?

A) Temperature has no effect on enthalpy   B) Higher temperature decreases enthalpy

C) Higher temperature increases enthalpy

D) Enthalpy is inversely proportional to temperature

Answer: C

4. The (Cp - Cv) relation in thermodynamics describes the difference between:

A) Specific heat capacity at constant pressure and constant volume

B) Internal energy and enthalpy   C) Heat and work   D) Enthalpy and entropy

Answer: A

5. Work in thermodynamics is defined as:

A) Energy transferred due to temperature difference

B) Energy transferred due to pressure difference

C) Energy transferred due to volume change

D) Energy transferred due to chemical reactions

Answer: C

Short Answer Questions:

1. Explain the First Law of Thermodynamics and its significance in energy conservation.

2. Define Enthalpy (H) and explain its role in thermodynamics.

3. How does temperature affect the behavior of substances in thermodynamic processes?

4. What is the (Cp - Cv) relation, and how does it relate to specific heat capacities?

5. Describe the concept of work in thermodynamics and provide examples of different
   types of work.

6. What is the Joule-Thomson effect, and how does it occur in gas expansion processes?

7. Discuss the practical applications of the Joule-Thomson effect in industrial processes.

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Chapter: 3

Second Law of Thermodynamics

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Objectives:

- Understand the Second Law of Thermodynamics and its implications for natural processes.
- Grasp the concept of entropy and its role as a measure of disorder in thermodynamic systems.
- Explore the significance of free energy in predicting the spontaneity and feasibility of chemical reactions and phase transitions.
- Identify the conditions under which a process occurs spontaneously based on changes in free energy, enthalpy, and entropy.
- Learn about the Gibbs-Helmholtz equation and its role in relating changes in Gibbs free energy to temperature variations

3.1 Introduction

In the realm of thermodynamics, the Second Law stands as a fundamental pillar governing the behavior of energy and matter. It encapsulates profound principles that shape our understanding of natural processes, from the simple to the complex. At its core lies the concept of entropy, a measure of disorder or randomness within a system. In this chapter, we delve into the Second Law, exploring its significance, implications, and key concepts such as entropy, free energy, and the conditions for spontaneity.

3.2 The Second Law of Thermodynamics

According to the Second Law, the total entropy of an isolated system cannot decrease over time; it can only stay constant or increase. This law embodies the irreversibility of natural processes, highlighting the tendency of systems to evolve towards states of higher disorder. While individual processes may exhibit reversibility, the overall trend towards entropy maximization governs the behavior of macroscopic systems. Second law affirms that a natural process progresses in a singular direction and is irreversible. In essence, while it's feasible to reverse the state of a natural system, doing so inevitably results in an increase in the entropy of the system. Therefore, the complete reversal of both the system's state and the surroundings simultaneously, without the implication of entropy destruction, is unattainable.

For example Consider a cup of hot coffee placed on a table in a room at a lower temperature. Heat will spontaneously flow from the hot coffee to the cool room until thermal equilibrium is reached, according to the Second Law. This process increases the entropy of the system as heat disperses, and the molecules in the system become more randomly distributed.

Another example is the diffusion of a gas into an empty chamber. Initially, the gas molecules are confined to one side of the chamber, leading to a low entropy state. As time progresses, the molecules disperse evenly throughout the chamber, resulting in a higher entropy state. This spontaneous diffusion illustrates the Second Law in action, as it leads to an increase in overall disorder.

3.2.1 Various statements of the second law

The second law of thermodynamics may be stated in many ways:

- Clausius statement:

Clausius statement asserts that heat cannot spontaneously transfer from cold to hot regions without external work being done on the system. For example, in a refrigerator, heat is conveyed from cold to hot, but only when forced by an external means.

- Kelvin statement:

Kelvin statement shows that it is impossible to construct a heat engine that operates in a cycle and produces no other effect than the extraction of heat from a single thermal reservoir and the performance of an equivalent amount of work.

- Planck's statement:

Planck statements elucidate that no device operating on a cycle can take heat from a single reservoir and convert it entirely into work without any other changes

3.3 Entropy: The Measure of Disorder

Entropy (S) is a elementary concept of thermodynamics, which represents the degree of disorder/ randomness within a system. It enumerates the number of microscopic configurations corresponding to a given macroscopic state. Systems naturally tend towards states of higher entropy, reflecting the tendency of energy to disperse and become more evenly distributed. From a statistical perspective, entropy provides insights into the

probability distribution of different microstates within a system, offering a bridge between microscopic and macroscopic behavior.

3.4 Free Energy: The Potential for Work

A thermodynamic potential known as free energy (G) quantifies the most work that can be extracted from a system while maintaining a constant temperature and pressure. It consists of two components: enthalpy (H) and entropy (S). The Gibbs free energy (G) expressed as:

$$G = H - TS$$

where T is temperature in Kelvin. A decrease in free energy indicates a spontaneous process, while an increase suggests a non-spontaneous one. Free energy serves as a powerful tool for predicting the directionality of chemical reactions and phase transitions, offering insights into the feasibility and equilibrium of processes.

3.5 Conditions for Spontaneity

The spontaneity of a process is governed by the change in free energy (ΔG). A process is spontaneous if the change in free energy is negative ($\Delta G < 0$) at constant temperature and pressure, which is in accordance with second Law of Thermodynamics. This criterion can be expressed as:

$$\Delta G = \Delta H - T\Delta S < 0$$

ΔH represents the Enthalpy change, T is temperature, and ΔS represent the change in Entropy. Thus, for a process to occur spontaneously, it must either release energy ($\Delta H < 0$) or increase entropy ($\Delta S > 0$), or both. Conversely, if ΔG is positive ($\Delta G > 0$), the process is non-spontaneous under the given conditions.

3.6 Gibbs Free Energy

Gibbs free energy, denoted as G, is a elemental conception in thermodynamics which plays a pivotal role in predicting the spontaneity and equilibrium of chemical reactions and phase transitions. It was developed by Josiah Willard Gibbs; this thermodynamic potential provides insights into the maximum sum of useful work that can be extracted from a system at the condition of constant temperature and pressure.

3.6.1 Understanding Gibbs Free Energy

'Gibbs free energy' is termed as the difference between the enthalpy (H) and the product of temperature (T) and entropy (S):

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

This equation demonstrates the balance amid the internal energy (enthalpy) of system and its tendency to increase disorder at a given temperature. A negative(*-ve*) change in Gibbs free energy ($\Delta G < 0$) specifies a spontaneous process, while a positive(*+ve*) change ($\Delta G > 0$) suggests a non-spontaneous one.

3.6.2 Applications of Gibbs Free Energy

Gibbs free energy finds wide-ranging applications in chemistry, physics, biology, and engineering:

1. **Chemical Reactions:** In chemical reactions, the change in Gibbs free energy, ΔG, helps determine whether a reaction will proceed spontaneously or requires external energy input.If ΔG is less than zero, the reaction is exergonic and spontaneous; if ΔG is greater than zero, the reaction is endergonic and non-spontaneous..

2. **Phase Transitions:** Gibbs free energy is crucial for analyzing phase transitions, such as melting, vaporization, and condensation. At equilibrium, the Gibbs free energy of the system is minimized, facilitating the prediction of phase diagrams.

3. **Biochemical Processes:** In biological systems, Gibbs free energy governs cellular metabolism, enzyme catalysis, and the spontaneity of biochemical reactions essential for life processes.

4. **Engineering Applications:** Gibbs free energy informs the design and optimization of energy conversion systems, such as fuel cells, batteries, and refrigeration cycles.

3.7 Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation offers a relationship between the change in Gibbs free energyand temperature for a reaction at constant pressure:

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

Where:

ΔG is the change in Gibbs free energy.

ΔH is the change in enthalpy.

T is the temperature in Kelvin.

ΔS is the change in entropy.

This equation highlights the interplay between enthalpy, entropy, and temperature in determining the spontaneity of a process. A negative value of ΔG at a given temperature indicates a spontaneous reaction, while a positive value suggests a non-spontaneous one.

Summary

The 'Second Law of Thermodynamics' states that the entropy, or disorder, of an isolated system always increases over time. This means that natural processes are irreversible and tend to move toward greater disorder, explaining why energy conversions are never 100% efficient and some energy is always dissipated as heat. Entropy, a measure of system disorder, is crucial in thermodynamics for predicting spontaneous processes. Higher entropy signifies a more disordered system, and the Second Law indicates that in an isolated system, entropy continually rises. Free energy represents the usable energy in a system available to perform work. The spontaneity of a process at constant temperature and pressure is determined by the change in Gibbs free energy (ΔG). A negative ΔG signifies a spontaneous process, whereas a positive ΔG denotes a non-spontaneous process. Gibbs free energy (G) integrates enthalpy (H), entropy (S), and temperature (T) to quantify the maximum reversible work a system can perform. The Gibbs-Helmholtz equation describes the relationship between Gibbs free energy and temperature, aiding in the understanding of how Gibbs free energy varies with temperature, which is essential for analyzing the thermodynamics of chemical reactions.

Keywords:

- **Second Law of Thermodynamics**: Entropy of an isolated system always increases, showing the irreversibility of natural processes
- **Entropy:** A measure of the disorder or randomness in a system; higher entropy means greater disorder.
- **Free Energy:** The energy available in a system to do work; specifically, Gibbs free energy is used to predict the spontaneity of processes.
- **Spontaneity:** The tendency of a process to occur without external intervention, determined by a negative change in ΔG.
- **Gibbs Free Energy (G):**A thermodynamic potential combining enthalpy, entropy, and temperature to forecast a system's maximum reversible work.

- **Gibbs-Helmholtz Equation:** An equation that relates the temperature dependence of Gibbs free energy to enthalpy.

MCQs

1. The Second Law of Thermodynamics states?

A. Energy cannot be generate or destroyed.

B. For the isolated system entropy always increases.

C. The total energy of an isolated system remains constant.

D. Heat flows from a colder body to a hotter body.

Answer: B

2. Entropy is a assess of----

A. Energy content of a system.   B. Disorder or randomness of a system.

C. Enthalpy of a system.   D. Work done by a system.

Answer: B

3. Free energy is defined as:

A. The total energy of a system.   B. The energy available to do work.

C. The heat content of a system.   D. The internal energy of a system.

Answer: B

4. For a process to be spontaneous at constant temperature and pressure, ΔG must be..:

A. Positive   B. Negative   C. Zero   D. Undefined   **Answer: B**

5. Gibbs free energy change (ΔG) is given by the equation:

A. $\Delta G = \Delta H - T\Delta S$ B. $\Delta G = \Delta S - T\Delta H$

C. $\Delta G = \Delta U + P\Delta V$ D. $\Delta G = T\Delta S - \Delta H$ **Answer: A**

Short Answer Questions:

1. What is the Second Law of Thermodynamics and how does it apply to natural processes?
2. Define entropy and explain its significance in thermodynamics.
3. What is Gibbs free energy and how does it determine the spontaneity of a process?
4. Derive the relationship between Gibbs free energy, enthalpy, and entropy.
5. State and explain the Gibbs-Helmholtz equation.

Chapter: 4

Chemical Equilibrium

Objectives

- Recognize chemical equilibrium, or the change in free energy during a chemical process.
- Derive the law of chemical equilibrium via thermodynamic derivation.
- The idea of Le Chatelier and the differentiation between ΔG and ΔGo
- Analyse Kp, Kc, and Kx relationships for reactions using ideal gases

4.1 Introduction

A **Chemical Reaction** involves the transformation of one or more substances into different substances through the breaking and forming of chemical bonds.

Types ofChemicalReactions

(a) Irreversible Reactions
(b) ReversibleReactions

(a) **IrreversibleReactions -** Reactions which takes place in one direction i.e. product cannot convert to the reactant.

Ex.

$$BaCl_2 \text{ (aq)} + H_2SO_4\text{(aq)} \longrightarrow BaSO_4 \text{ (ppt)} + 2 \text{ HCl (aq)}$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
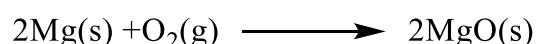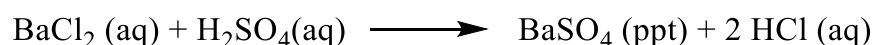
(b) **ReversibleReactions** – which takes place in both direction forward and backward,*i.e,* reactant converted into product and product convert into reactant there for never go on to completion. Reversible reactions always takes place in close container

Ex.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$
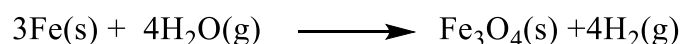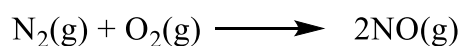
Spontaneous Reaction - Reaction which proceeds itself is known as spontaneous reaction.

Example- carbon (graphite) on ignition undergoes complete combustion to give CO_2

Free energy of Spontaneous reaction: A chemical reaction is considered viable if its free energy change is negative, indicating that the reaction occurs spontaneously. The reaction is in an equilibrium state if free energy change is zero and if the free energy change is positive, the reaction is not possible or feasible.

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

There are two factors which contribute to the value of ΔG, first energy factor ΔH and the entropy factor $T\Delta S$.

Standard Gibbs free energy is $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

4.2 Chemical Equilibrium-

Chemical equilibrium occurs when reactant and product concentrations stabilize, and the rates of forward and reverse reactions balance each other. Although there is no net change in the amount of reactant and product molecules, equilibrium is a dynamic process where reactions of reactants to products and products to reactants continue.

Example: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
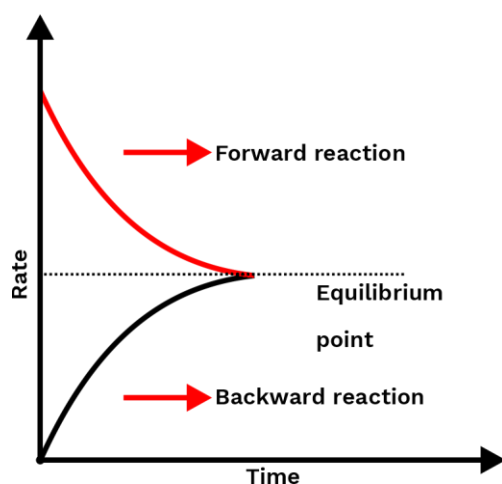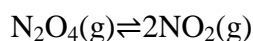
4.2.1 Law of Mass action- The law of mass action states that a reaction's rate is directly correlated with its active mass.

Think about the following reaction: $aA + bB \rightleftharpoons cC + dD$

Law of mass action states that

Rate of forward reaction is- $r_f \alpha [A]^a. [B]^b = k_f[A]^a. [B]^b$

Rate of reverse reaction is- $r_r \alpha [C]^c. [D]^d = k_r [C]^c. [D]^d$

Where k_f and k_r are proportionally constant and square brackets show molar concentration of reactant and product. The forward and reverse reaction rates are equivalent at equilibrium.

$k_f [A]^a . [B]^b \quad = k_r [C]^c . [D]^d$

$k_f/k_r = K_{eq} = [C]^c [D]^d \quad / [A]^a [B]^b$

The equilibrium constant is denoted by Keq.

Example: $\quad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$
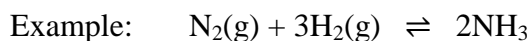
$Kc = [NH_3]^2 /[N_2][H^2]^3$

Kc = The equilibrium constant represents the ratio of the product's equilibrium concentration over the reactant's equilibrium concentration, each raised to the power of its stoichiometric coefficient.

4.2.2 Constant of equilibrium with respect to partial pressure (Kp):

The equilibrium constant can also be computed in terms of partial pressure when all of the reactant and products are in the gaseous state. The general ideal gas equation yields the relationship between the molar concentration and the partial pressure (P) of any one gas in the equilibrium mixture.

$PV = nRT$

$P = (n/V) . RT$

Where (n/V) is molar concentration.

$P = $ Molar concentration $\times RT$

In other words, at a given temperature, the partial pressure (P) of a gas in the equilibrium mixture is directly proportional to its molar concentration.

$n L(g) + mM(g) \rightleftharpoons yY(g) + zZ(g)$

$Kp = [pY]^y . [pZ]^z / [pL]^n . [pM]^m$

Example : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$

$Kp = [pNH_3]^2 / [pN_2]. [pH_2]^3$

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
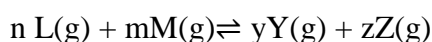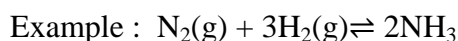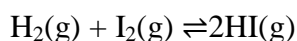
$Kp = [pHI]^2 / [pH_2] . [pI_2]$

4.2.3 Relation between Kp and Kc

Taking example of ageneralreaction,

$$aB + bB \rightleftharpoons cC + dD$$
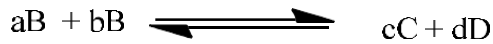
Intermsofconcentrations(moles/liter) value of equilibrium constantis

In case where the reactants and products are gaseous, partial pressure may be used in place of the concentration terms. Kp, the equilibrium constant, is expressed as,

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \dots\dots (i)$$

$$Kp = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b} \qquad \dots\dots\dots (ii)$$

Foranidealgas,

$$pV = nRT \ or \ p = \frac{n}{V}RT = CRT,$$

C stands for the molar concentration . We can write for various gases A, B, C, and D.

$P_A = C_A . RT$, $P_B = C_B RT$, $P_C = C_C RT$, $P_D = C_D RT$

Using equation (ii) with these values, we obtain

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b}$$

$$or \qquad K_p = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^{(c+d)-(a+b)}$$

Where

$$\boxed{K_p = K_c (RT)^{\Delta n}} \qquad \dots\dots\dots (iii)$$

$\Delta n = (c + d) - (a + b)$ = [number of moles of products]- [number of moles of reactants]

4.3 Thermodynamic derivation of the law of mass action–

Consider a general reaction

$aA + bB \rightleftharpoons cC + dD$
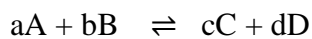
 Consider a general reaction Equilibrium constant (K) in terms of activity is given by

$K = aC^c \times aD \ / \ ^a \times aB^b$

This equation shows how a substance's chemical potential (μ) in a mixture relates to activity.

$\mu = \mu \circ + RT\ln a$

Where, μ = is chemical potential of pure substance, T is the absolute temperature, while R is the gas constant.

For one mole of the substance one way to express an equation is as

$a\mu_A = (\mu \circ A + RT \ln \ )$

Similarly for substance B, C, and D equations can be written as follows

$b\mu_B = (\mu \circ B + RT \ln \ )$

$c\mu_C = (\mu \circ C + RT \ln \ )$

$d\mu_D = (\mu \circ D + RT \ln \ )$

The change in free energy (ΔG) for the reaction is

$\Delta G = \Delta Gproduct - \Delta Greactant$

$\Delta G = [\ \mu_D + c\mu_C] - [\ a\mu_A + b\mu_B\ ]$

$\Delta G = \{(\mu \circ D + RT \ln \ )\} + \{c(\mu \circ C + RT \ln a_C)\} - \{a(\mu \circ A + RT \ln a_A)\} + \{b(\mu \circ B + RT \ln a_B)\}$

$\Delta G = [\ \mu \circ C + d\mu \circ D] - [a\mu \circ A + b\mu \circ B\ ] + RTlnaC^c \times aD^d/\ aA^a \times aB^b$

As $\Delta G^\circ = [c\mu \circ C + d\mu \circ\ ] - [\ a\mu \circ A + b\mu \circ B]$

$\Delta G = \Delta G^\circ + RTlnaC^c \times aD^d/\ aA^a \times aB^{b}$

At   equilibrium   change   in   Gibbs   free   energy   is   zero

$\Delta G^\circ = -RTln\frac{aC^c \times aD^d}{aA^a \times aB^b} = -RTln\ K$

Thus change in free energy (ΔG) in terms of log for the reaction can be written as

$\Delta G^\circ = -2.303RTlog\ K$

As R and T are constant we can infer 3 cases

- If ΔG° is negative log K must be positive and reaction proceeds spontaneously as product of concentration terms is more than product of reactant concentration terms.

- If ΔG° is positive log K must be negative and reaction does proceeds spontaneously as product of concentration terms is less than product of reactant concentration terms.

- If ΔG° is zero log K must be 0 and reaction has reached equilibrium as product of concentration terms is equal to product of reactant concentration terms.

  Definition of ΔG and ΔG∘

  The thermodynamic quantity known as Gibbs-Free energy (**ΔG**) is the difference between enthalpy and the product of the system's entropy and absolute temperature. A thermodynamic quantity known as standard Gibbs-Free energy(**ΔG∘**) is the difference

between enthalpy and the product of the system's entropy at standard state conditions and absolute temperature.

G = H – TS

H= enthalpy; T= temperature; S= entropy Change

Gibbs free energy in system at constant temperature is $\Delta G = \Delta H – T\Delta S$ At standard state conditions Change

4.4 Le- Chatelier's principle:

Henry Le Chatelier (1884) - French Chemist "When a change is applied on a system in equilibrium, the system tends to adjust itself so as to reduce the change."

This principle states that when a system is in equilibrium and a variable, like pressure, temperature, or concentration, is changed, the system will try to minimize the impact of the change as much as possible.

- If concentration is raised, equilibrium will move in the direction of the component's decreasing concentration.
- The equilibrium will move toward low pressure if the pressure is raised.
- An increase in temperature will cause the equilibrium to move toward a lower temperature.

1. **Effect change in concentration**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$$
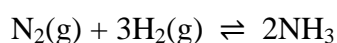
- An equilibrium will move forward when the concentration of either nitrogen or hydrogen increases, causing an increasing amount of N_2 and H_2 to convert to NH_3.
- A rise in reactant concentration that moves the equilibrium forward
- A rise in product concentration that causes the equilibrium to move backward direction.

Examples:

1. Clothes dry more quickly in the presence of a breeze or constant shaking. This occurs as a result of the surrounding air's water vapor being evacuated, and the cloth losing more water vapor to restore equilibrium with the environment.

2. When we sit under a fan, the sweat we produce on humid days evaporates. As a result of our skin's inability to lose more water vapor to the surrounding air's high concentration,

we sweat more. Evaporation begins from the skin as soon as the fan removes the humid air.

2. **Effect change in pressure**

Increased pressure causes the equilibrium to move in the direction of a decrease in the number of moles.

A. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ where $\Delta n = -2$
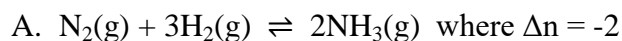
A negative value of Δn indicates that pressure increases will cause the equilibrium to move ahead. A drop in pressure will cause the equilibrium to move backward.

B. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ where $\Delta n = 1$
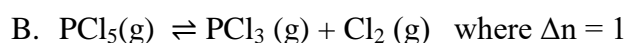
When Δn is positive, pressure increases will cause the equilibrium to move in the backward direction. The equilibrium will move in forward direction as the pressure decreases.

C. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ where $\Delta n = 0$
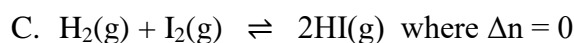
$\Delta n = 0$ means No change in equilibrium on increasing and decreasing the pressure.

D. Effect of change in temperature

A. Exothermic reaction –If there is increasing in temperature then equilibrium will shift in backward direction. decreasing in temperature then equilibrium will shift in forward direction

B. Endothermic reaction –If there is increasing in temperature then equilibrium will shift in forward direction. decreasing in temperature then equilibrium will shift in backward direction

4.5 Applications of Le-Chatelier Principle:

1. Physical Equilibria:

a. Melting of Ice: Ice melts at its melting point as its volume decreases and it absorbs heat.

$$H_2O\ (s) \rightleftharpoons H_2O\ (l).$$
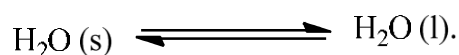
For example,

It is shown as:

$$\underset{\text{(More volume)}}{\text{Ice}} \underset{}{\overset{0^0C}{\rightleftharpoons}} \underset{\text{(Less volume)}}{\text{Water}} \quad \text{Heat}$$
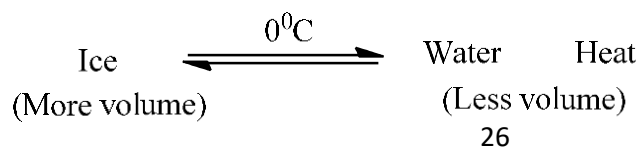
A rise in temperature or pressure will cause the equilibrium to move from left to right. Put another way, a rise in temperature or pressure lowers the melting point of ice.

b. Water vapourization: This illustrates the equilibrium between steam and water as:

$$\text{Water} \ (\text{Less volume}) \rightleftharpoons \text{Water vapour} \ (\text{More Volume}) \ - \text{Heat}$$

The equilibrium will move toward the direction of heat absorption—a forward reaction—as the temperature rises. Thus, more steam will be generated. Likewise, when pressure increases, the equilibrium will move in the direction of the volume decrease, or a backward reaction. Steam will therefore condense into liquid. Stated differently, the generation of steam will be favorably impacted by temperature increases and pressure decreases.

c. Solubility of substances: Some substances, such as sugar, NaCl, etc., dissolve when heat is absorbed.

$$\text{Sugar} + \text{aq.} \rightleftharpoons \text{Sugar (aq)} - \text{Heat}$$
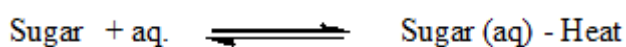
Temperature rise will therefore cause the equilibrium to move to the right. Therefore, when the temperature rises, solubility of these chemicals increases. Some chemicals dissolve when the temperature rises, such as $Ca(OH)_2$ and others.

$$Ca(OH)_2 + \text{aq.} \rightleftharpoons Ca(OH)_2 \text{(aq)} + \text{Heat}$$
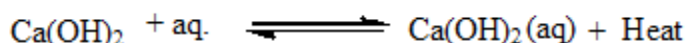
Therefore, when the temperature rises, the equilibrium—or the direction in which heat is absorbed—will shift to the left. Therefore, when the temperature rises, these compounds become less soluble.

2. Chemical equilibria:

a. SynthesisofammoniabyHaber'sprocess:

$$\underset{\text{1 vol.}}{N_2 \text{ (g)}} + \underset{\text{3 vol}}{3H_2 \text{ (g)}} \rightleftharpoons \underset{\text{2 vol}}{2NH_3 \text{ (g).,}} \qquad \Delta H = -22 \ kcal$$
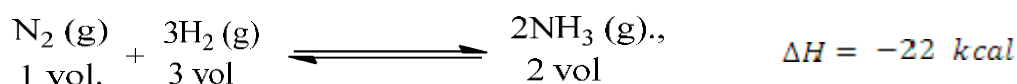
(i) Temperature effect: According to Le Chatelier's principle, if the reaction's temperature is dropped, the equilibrium must change in a way that tends to raise the temperature once again. In other words, ammonia synthesis is required to release heat. That low temperature is more

advantageous for ammonia's production. However, decreasing the temperature also lowers the rate of reaction; therefore, even at relatively low temperatures, a catalyst that provides a suitable reaction rate must be used.

(ii) The impact of pressure: When its elements are reduced in volume, ammonia is created. As a result, if the system is in equilibrium and the pressure is increased, Le-Chatelier's principle states that the equilibrium must change in a way that tends to reduce the pressure. This can only be accomplished by producing additional ammonia in order to lower the volume. In other words, ammonia forms more readily under high pressure.

(iii) Effect of concentration: Le -Chatelier's principle states that when more N_2 is given to a system that is already in equilibrium in order to increase its concentration, the equilibrium will shift in a way that tends to decrease the concentration of N_2. In other words, in order to used up N_2, more ammonia will be created. This raises the production of ammonia in relation to H_2, and increases the concentration of H_2 in the opposite way. Than formation of Ammonia favoured the following condition:

- Low temperature
- High pressure
- High concentration of reactants.

b. Formation of nitric oxide: Reaction is shown as

(i) Effect of pressure: Since there is no volume change while nitric oxide is forming, pressure will not affect the equilibrium.

(ii) The effect of temperature: as the temperature rises, the equilibrium will move forward, in the direction that heat is absorbed. Thus, the production of nitric oxide is favored by high temperatures.

(iii) Effect of concentration: adding N_2 to an equilibrium system will cause the equilibrium to change in a way that lowers the N_2 concentration. Consequently, more nitric oxide will be produced. The impact of introducing oxygen is comparable. Than formation of nitric oxide favoured the following condition:

- High temperature
- High concentration of N_2 or O_2

Summary: When two opposing reactions happen at the same pace and the concentrations of reactants and products do not change over time, the situation is known as chemical equilibrium. A reaction that exhibits both forward and backward motion at the same time is referred to as reversible. Dynamic balance is the same as chemical equilibrium. • According to the law of mass action, the reactant's active masses determine how quickly a chemical reaction proceeds. Le-Chatelier's principle explains that when concentration, pressure, or temperature are changed in an equilibrium system, the equilibrium moves in a way that tends to counteract the effects of the change.

Keywords:

Chemical Equilibrium: when the rates of forward and reverse reactions are equal, leading to constant concentrations of reactants and products.

Equilibrium constant (K): Equilibrium constant (K) quantifies the ratio of product to reactant concentrations at equilibrium in a chemical reaction, with its definition varying for different reaction types.

Law of mass action: A principle that states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants, each raised to the power of its stoichiometric coefficient.

Homogeneous Equilibrium: Chemical equilibrium that occurs in a homogeneous system, where all reactants and products are in the same phase (e.g., all in the gas phase or all in the liquid phase).

Heterogeneous Equilibrium: Chemical equilibrium that occurs in a heterogeneous system, where reactants and products are in different phases (e.g., gas and solid or liquid and solid).

Dynamic Equilibrium: The condition in a reversible reaction where the rates of the forward and reverse reactions are equal, and there is no net change in the concentrations of reactants and products, although reactions are still occurring.

MCQs

1. N_2 (g) + $3H_2$(g) ⇅ $2NH_3$ + Heat is the reversible reaction. The equilibrium moves forward in the following ways:
   (A) by raising the NH_3(g) concentration (B) by lowering pressure
   (C) by lowering N_2 and H_2 concentrations
   (D) by raising pressure and lowering temperature.

Answer: (D)

2. In reversible reactions as the reactant concentration increasesthan the equilibrium constant will

   (A) Depend on the concentration (B) Decreases

   (C) Remain the same (D) Increases

   Answer: (C)

3. In equilibrium value of ΔG is ?

   (A) Negative (B) Positive (C)Zero (D)None

   Answer: (C)

4. The value of 'Equilibrium constant' for different chemical reactions at a particular temperature is _____

   (A) constant (B) unique (C) the same (D).cannot say

   Answer: (C)

5. What is the **E**quilibrium constant of the following reaction: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$?

   (A) $[NO][H_2O]/[NH_3][O_2]$ (B) $[C]^c[D]^d/[A]^a[B]^b$

   (C) $[NO_4[H_2]^6/NH_3]^4[O_2]^5$ (D) $[NO]^4[H_2O]^6/[NH_3]^4[O_2]^5$

   Answer: (C)

Short Answer Question:

1. The mass action statute of the state.

2. Elucidate the Le-Chatelier principle.

3. Create an equation that shows how temperature and equilibrium constant are relate.

4. Put KP and Kc in a relationship.

Chapter: 5

Ionic equilibrium-I

Objectives

- Understand Ionic Equilibrium and different Types of electrolytes

- Calculate constant of ionization constant,Degree of ionization and ionic product of water.

- Examine the pH scale, common ion effect and ionization of weak acids and bases.

5.1 Introduction: It's common knowledge that sugar in aqueous solution doesn't conduct electricity. Nevertheless, adding ordinary salt (NaCl) to water causes it to conduct electricity. Furthermore, as the concentration of common salt rises, so does the conductivity of electricity. Based on their capacity to conduct electricity, Michael Faraday divided the materials into two groups. A class of materials known as electrolytes is defined as those that conduct electricity in their aqueous solutions, whereas non-electrolytes are defined as those that do not. Strong and weak electrolytes are the further classifications made by Faraday for electrolytes. While weak electrolytes only partially dissolve upon breakdown in water, strong electrolytes almost entirely ionize.

Note that equilibrium between ions and unionized molecules is established in weak electrolytes. Ionic equilibrium is the term used to describe this kind of equilibrium involving ions in an aqueous solution. Electrolytes include bases, acids, and salts. They can function as strong or weak electrolytes.

5.2 Acid and Base

There are now three different ways that acids and bases are conceptualized. Everyone has unique benefits of its own.

- Arrhenius concept
- Bronsted-Lowery Concept
- Lewis concept

5.2.1 Arrhenius theory – This concept is given by SvanteArrhenius(1884). According to this concept an acid is a substance that dissociates to give hydrogen ion(H^+) when dissolved in water. Example: $HCl, CH_3COOH, HNO_3, H_2SO_4, H_3PO_3, H_2CO_3$

$$HCl(aq) \longrightarrow H^+(aq) \quad Cl^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) \quad OH^-(aq)$$
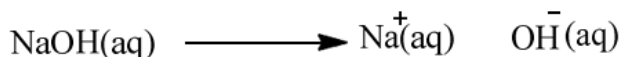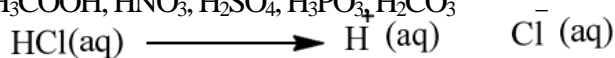
Abase is a substance which dissociate in to hydroxylion(HO^-) when dissolved in water.

$$NaOH(aq) \rightleftharpoons Na^+(aq) + HO^-(aq)$$
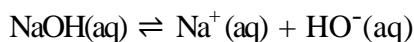
The stronger an acid or basic is, the more H + or OH-ions it releases into the water.

Drawbacks of Arrhenius theory,

- Itisrestrictedtoonlyaqueoussolutions.Water is devoid of free H+ and OH- ions. In the free state of water, there is no H^+ or OH^- ions created by bases or acids, respectively. By forming hydrogen bonds with water molecules, they combine to produce complex ions. The H^+ (aq) ion when attached with H_2O molecule, form H_3O^+ ion which is known**Hydroniumion.**

Hydronium ion
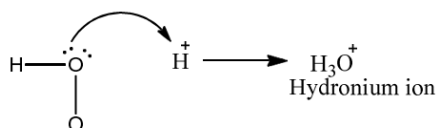
   In the same way, the OH- ion creates the $H_3O_2^-$ complex.

- It is insufficient to explain why components without hydrogen behave acidically. Example $AlCl_3$. Similarly it does not explain the basic character of substances likeNH_3andNa_2CO_3whichdonothave OH group

5.2.2 Bronsted and Lowry Concept – A more inclusive definition of bases and acids was proposed by Lowry and Bronsted. They define a Base as a substance that has a tendency to absorb a proton (H^+) from any other substance, and an acid as a substance that has a tendency to donate a proton to any other substance. Stated differently, a base is an acceptor of protons and an acid is a giver of protons.

The portion of an acid that remains after losing a proton tends to get it again. It acts like a base as a result. As a result, the general equation defines an acid and a base.

$$Acid \rightleftharpoons \underset{proton}{H^+} + Base \qquad ....(i)$$
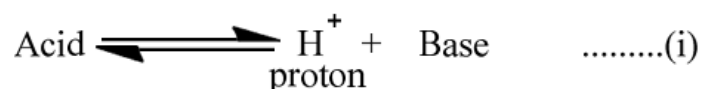
A combination of bases and acids. Consider the following representation of the dissociation of acetic acid in water:

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3\overset{+}{O}} + \underset{\text{Base}}{CH_3CO\overset{-}{O}} \quad ....(ii)$$
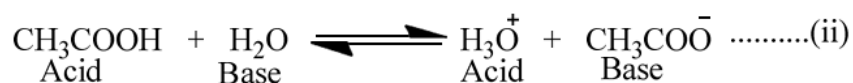
It is clear that acetic acid functions as an acid by giving water a proton. Water functions as a base because it can take up a proton. In the opposite process, the hydronium ion (H_3O^+) functions as an acid by giving the acetate ion a proton. Because it has the ability to take up a proton, the acetate ion functions as a base. Conjugate acid base pairings are those substance pairs that can be created from one another by gaining or losing a proton. As such, acetate ion is the '**Conjugate Base**' of acetic acid, while acetic acid is the '**Conjugate Acid**' of acetate ion. In a similar, '**Hydronium ion**' is the conjugate acid of water and water is the conjugate base of '**Hydronium ion**'.

The conversation that follows leads to the following conclusions:

1. First of all, it is obvious that a substance can only exhibit an acidic character in the presence of another substance that is able to take a proton. Since benzene cannot take up protons, for instance, acetic acid in benzene is not acidic.

2. Secondly, the hydrogen ion in an aqueous solution is known as the hydrated ion, or H_3O^+ ion, rather than the H+ ion. Since it resembles ammonium ion (NH_4^+), it is also known as hydronium ion.

Thirdly, ions as well as molecules can function as bases and acids.

Acetic acid dissociation in water can be shown as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

Both Acid1 and Base1, as well as Acid2 and Base2, are conjugate acid-base pairs.

The dissociation of an acid HA in water can generally be described as

$$HA + H_2O \rightleftharpoons H_3\overset{+}{O} + A^-$$

Similar to how an acid's dissociation needs a solvent capable of absorbing a proton. Similar to this, in order for a base to dissociate, it needs a solvent that is willing to give up a proton. Water is both basic and acidic. Thus, in water, both bases and acids can dissociate. Water therefore functions as a base (a proton acceptor) toward acetic acid and as an acid (a proton donor) towards ammonia. These materials are referred to as amphoteric or amphiprotic.

$$HA + B \rightleftharpoons A^- + HB^+$$
acid   base   conjugate base   conjugate acid

Accepts proton

$$H_2O + NH_{3(aq.)} \rightleftharpoons NH_4^+{}_{(aq.)} + OH^-_{(aq.)}$$
Ammonia

Donates proton

Accepts proton

$$HCl_{(aq.)} + H_2O \rightleftharpoons Cl^-_{(aq.)} + H_3O^+_{(aq.)}$$

Donates proton
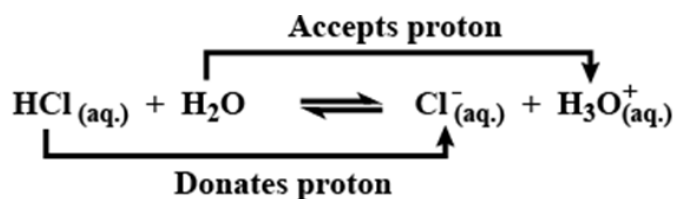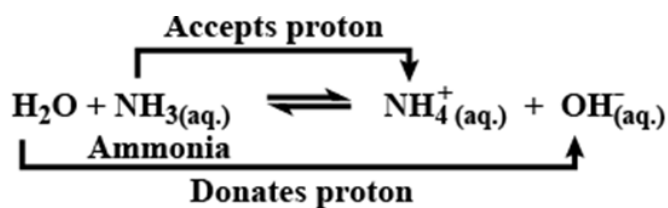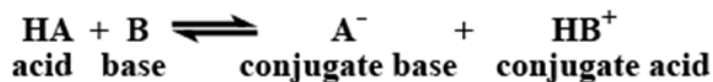
Acid-Base pairings' relative strengths: The idea of Lowry and Bronsted states that a base's strength is determined by its protons-gaining tendency, while an acid's strength is determined by its proton-losing tendency. An acid that is strong, like HCl, will have a strong propensity to donate protons.

As a result, the equilibrium,

$$HCl + H_2O \rightleftharpoons H_3\overset{+}{O} + \overset{-}{Cl}$$

resides significantly to the right, and a very tiny amount of the opposite reaction—which represents the proton uptake by the chloride ion and the subsequent reformation of HClwill occur. The chloride ion is a weak base as a result. Generally speaking, the conjugate base of a stronger acid must be weaker, and vice versa. A strong acid, such as HCl, has a weak conjugate base, Cl-. A base that is strong, like CH$_3$COO-, will have a weak conjugate acid, like CH$_3$COOH.

5.2.3 Lewis concept Even more broadly, G. N. Lewis suggested a model of acids and bases in the beginning of the 1930s.

Lewis theory states that an acid is an electron pair acceptor. An electron pair donor is a base.

A   B   A——B
Lewis acid   Lewis base   Complex
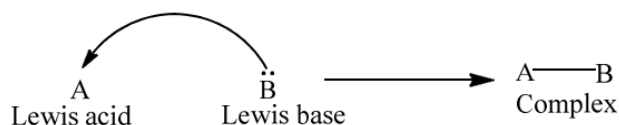
Notably, all anions or molecules with an electron pair function as Lewis bases, while all cations or neutral compounds lacking an electron function as Lewis acids. A couple of examples are:

$$BF_3 \ + \ NH_3 \longrightarrow BF_3NH_3$$
$$\text{Acid} \qquad \text{Base}$$

$$BF_3 \ + \ F^- \longrightarrow BF_4^-$$
$$\text{Acid} \qquad \text{Base}$$

$$H^+ \ + \ \overset{..}{N}H_3 \longrightarrow NH_4^+$$
$$\text{Acid} \qquad \text{Base}$$
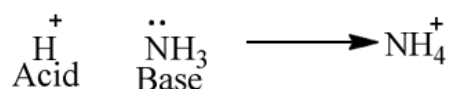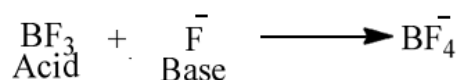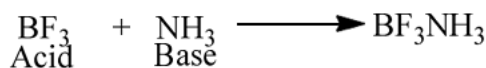
5.3 Electrolyte - Strong and weak electrolytes and Ionic equilibrium

An aqueous solution or molten state of a substance that conducts electricity is called an electrolyte. Conversely, a non-electrolyte is a substance that does not conduct electricity in its molten or watery condition.

An electrolyte's conductance results from the ions that are created when a material dissociates. Different electrolytes, however, dissociate to varying degrees.

The term "degree of dissociation" or "ionization" refers to the percentage of all molecules that separate into ions. The degree of dissociation is the fraction of all molecules that separate into ions; it is commonly denoted as α.

$$\alpha = \frac{\text{Numer of moles dissociated}}{\text{Total number of moles taken}}$$

- The electrolytes are categorized as "strong electrolytes" or "weak electrolytes" based on the degree of dissociation.

- **Strong Electrolytes:** These compounds exhibit high electrical conductivity because they nearly entirely disintegrate into ions in aqueous solution. Examples example strong acid, base and salt like KOH, NaCl, H_2SO_4, KNO_3.

- **Weak Electrolytes:** These are the materials that, when slightly dissociated in an aqueous solution, also slightly conduct electricity. Examples: example weak acid, base and salt like NH_4OH, CH_3COOH.

- **Non electrolyte** – Compound does not conduct electricity eg. Sugar, urea

5.3.1 Ionization constant of weak electrolyte

Weak acids and bases are the example of weak electrolyte which are dissociate in small extant.

$$HA\,(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

Initial concentrations (in moles)	c	0	0
Equilibrium concentrations	$c(1-\alpha)$	$c\alpha$	$c\alpha$
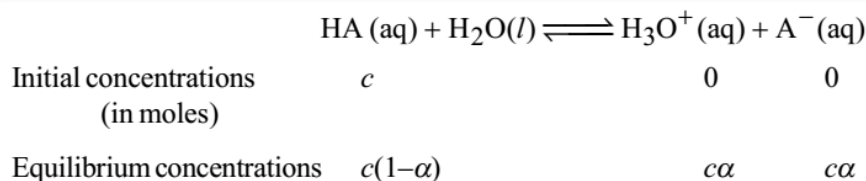
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{[c\alpha][c\alpha]}{c[1-\alpha]} = \frac{c^2\alpha^2}{c[1-\alpha]} = \frac{c\alpha^2}{(1-\alpha)}$$

Given how weak the acid HA is, $\alpha \ll 1$. When compared to 1, you can ignore α.

$$K_a = c\alpha^2$$

The degree of dissociation or extent of ionization is represented by α, while Ka is the acid's ionization or dissociation constant. Since the H+ concentration and Ka are strongly correlated, stronger acids are those with higher Ka values.

5.3.2 Likewise, the weak base equilibrium constant Kb.

$$MOH\,(aq) \rightleftharpoons M^+\,(aq) + OH^-\,(aq)$$

At equilibrium, MOH has (c – cα) moles/lit, while M+ and OH–have (cα) moles/lit if the initial concentration of MOH is c mole/lit and the degree of dissociation is α. Thus, the Kb will be:

$$K_b = [M^+]\,[OH^-]/\,[MOH]$$

or

$$K_b = c\alpha^2\,/\,(1-\alpha)$$

$$K_b = c\alpha^2$$

Because Kb and OH-concentration are strongly correlated, bases with higher Kb values are stronger.

5.4 Dissociation constant of water (ionic product of water) Pure water has a low electrical conductivity. This demonstrates that water is a weak electrolyte, meaning that it is only slightly ionized.

Dissociation of H_2O: $H_2O \leftrightarrow H^+ + OH^-$

Using the chemical equilibrium law, its dissociation constant, Kc, is obtained as follows:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad \ldots (i)$$

It is possible to think of the concentration of undissociated water molecules, $[H_2O]$, as constant, say k, because dissociation occurs to very small constants.

$$\therefore \qquad K_c \times k = [H^+][OH^-]$$

An additional constant denoted by Kw is obtained by multiplying the two constants, Kc and k.

$$K_w = [H^+][OH^-] \qquad \ldots\ldots\ldots (ii)$$

where Kw is referred to as the ionic product of water or, more widely, the dissociation constant of water.

The result of the molar concentration of H+ and OH- ions is hence the ionic product of water. Typically, Kw is calculated as follows: Kw = 1.00×10^{-14} at 298 K (25^0 C).

Temperature's impact on Kw. As temperature rises, the ionic product of water (Kw) increases. This is a result of the fact that water ionization rises in proportion to temperature.

$$\therefore \quad [H^+][H^+] = 1.0 \times 10^{-14}$$

$$or \quad [H^+]^2 = 1.0 \times 10^{-14}$$

$$or \quad [H^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \, moles/litre$$

Therefore, at 250 C in pure water,

$$[H^+] = [OH^-] = = 1.0 \times 10^{-7} M$$

5.5 Common ion effect- Suppression of AB dissociation occurs when a soluble salt (A+C-) is added to a solution of another salt (A+B-) that contains a common ion (A+).

$$AB \rightleftharpoons A^+ + B^-$$

When salt (AC) is added, the concentration of A+ rises. Consequently, the equilibrium will move to the left, lowering the concentration of A+ ions in accordance with Le-Chatelier's principle. or that there will be less of an AB separation.

The term "common ion effect" refers to the loss of dissociation degree of a salt caused by the addition of a common ion.

To further understand the common-ion effect, let's look at a few examples.

Example 1: In a silver chloride saturated solution, we have the equilibrium

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The concentration of Cl- ions will rise when NaCl is added to the mixture. More of the solid AgCl will form if the equilibrium indicated above is moved to the left. AgCl's solubility will consequently decreses.

Example 2: NH4OH solution and solid NH4Cl are combined, and the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Move to the left. As a result, the OH-concentration falls.

Summary:

Ionic equilibrium is the state in which ions are present in an aqueous solution.An aqueous solution or melt that conducts electricity is called an electrolyte. Additionally, a substance whose aqueous solution or melt form does not conduct electricity known as non electrolytes. The degree of dissociation is the fraction of all molecules that separate into ions; it is commonly denoted as α.Strong Electrolytes: these are materials that, in an aqueous solution, virtually entirely dissolve into ions, making them excellent electrical conductors. Among them are NaOH, KOH, H_2SO_4, NaCl, and KNO_3. Weak Electrolytes: These are the materials that, when slightly dissociated in an aqueous solution, also somewhat conduct electricity. NH4OH and CH_3COOH are a few examples.

Bronsted and Lowery state that a base is a 'Proton-acceptor' and an acid is a 'Proton-donor'. In Lewis theory, a base donates electron pairs, while an acid accepts them. The common ion effect reduces salt dissociation due to the addition of a shared ion.

Keywords:

Dissociation: The separation of ions that occurs when an ionic compound dissolves in a solvent, such as water, breaking into its constituent ions.

Ionic product: The product of the concentrations of the ions in a solution, each raised to the power of their coefficients in the dissociation equation.

Common ion effect: The reduction in the degree of ionization of a weak electrolyte when a strong electrolyte that has a common ion is added to the solution.

Equilibrium constant (Kc): A numerical value that expresses the ratio of the concentrations of products to reactants at equilibrium for a chemical reaction.

Ionization: The process by which an atom or molecule gains or loses electrons, resulting in the formation of ions.

MCQs

1. Calculate the pH of 0.1 M HCL
    A. 10
    B. 20
    C. 1
    D. 0   (Ans. C)

2. Example of strong acid is
    A. HCl
    B. NaOH
    C. CH_3COOH
    D. All   (Ans. A)

3. Which of the following act as a lewis base
    A. HCl
    B. NaOH
    C. NH_3
    D. All(Ans. C)

Short Answer Questions:

1. Explain the term Common ion effect.
2. Define strong and weak electrolytes with example.
3. Illustrate conjugated acid-base pairs with suitable examples.
4. What is degree of dissociation?
5. Explain different concepts for acid bases

Chapter: 6

Ionic equilibrium-II

Objectives:

- Determining the hydrolysis constant for salt water
- The pH and level of hydrolysis for various salts.
- Offers solution buffers. Salts that are sparingly soluble and their solubility products
- Uses of the principle of soluble product

6.1 Salt Hydrolysis- The reaction between a salt and water that yields back the acid and base is known as **Salt Hydrolysis**. When dissolved in water, salts act as strong electrolytes, fully dissociating into positively charged cations and negatively charged anions. They are categorized into four groups.

a. Salt of strong acid and strong base – KCl, NaCl, NaNO$_3$
b. Salt of strong acid and weak base – NH$_4$Cl
c. Salt of strong base and weak acid – KCN, CH$_3$COONa
d. Salt of weak acid and weak base – CH$_3$COONH$_4$

6.2 Hydrolysis Constant:

A salt (BA) can be hydrolyzed generally using the following equation:

$$BA + H_2O \rightleftharpoons BOH + HA$$

$$\frac{[HA][BOH]}{[BA][H_2O]} = K, \text{ The equilibrium constant}$$
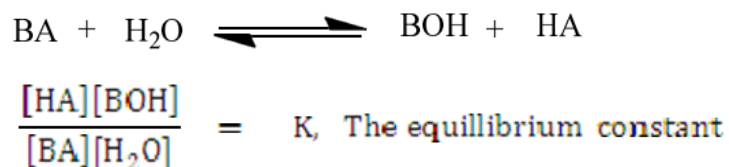
When the chemical equilibrium law is applied, we obtain

Since there is a significant excess of water in aqueous solution, its concentration [H2O] can be thought of as constant, meaning that we have

$$\frac{[HA][BOH]}{BA} = K[H_2O] = K_h$$

where the hydrolysis constant is denoted by Kh.

6.3 Hydrolysis of Salt of strong acid and strong base –

Example: $NaCl, NaNO_3, Na_2SO_4, KCl$

Consider the hydrolysis of NaCl as an example. Perhaps we could write:

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

$$\text{or } Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- - H^+ + Cl^-$$

$$\text{or } H_2O \longrightarrow H^- + OH^-$$
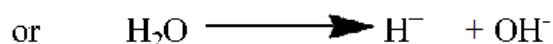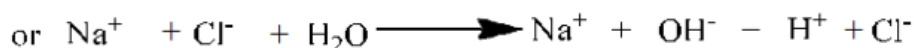
Therefore, there is no hydrolysis involved—just ionization. Moreover, at the final solution, [H+] = [OH-]. Thus, there is no solution. It is therefore often true that strong acid and strong base salts do not hydrolyze and produce a neutral solution.

6.4 Salt of strong acid and weak base –

In the case of salt BA, the hydrolysis can be expressed as

$$\underset{\text{salt}}{BA} + H_2O \rightleftharpoons \underset{\text{weak}}{BOH} + \underset{\text{strong}}{HA}$$

That means, cation hydrolysis is occurring.

For the reaction mentioned above, the hydrolysis constant Kh will be provided by

$$K_h = \frac{[BOH][H^+]}{[B^+]} \qquad \dots \dots \text{(i)}$$

The dissociation equilibrium for the weak base BOH is
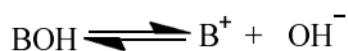
$$BOH \rightleftharpoons B^+ + OH^-$$

The dissociation constant is going to be provided by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \dots \dots \text{(ii)}$$

Ionic product of water,

$$K_w = [H^+][OH^-] \qquad \dots \dots \text{(iii)}$$

Multiplyingequation(i)with(ii)anddividingbyequation (iii),weget

$$K_h = \frac{K_w}{K_b} \qquad \dots \text{(iv)}$$

Degree of Hydrolysis of the salts of strong acid and weak base:

$$h = \sqrt{\frac{K_w}{K_b \cdot c}}$$

Example: NH_4Cl, $CuSO_4$, NH_4NO_3, $AlCl_3$, $CaCl_2$ etc.

For example, the hydrolysis of NH_4Cl can be shown as follows:

$$NH_4Cl + H_2O \rightleftharpoons NH4OH + HCl$$

$$Or \quad NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$Or \quad NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$
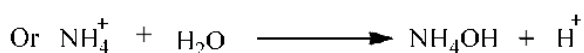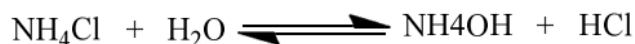
Such a salt has an acidic solution because it generates H+ ions.

6.6 Salt of strong base and weak acid – this type of solution having pH >7.

Representing the salt using BA as normal, the hydrolysis can be shown as follows:

$$BA + H_2O \rightleftharpoons BOH + HA$$
Salt $\qquad\qquad$ Strong $\quad$ Weak

$$Or \quad B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA$$

$$Or \quad A^- + H_2O \rightleftharpoons OH^- + HA$$

Original conc: $\qquad$ c $\qquad\qquad\qquad\qquad$ 0 $\qquad$ 0
Conc. at eqm: $\quad$ c(1-h) $\qquad\qquad\qquad$ ch $\qquad$ ch
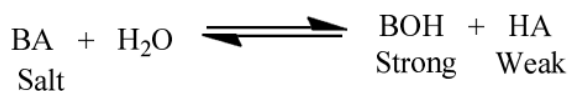
Given the process above, the hydrolysis constant Kh will be provided by

$$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{ch.ch}{c(1-h)} = \frac{ch^2}{1-h} \qquad \dots\dots (i)$$

The dissociation equilibrium for the weak acid HA is

$$HA \rightleftharpoons H^+ + A^-$$
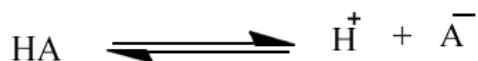
The acid HA's dissociation constant, Ka, will be determined by

$$K_w = [H^+][OH^-] \qquad \dots (iii)$$

Multiplying equation(i) with(ii) and dividing by equation(iii), we get

42

$$K_h = \frac{K_w}{K_a} \qquad\qquad \dots\dots\dots (iv)$$

We can take 1-h=1 if h is very small in relation to 1, making the equation 1 as:

$$ch^2 = K_h \ or \ h^2 = \frac{K_h}{c}$$

$$h = \sqrt{\frac{K_h}{c}}$$

Example: $CH_3COONa, Na_2CO_3, NaCN, K_2CO_3$ etc.

The hydrolysis of sodium acetate (CH_3COONa) can be shown, for example, as follows:

$$CH_3COONa + H_2O \rightleftharpoons CH3COOH + NaOH$$

$$Or \ CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$Or \ CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$
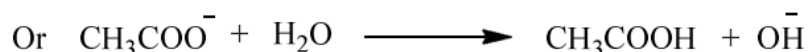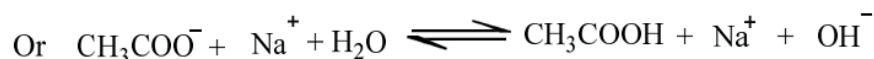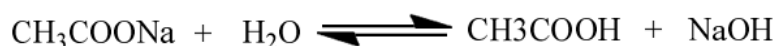
Such a salt has an alkaline solution because it generates OH- ions.

6.7 Salt of weak base and weak acid – this type of solution having pH >7.

$$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$$

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$
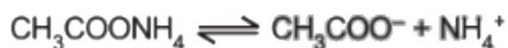
$$C(1-h) \quad C(1-h) \qquad\qquad Ch \qquad Ch$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

$$K_h = \frac{K_w}{K_a.K_b} = \frac{(Ch)(Ch)}{C(1-h)C(1-h)} = \frac{h^2}{(1-h)^2} = h^2$$

$$h = \sqrt{\frac{K_w}{K_a.K_b}}$$

Example: $CH_3COONH_4, (NH_4)_2CO_3, AlPO_4$ etc.

Such a salt has an alkaline solution because it generates OH⁻ ions.

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Or $CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH$
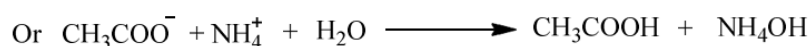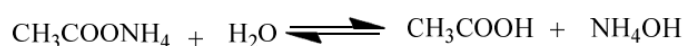
As a result, both cationic and anionic hydrolysis are involved. As a result, the final answer is impartial.

6.8 pH calculation:

6.8.1. pH of salt of weak acid and strong base:

For example:

	A^-	H_2O $\rightleftharpoons$	OH^-	$+$ HA
Original conc:	c		0	0
Conc. at eqm:	c(1-h)		ch	ch
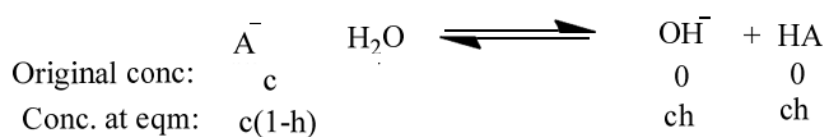
i.e,   [OH⁻]=ch

$$H^+ = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

$$[H^+] = \frac{K_w}{c}\sqrt{\frac{K_a \cdot c}{K_w}}$$

$$or \ [H^+] = \sqrt{\frac{K_w \cdot K_a}{c}}$$

$$pH = -log[H^+] = -log\sqrt{\frac{K_w \cdot K_a}{c}}$$

$$= log\left(\frac{K_w \cdot K_a}{c}\right)^{1/2}$$

$$or \ pH = -\frac{1}{2}[logK_w + logK_a - logc]$$

It is therefore possible to determine the pH of the solution by knowing the molar concentration (c) of the solution and the dissociation constant (Ka) of the weak acid involved.

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

6.8.2. pH of salt of strong acid and weak base:

$$B^+ + H_2O \xrightleftharpoons{K_h} BOH + H^+$$

Initial concentration	c	0	0
Concentration at equilibrium	c(1 − h)	ch	ch
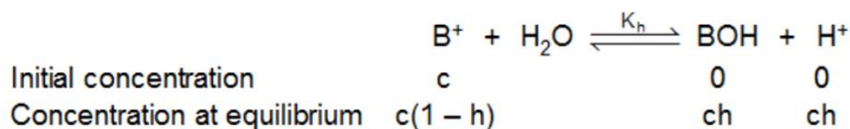
Now,

$$K_h = \frac{[H^+][BOH]}{[B^+]} = \frac{ch \times ch}{c(1-h)} = \frac{ch^2}{1-h}$$

$$K_h = ch^2 \qquad (1 - h = 1 \text{ for weak electrolyte})$$

$$h = \sqrt{\frac{K_h}{c}}$$

$$h = \sqrt{\frac{K_w}{K_b \times c}}$$

$$[H^+] = ch = c \times \sqrt{\frac{K_w}{K_b \times c}} = \left(\frac{K_w \times c}{K_b}\right)^{1/2}$$

$$pH = -\log[H^+] = -\log\left[\frac{K_w \times c}{K_b}\right]^{1/2}$$

$$pH = -\frac{1}{2}[\log K_w - \log K_b + \log c]$$

$$\boxed{pH = 7 - \frac{1}{2}[pK_b + \log c]} \text{ at 298 K}$$

6.9 Buffer solution: A solution that remains stable in pH even after adding an acid or base is referred to as a buffer solution.

Example $NaCl + H_2O \rightleftharpoons NaOH + HCL$
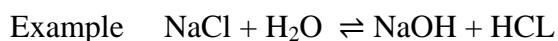
pH $= 7$ if add HCl pH$<$7

if add NaOH pH$>$7

while $CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

If add HCl $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$
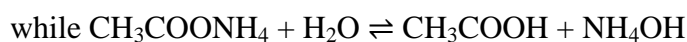
If add NaOH $NH_4^+ + OH^- \rightleftharpoons NH_4OH$ No change in pH

6.9.1 Type of buffer -

a. Simple buffer – A buffer is created by mixing a weak acid salt with a weak base, such as ammonium acetate (CH_3COONH_4).

b. Mixed buffer are two type

Acidic buffer: A weak acid and its salt, such as $CH_3COOH + CH_3COONa$, are mixed together to form the solution with strong base

Basic buffer: It is a solution made up of a weak base and its salt (such as $NH_4OH + NH_4Cl$) combined with a strong acid.

6.10 Buffer Action: Buffer action refers to a buffer solution's ability to maintain its pH level even when small amounts of an acid or base are introduced.

6.10.1 Buffer Action of Acidic Buffer:

Consider the buffering effect of an acidic buffer that contains CH_3COOH and CH_3COONa. In the aqueous solution, sodium acetate almost entirely dissociates while acetic acid dissociates to a minor level as follows:

$$CH_3COOH + H_2O \rightleftharpoons CH_3CO\bar{O} + H_3O^+$$

$$CH_3COONa \longrightarrow CH_3CO\bar{O} + Na^+$$
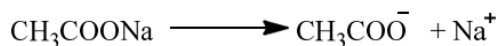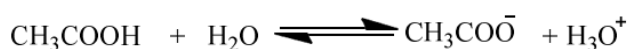
The "common ion effect" further suppresses the ionization of CH_3COOH. Consequently, the solution contains a modest amount of H+ ions and an excess of acetate (CH_3COO^-).

The H+ ions provided by the acid react with the CH_3COO^- ions in the mixed solution above, forming weakly ionized molecules of CH_3COOH, when a few drops of an acid are added.

$$CH_3CO\bar{O} + H^+ \longrightarrow CH_3COOH$$
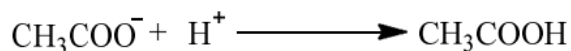
As a result, the pH of the solution and the H+ ion concentration stay relatively constant. Likewise, the addition of a few drops of a base results in the formation of weakly ionized molecules of H2O as the base's ions mix with the previously existing ions.

$$H^+ + O\bar{H} \longrightarrow H_2O$$
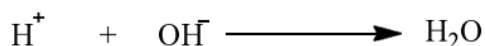
When the H+ ions are used up, the equilibrium moves to the right. In order to make up for the loss of H+ ions, more CH_3COOH dissociates. As a result, neither the pH nor the concentration of H^+ ions in the solution alter.

6.11.2 Buffer action of Basic Buffer:

Another effective buffer is a combination of equimolar solutions of ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl), the element that has almost entirely separated from the hydroxide. Undissociated NH_4OH, NH_4+, and ions are all present in the combination. Now let's talk about this mixture's buffering properties.

In the event of a significant acid addition, the base NH_4OH neutralizes the H+ ions added:

$$H^+ + NH_4OH \longrightarrow H_2O + NH_4^+$$
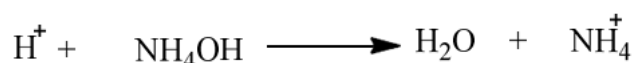
A strong base is added, and the NH4+ ions neutralize the additional ions to generate very slightly dissociated NH4OH.

It appears that in this instance, the presence of NH4+ ions is responsible for reserve acidity, and the presence of NH4OH is responsible for reserve alkalinity.

Buffer capacity: The quantity of acid or base moles needed to be added to one liter of buffer solution in order to raise the pH by one unit. Consequently

$$\text{Buffer capacity}(\beta) = \frac{\text{No. of moles of the acid or base added to \quad litre of the buffer}}{\text{Change in pH}} = \frac{n}{\Delta pH}$$

6.11 Henderson Equation:

First, let us consider a buffer solution that contains the highly dissociated salt NaA and the weak acid HA. The equation provides the hydrogen ion concentration of such a solution is:

$$[H^+] = K_a \, [\text{salt}]/[\text{acid}]$$

$$Ka = \frac{[H+][A-]}{[HA]}$$

Now taking negative log on both of the equation gives:

$$-logK_a = -log\frac{[H+][A-]}{[HA]}$$

$$-logK_a = -log[H^+] + (-log\frac{[A-]}{[HA]})$$

By the definition:

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

Thus,

$$pK_a = pH - \log\frac{[A-]}{[HA]}$$

This equation is then arranged to form the Henderson Hasselbalch equation as:

$$pH = pK_a + \log\frac{[A-]}{[HA]}$$

6.12: Application of buffer: Two buffer systems keep the pH of blood at roughly 7.4.

Primary buffers: acid/alkali sodium salt of phosphoric acid and carbonic acid/carbonate are found in plasma.

Hemoglobin, oxy-hemoglobin, and the acid/alkali potassium salt of phosphoric acid are the secondary buffers found in erythrocytes.

6.13 Uses of buffer :

- Calibration of pH meter
- Control of pH in industrial reaction
- Wine making
- Minimizing effect of acid rain
- Maintain soil pH
- Maintain water quality

Summary: The process by which a salt combines with water to yield back the base and the acid is known as salt hydrolysis.A buffer solution is one that doesn't react negatively to the addition of an acid or base, changing its pH.The amount of acid or base moles needed to be added to one liter of buffer solution in order to modify the pH by one unit is known as the buffer capacity. The quantity of a chemical in moles per liter of solution is known as its molar solubility. An indicator is a material that is typically added to the solution in the titration flask in order to determine the equivalency point.

Key wards:

Buffer solution: A solution that resists changes in pH when small amounts of an acid or a base are added to it.

Salt hydrolysis: The reaction of the ions of a salt with water, resulting in the formation of acidic or basic solutions.

Amphiprotic substances: Substances that can act as both acids and bases, depending on the conditions.

Henderson-Hasselbalch equation: An equation utilizes to determine the pH of a buffer solution.

Acid dissociation constant (Ka): Acidity strength is a measure of an acid's potency in a solution, denoted by the equilibrium constant for its ion dissociation

Base dissociation constant (Kb): Basicity strength refers to the potency of a base in a solution, quantified by the equilibrium constant for its ion dissociation..

MCQ:

1. An aqueous solution's pH is 4. [OH⁻] for it is-

(A) 10   (B)10^{-4} (C) 10^{-10} (D) 3

Answer (C)

2. The ability to withstand changes in a solution's

(A) pH,   (B) Concentration   (C) Ionization   (D) Salt concentration

Answer (A)

3. Salt that is only weakly soluble at ambient temperature has a solubility product of 4.0×10^{-6} M^2. The molar solubility of it is:

(A) $4.0 \times 10^{-6} M$ (B) $4.0 \times 10^{-6} M^2$ (C) 4.0×10^{-3} (D) $0 \times 10^{-3} M^2$

Answer: (C)

Short Answer Questions:

1. Discuss buffer capacity and its action
2. What do you mean by pH.
3. Define degree of ionization.
4. Explain ionic product of water.

Chapter: 7

Aromatic Hydrocarbon: Benzene

Objectives:

- Identify and differentiate aromatic and anti-aromatic compounds based on their structural similarities.

- Understand what characteristics aromatic substances have and how aromaticity affects chemistry.

- An overview of polycyclic aromatic compounds and aromatic heterocycles.

- Identify and be proficient in writing the electrophilic aromatic substitution mechanism.

- Capable of summarizing the electrophilic aromatic substitution reaction that includes Friedel-Craft acylation and alkylation, nitration, sulphonation, and halogenation.

7.1 Introduction:

Aromatic compounds are a class of organic compound with a common pleasant odor and unknown structures that were produced from natural resources, such as resins, balsams, and the like. Six carbons were present in the majority of simple aromatic compounds. Furthermore, aromatic compounds often created benzene or its derivatives when they underwent various forms of treatment. Benzenoid compounds, often known as aromatic compounds, were closely related to benzene.

Benzene: Faraday extracted C_6H_6 for the first time from cylinders of compressed illumination gas that came from natural sources. Hofmann discovered benzene in coal tar, which remains the primary source of benzene and its derivatives today.

7.2 Nomenclature of aromatic organic compounds:

The parent aromatic hydrocarbon benzene is called substituted benzene if a substitution is present on the benzene ring. Certain areas' trival names have been approved by the I.U.P.A.C. system.

Monosubstituted benzene: The name of the substituent is prefixed to "benzene" to name them.

Examples:

Chloro benzene   Nitrobenzene   Benzene sulphonic acid

Phenol   Aniline   Benzoic Acid   Toluene
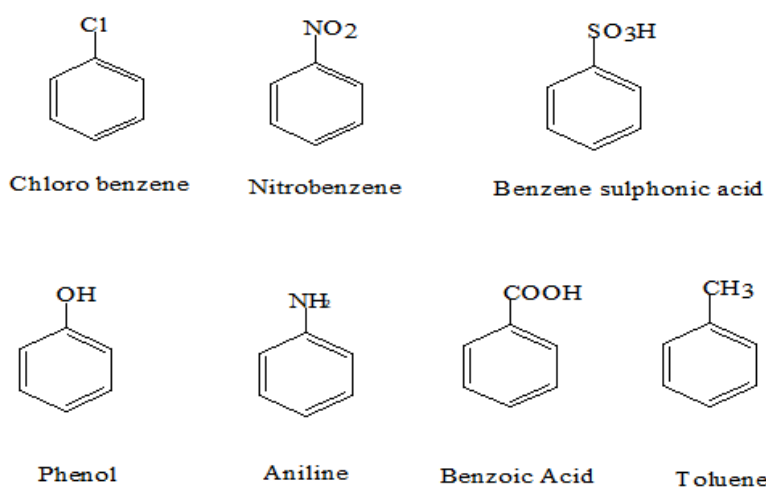
Disubstituted benzene: Two substitutents on the ring allow for the possibility of three positional isomers, which can be identified by numbers or by the symbols ortho, meta, and para.

1,2-dibromo benzene
ortho benzene

1,3-dibromo benzene
mete benzene

1,4-dibromo benzene
para benzene
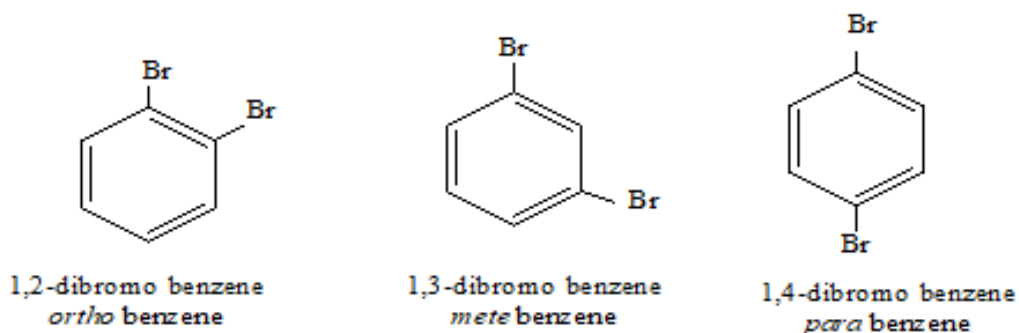
Polysubstituted benzene: Numbers are used to identify the position of substituents on benzene when three or more are present.
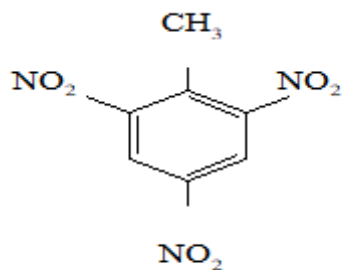
2,4,6-trinitro toluene

Fused polycyclic arenes: Numerous polycyclic arenes have one or more benzene rings fused in orthogonal orientations.
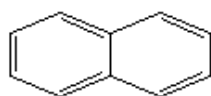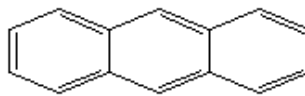
Naphthalene   Anthracene

7.3 Structure of Benzene:

7.3.1 Kekule structure and Molecular formula:

The following points lead to the deduction of benzene's structure.

a. Molecular Formula: Its empirical formula, as determined by the analytical measurement, is CH, and its molecular mass is 78.
Empirical equation is equal to CH

Empirical Weight = 12+1= 13

Weight in molecules = 78.
Empirical weight X n = Molecular weight

13 X n = 78

Given that the chemical formula is CH X 6 = C_6H_6

b. Kekule structure of benzene: Scientist Kekule revealed the unique structure of C_6H_6 in 1865. He explained that the compound exhibits two resonating structures, or Kekule

structures, but that these structures are unable to fully explain the properties of benzene. As a result, the compound has resonance hybrid, with a resonating energy of 36 K Cal/mol.

Kekule structure   Resonance hybrid
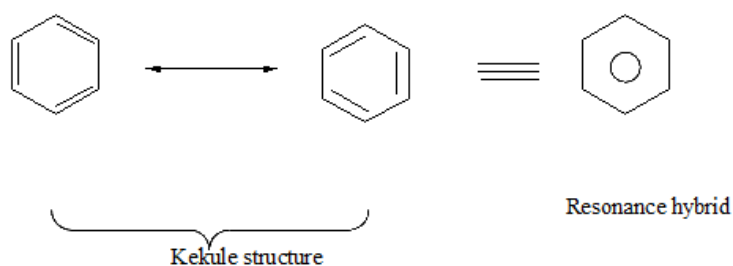
Six carbons make up its cyclic planar structure, which alternates between single and double bonds. There is a constant oscillation between the two forms because each carbon is connected to one hydrogen atom.

7.3.2 Resonance and MO picture:

Resonance structure: According to valence bond theory, benzene is a resonance hybrid of three dewar and two kekule structures, with the kekule structure accounting for the majority of the structure's contributions. Compared to other structures, benzene should be more stable as resonant structures are more stable.

Diwar benzene   Resonance hybrid
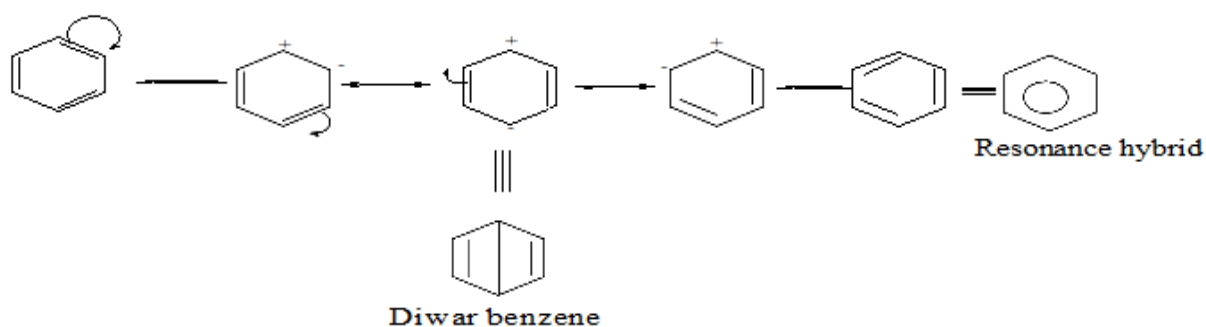
Molecular orbital (MO) picture: Benzene has six carbon atoms that are all Sp^2 hybridized. Each hybrid orbital forms a σ bond by overlapping with the s-orbitals C-C and C-H bonds. In the current structural perspective, every carbon in benzene is an Sp^2 hydride with a bond angle of 1200. Thus, it is planner and cyclical. Every carbon has a single unhybrid p orbital (pz), which is perpendicular to the σ plane and π-e-undergoes delocalization, each carbon overlap with two other carbon atoms to form a Sp^2-Sp^2 σ bond and with an H-atom to generate a Sp2-S σ bond.

C in ground state = $1S^2, 2S^2, 2p^2$ =
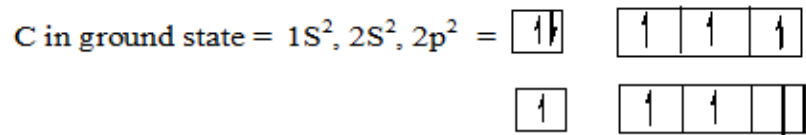
C in excited state =
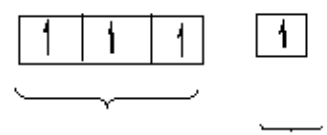
C in hybridization state =

SP2 hybrid orbital   pz unhybrid orbital

SigmaFrame work of benzene

π-Frame work of benzene:

→ pz orbital
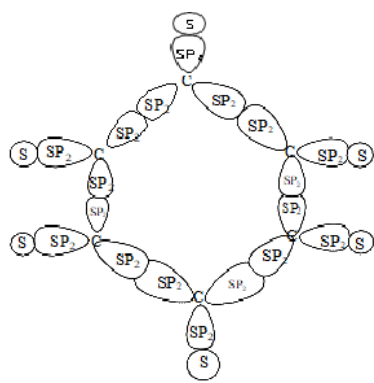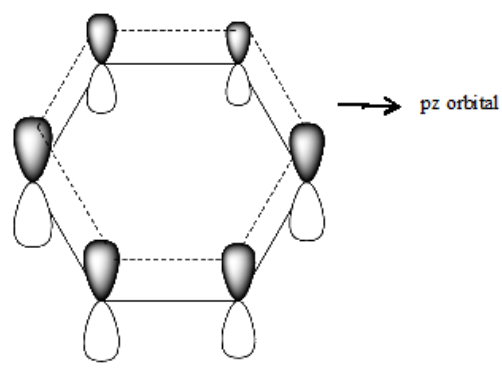
Complete structure of benzene·

H   1.39A⁰   H

H 120^0

H   1.09 A⁰
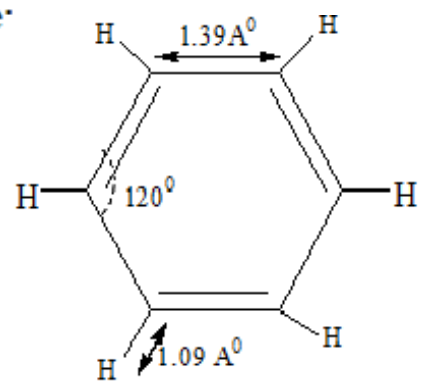
7.4 Aromaticity: Huckel's Rule:

Compared to a comparable cyclic molecule with localized electrons, an aromatic compound exhibits greater stability. On the other hand, compared to a similar cyclic compound containing localized electrons, an antiaromatic compound is less stable. In contrast to antiaromaticity, aromaticity is characterized by stability.

Aromaticcompound>cycliccompoundwithlocalized electrons>antiaromaticcompound

The unique stability of aromatic compounds—known as aromaticity—comes from their alternating single and double bonds. To be considered aromatic, a compound must meet these conditions.

1. A chemical that is aromatic is planar and cyclic.
2. Each atom in an aromatic ring has a p-orbital.
3. A molecule that is aromatic must have $(4n+2)$ π electrons in its cyclic p-orbital arrangement. This rule is called Huckel rule. An anti-aromatic system will exist if such systems have four $n\pi$ electrons.

Example:
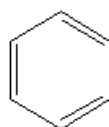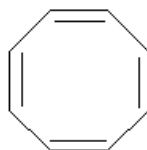
Benzene   Cyclooctatetraene

7.5 Methods for Preparing Benzene

7.5.1 From Petroleum: Naturally occurring aromatic chemicals in petroleum can be removed. Additionally, two processes are used to manufacture them from the non-aromatic components of petroleum –

i. Hydroforming or Catalytic reforming: The aromatic compounds produced by this process, which is based on the reactions of dehydrogenation, cyclization, and isomerization, has the same number of carbon atoms as the aliphatic starting components. Oxides of chromium, vanadium, and molybdenum supported on alumina are excellent catalysts that cause dehydrogenation and cyclization. In the presence of a catalyst, hydroforming is done at 480–550 degrees Celsius and 150–300 Ib/sq. in. of pressure.

Any paraffin or olefin with at least six carbon atoms arranged in a straight chain is capable of undergoing cyclization. Before the olefin cyclizes to produce the aromatic hydrocarbons, the

paraffin is first dehydrogenated to do this. The key illustrations of hydroforming are as follows:

$$CH_3.(CH_2)_4.CH_3 \longrightarrow C_6H_6 + 4H_2$$
$$\text{n-hexane} \qquad\qquad \text{Benzene}$$

$$CH_3.(CH_2)_5.CH_3 \longrightarrow C_6H_5.CH_3 + 4H_2$$
$$\text{n-heptane} \qquad\qquad \text{Toluene}$$

$$CH_3.(CH_2)_5.CH_3 \longrightarrow C_6H_4.(CH_3)_2 + C_6H_5.C_2H_5$$
$$\text{n-Octane} \qquad\qquad \text{xylene} \qquad \text{ethyl benzene}$$
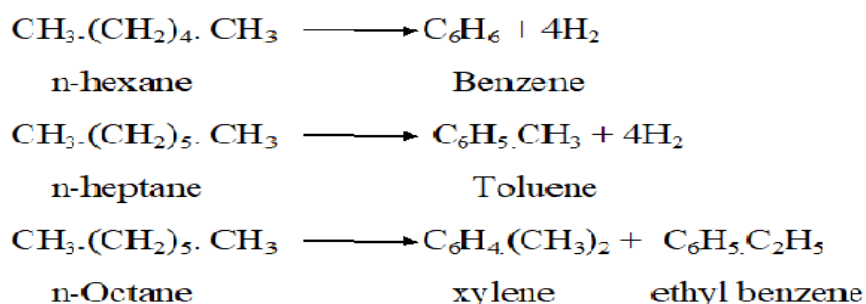
ii. High-temperature cracking in the presence of a catalyst: The charge stock can be cracked at temperatures between 650 and 680^0 when it is placed in tubes containing metallic dehydrogenation catalysts, which are the same catalysts used in hydroforming. By using this technique, numerous polynuclear hydrocarbons have been extracted from cracked paraffines, including benzene, toluene, xylenes, naphthalene, and anthracene. By producing low-molecular weight olefins and diolefins during the cracking process, which condense to form aromatic hydrocarbons, the Diel's-Alder reaction is the mechanism via which following aromatic compounds are formed-
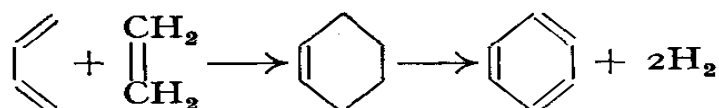
7.5.2 From sodium benzoate: Benzene is produced when sodium benzoate (C_6H_5COONa) reacts with sodalime (NaOH and CaO).

$$C_6H_5COONa + NaOH \xrightarrow{\text{CaO}} C_6H_6 + Na_2CO_3$$
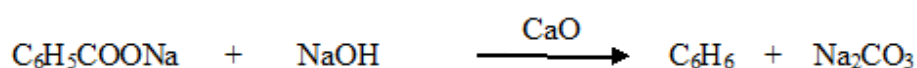
7.5.3 From Phenol: When phenol and zinc powder react yielding benzene. And zinc oxide is removed.
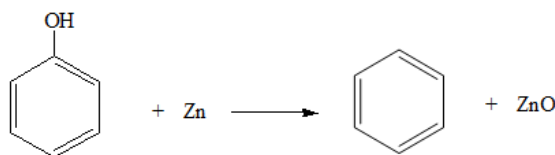
7.5.4 From Grignard Reagent: On hydrolysis Grignard, reagent (C_6H_5X) form benzene.
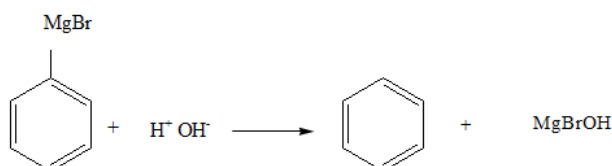
7.5.5 From Benzene sulphonic acid: Benzene is produced through the hydrolysis of benzene sulphonic acid.
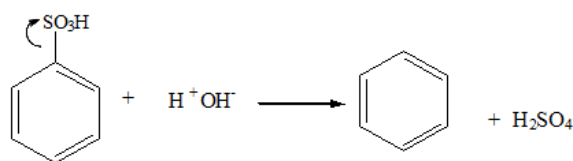
7.5.6 By polymerization reaction or acetylene: Acetylene on hydrolysis form benzene.
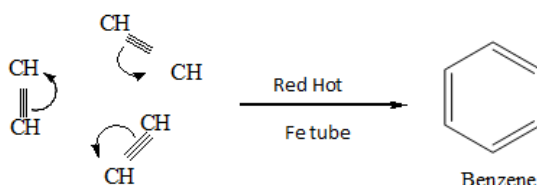
7.5.7 Industrial Preparation of benzene: Heating n-hexane to 500°C while supplying Al_2O_3 in presence of Cr_2O_3 results in cyclohexane, which on further dehydrogenates to get C_6H_6.
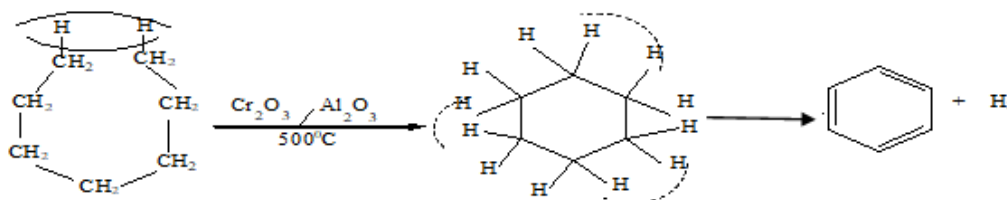
7.6 Physical properties of Benzene:

- Benzene is colorless liquid.
- It has an odd fragrance and m.p. of $5.5^{o}C$ and b.p. of $80^{o}C$.
- It is soluble in organic solvents but insoluble in liquids.
- Benzene is a good solvent itself and it works well as solvent with fats, resins, sulfur, and iodine.
- The dry cleaning industry uses it.
- Its fumes are toxic.

It is also utilized in the production of nitrobenzene, colors, medications, and motor fuel.

7.7 Chemical properties of Benzene:

7.7.1 Hydrogenation: When benzene reacts with H_2 at 160°C with a Ni catalyst present, cyclohexane is the byproduct.

57
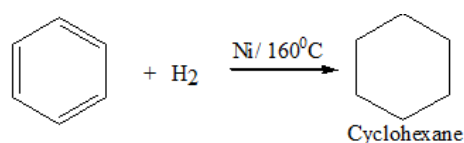
7.7.2 Ozonolysis: When benzene reacts with O_3 in the presence of CCl_4, benzene tri ozonoid is produced. Glyoxal is produced when this hydrolyzes in the presence of zinc.

benzene tri ozonoid
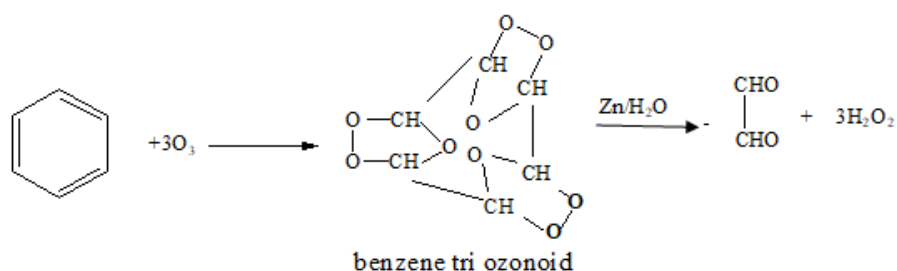
7.7.3 Chlorination: When benzene and Cl_2 react in the presence of sunlight, benzene hexa chloride ($C_6H_6Cl_6$, BHC) is the extra product. It goes by the names Lindane, 666, and gamaxine as well. It serves as an apestiside.

Benzene hexa chloride
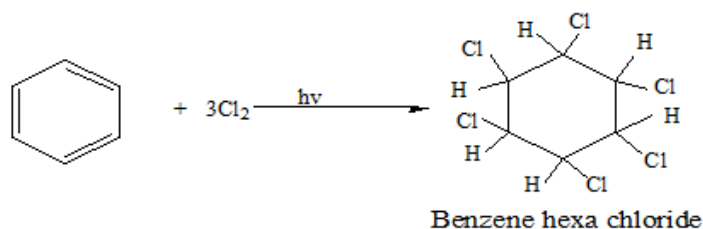
7.7.4 Electrophilic Substitution reaction:

i. Chlorination:C_6H_5Cl is produced when benzene reacts with Cl_2 in the absence of sunlight and in the presence of $FeCl_3$ or $AlCl_3$. The reaction is called electrophilic substitution reaction of benzene.
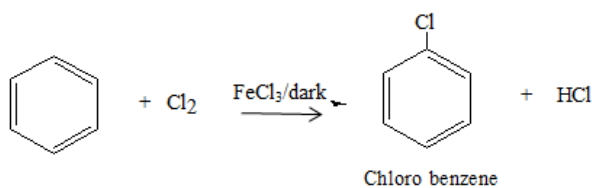
Chloro benzene
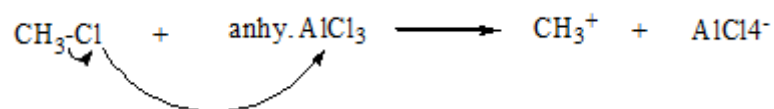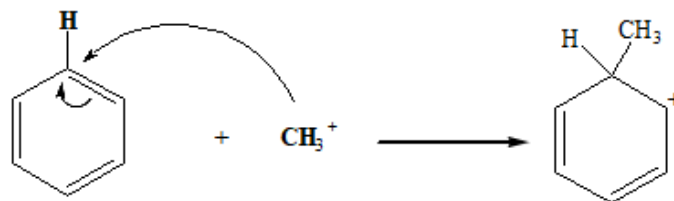
Mechanism:

Step I: Electrophile formation:
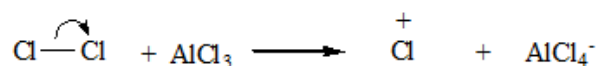
Step II: Electrophile attack to form arinium ion:

Arenium ion

Step III: Product formation:

Arenium ion

$+ H^+$
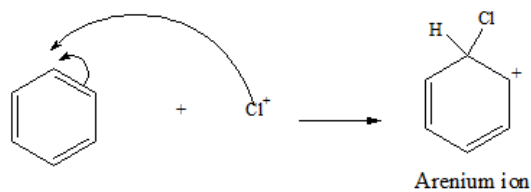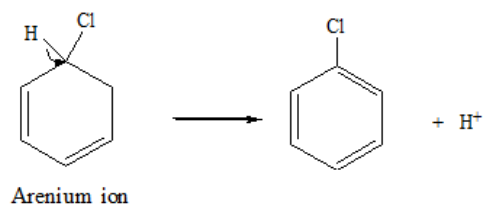
Step VI: Catalyst formation:

$$H^+ \; + \; AlCl4^- \longrightarrow AlCl_3 \; + HCl$$

ii. Nitration: Nitrobenzene is produced when benzene reacts with HNO_3 in the presence of H_2SO_4. We call this reaction nitration.

Nitro benzene

$+ \; H_2O$

Mechanism:

Step I: Electrophile formation:

$$OH\!-\!NO_2 \; + \; H_2SO_4 \longrightarrow NO_2^+ \; + HSO_4^- \; + \; H_2O$$
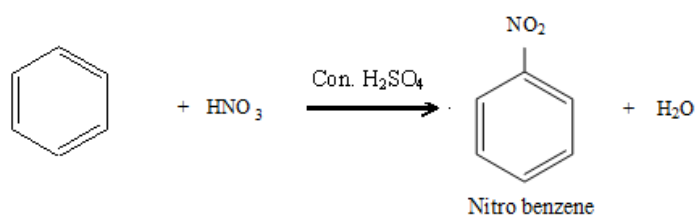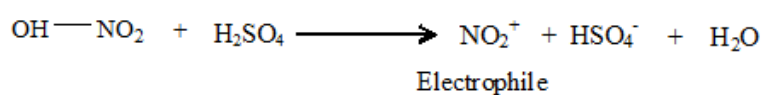
Electrophile

Step II: Attack of electrophile NO_2^+:
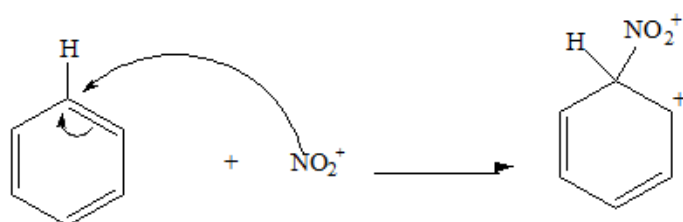
Step III: Formation of nitrobenzene:

Nitro benzene

Step IV: Catalyst formation:

$$H^+ \; + \; HSO_4^- \longrightarrow H_2SO_4$$
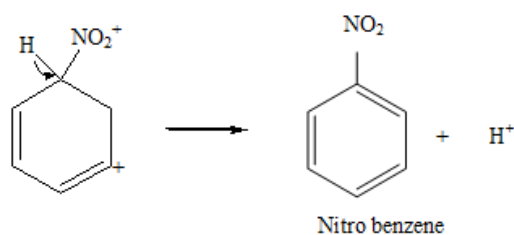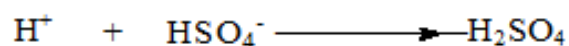
iii. Sulphonation: Benzene reacts with H_2SO_4 in the presence of H_2SO_4 to produce benzene sulphonic acid. We refer to this reaction as the sulphonation reaction.
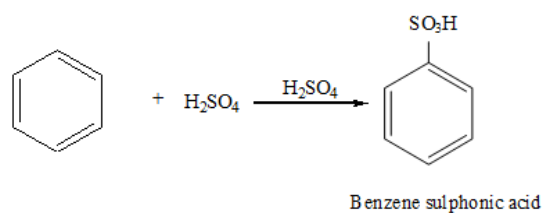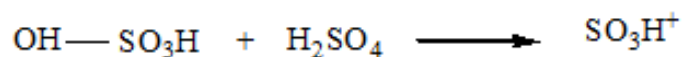
Benzene sulphonic acid

Mechanism:

Step I: Electrophile formation:

$$OH\text{---}SO_3H \; + \; H_2SO_4 \longrightarrow SO_3H^+$$

Step II: Attack of electrophile:

Step III: Product formation:

benzene sulphonic acid

Step IV: Formation of Catalyst:

$$H^+ \quad + \quad HSO_4^- \longrightarrow H_2SO_4$$
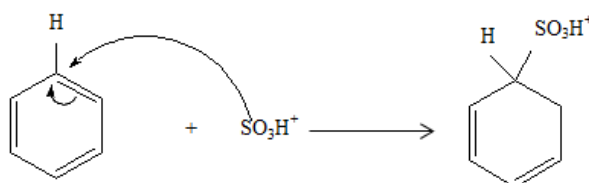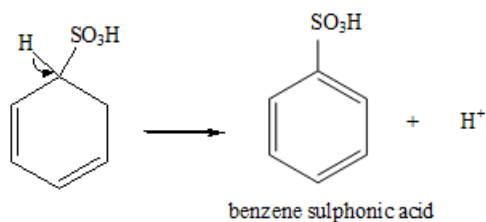
iv. Friedel Craft reaction:

    a. Friedel craft alkylation:

Benzene combines with R-X in the presence of anhydrous $AlCl_3$ to form alkyl benzene. This reaction is called Friedel Craft acylation.
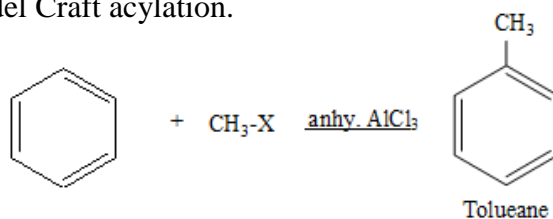
Example:
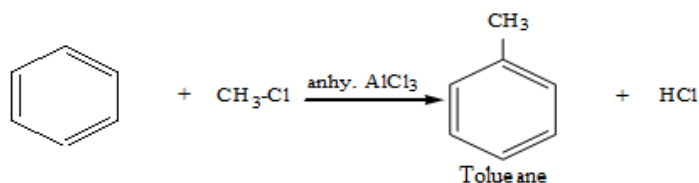
Mechanism:

Step I: Electrophile Formation:

Step II: Attack of electrophile:

Step III: Product Formation:

benzene sulphonic acid

Step IV: Catalyst Formation:

$$H^+ \ + \ AlCl4^- \longrightarrow AlCl_3 \ + \ HCl$$
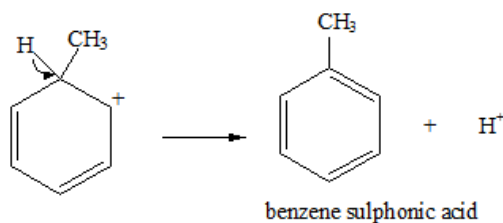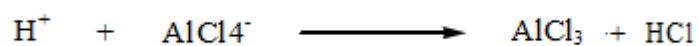
b. **Friedel craft acylation:** Aceto phenone is the product of the reaction between benzene and R-CO-X in the presence of anhydrous AlCl$_3$. Friedel Craft acylation is the term for this reaction.
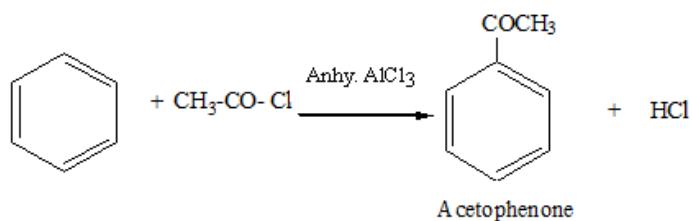
A cetophenone

Mechanism:

Step I: Electrophile Formation:
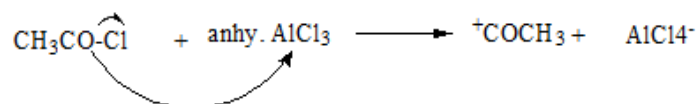
Step II: Attack of electrophile:
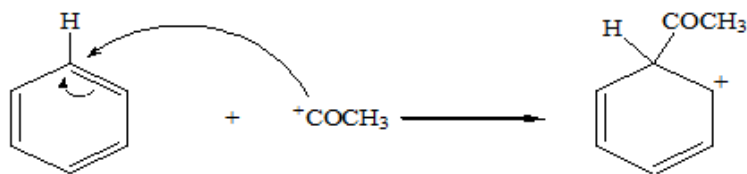
Step III: Formation of Acetophenone:

Acetophenone

Step IV: Formation of catalyst:

$$H^+ \; + \; AlCl_4^- \longrightarrow AlCl_3 \; + \; HCl$$
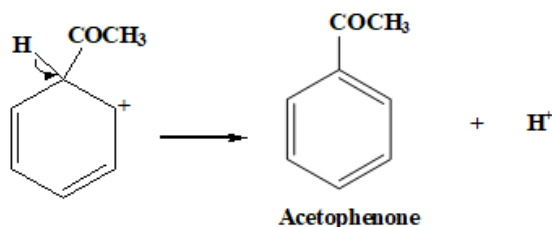
7.7.5 Birch reduction: An organic process known as the Birch reduction produces unconjugated cyclohexadienes by reducing aromatic rings by 1,4-reduction. Lithium or sodium metal conducted reductionin liquid ammonia in the presence of alcohol.

Cyclohexadienes
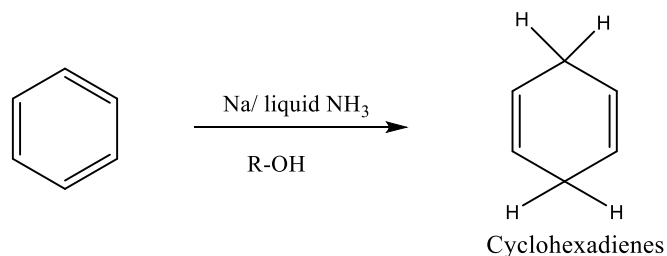
Mechanism:
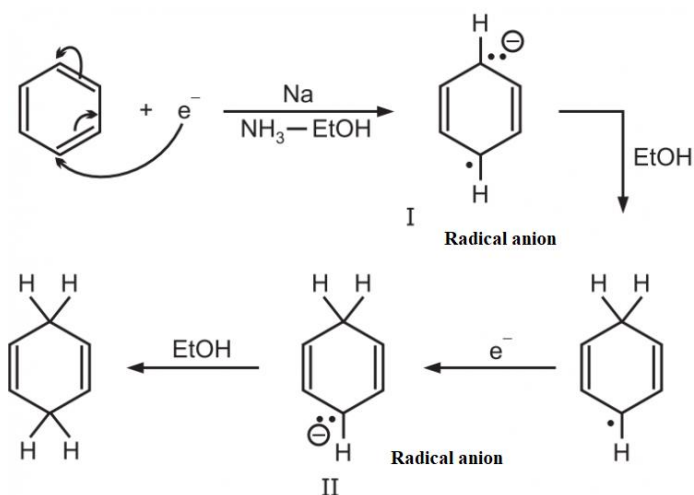
7.8 *ortho/para* ratio and orientation:

Each of the six hydrogen atoms is the same. As a result, they only create monosubstituate derivatives Under the I substituent group, the subsequent incoming electrophile will forward to the other state. So, "Directive influence" refers to the I substituent group's propensity to forward the II entering substituent group on ortho, para, or meta locations. ." I substituent group's type determines the directive influence.

Group classification based on directive influence: Based on directive influence, the groupings are divided into two classes:

(1) Ortho para Director Groups.

(2) The meta Director Groups.

The positions 2 and 6 in a C_6H_6 ring are comparable and create an ortho product.

Positions 3 and 5 are equivalent and produce a meta product.

Position 4 is special and provides a para product.

1. **Ortho&para Directing groups :** It is referred to as an o, p director if the first substituent group forwards to the incoming second substituent group, mainly to ortho and pera positions.
   Example: 57% o-nitro and 43% p-nitro phenol are formed on nitration of C_6H_5OH is nitrated.
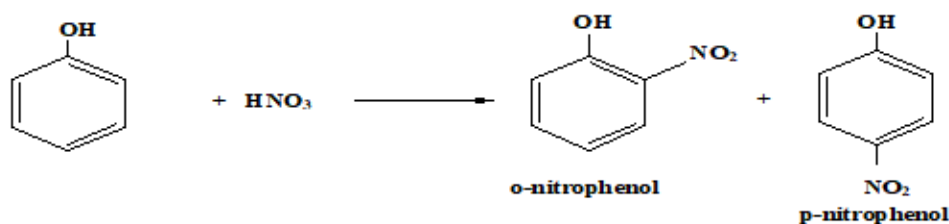

Condition for *o-p* director:

1. In nature *o,p*-directors are saturated.
2. They consist of a loan pair of electrons since they are electron rich (excluding –R groups).
3. These are ring activators, with the exception of the halogen family because of the –I effect.

Example of o,p-directors-

| Types	Strongly activator	Weak activator	Ring deactivator
Example	$-\ddot{O}H, -\ddot{N}H_2$ $-\ddot{R_2N}, -\ddot{O}R$	$-CH_3, -C_2H_5,$ $-R$	$-F, -Cl, -Br, -I$

Mechanism of o, p-director: Incoming electrophiles will more readily attack at positions o and p because the o, p-director group mechanism raises the density of e- at those locations. As a result, these activate rings.
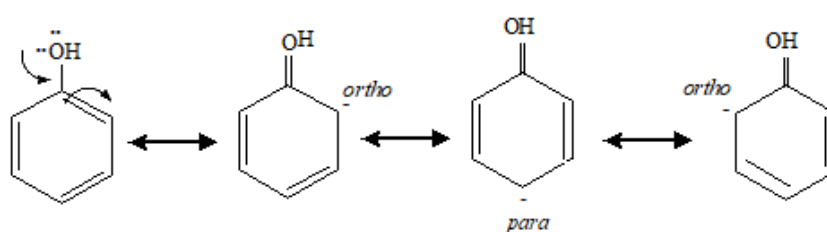
As a result, it is evident from the process above that the -OH group raises the density of e-at o and p-locations, making o and p-directors ring activators because the incoming electrophile will readily attack at these positions. However, due to the -I effect (inductive effect), halogen (-F,-Cl,-Br,-I) are ring deactivators but o,p directors.

2. **Meta-Directing Groups:** A group is called a meta director if it is the first substituent group to forward to the entering group at the meta position.

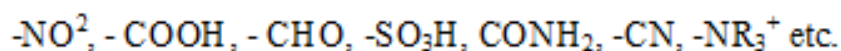   Example: 1, 3 dinitro benzene is formed when it passes through nitration.
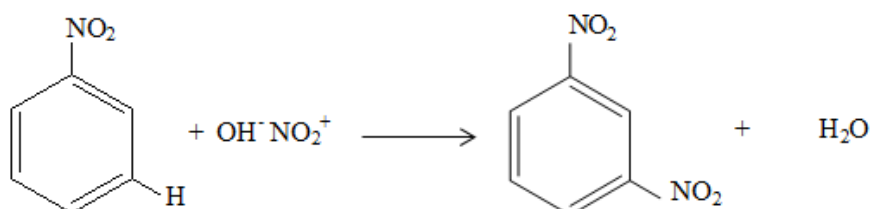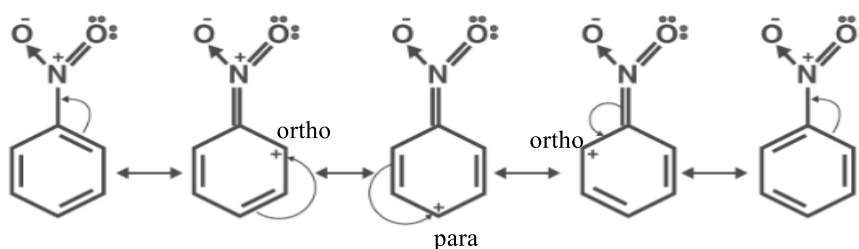

Requirement for meta directors:

(1) They are multibonded, with the exception of -NR3+.

(2) These are lacking in electrons.

(3) Because they pull the electron away from the ring and back towards themselves, these are ring deactivators.

Examples of meta directors:

$$-NO^2, -COOH, -CHO, -SO_3H, CONH_2, -CN, -NR_3^+ \text{ etc.}$$

Mechanism of meta directors:

Therefore, it is evident from the mechanism above that m-directors remove the electron from the ring. The ortho and pera positions consequently become partially + ve. The second electrophille that is approaching will therefore assault at the neutral meta location. Thus, these are both ring deactivators and meta directors.

Summary:

The term "arenes" refers to aromatic hydrocarbons. The name of benzene derivatives is dependent on the substituent that is added to benzene. The most important compound in arenes is benzene. Benzene aromaticity leads to electrophilic aromatic substitution processes; by substituent, benzene derivative is known by numerous names, including Toluene or Methylbenzene. Compared to dienes and alkenes, the nonaromatic addition products produced by their electrophilic addition processes would be far less stable. The electrophilic aromatic substitution reactions that occur most frequently include Friedel–Crafts acylation, alkylation, sulfonation, nitration, and halogenation.• Substituted benzenes, such as nitrobenzene and bromobenzene, are names for certain monosubstituted benzenes.

Lewis acid catalysts are needed for bromination or chlorination, while oxidizing agents are needed for iodination. Sulfuric acid acts as a catalyst in the nitric acid nitration process. For Friedel–Crafts acylation, which adds an acyl group to a benzene ring, one can utilize either an acyl halide or an acid anhydride. The main product in a Friedel–Crafts alkylation reaction will be the one containing the rearranged alkyl group if the carbocation produced from the

alkyl halide employed in the reaction can rearrange. The resonant structures influence the stability of benzene. We can simply determine benzene's stability by resonance. The Huckel Rule makes it simple to determine the aromaticity of benzene and a few other stable compounds.

Keywords:

Aromatic compound:A phrase used to group benzene and its derivatives is aromatic compound.

Arene: An aromatic hydrocarbon.

Aryl group:A group with the symbol Ar-that is created by taking out a H from an aromatic molecule (an arene).

Ar-: By analogy with R-for an alkyl group, the symbol for an aryl group.

Resonance energy: The energy differential between a resonance hybrid and its most stable possible contributing structure.

Polynuclear aromatic hydrocarbon:a hydrocarbon with two or more aromatic rings fused together.

Electrophilic aromatic substitution:a process wherein an aromatic ring's hydrogen is replaced by the electrophile E.

MCQ:

1. Hybridisation of c-atom in benzene is……………..
   (A) sp   (B)sp^2 (C)sp^3 (D)s^2p
   Answer (B)

2. Which is not an example of aromatic compound.
   (A)Napthalene   (B) Benzene   (C) Anthracene   (D)   Hexene
   Answer (D)

3. Benzene in the presence of iron catalyst react with chlorine to produce……..
   (A) Benzene hexachloride   (B) Benzyl chloride
   (C) Chlorobenzene   (D) Benzoyl chloride
   Answer (C)

4. Which is not an example of heterocyclic aromatic compound?
   (A)   Furan   (B)Pyridine   (C) Thiophene   (D)Tropolone

Answer (D)

5. Who explain that aromatic compounds have an odd number electron pairs which can be written mathematically as 4n+2.

   (A) Auguste Laurent   (B) Antoine Lavoisier

   (C) Jacob Berzelius   (D) Erich Huckel

   Answer (D)

Short Answer Questions:

1. How can you determine whether a substituent on Benzene is electron withdrawing?
2. How do substituents present on benzene affects electrophilic aromatic substitution?
3. Define aromatic and non aromatic compounds.
4. What do you mean by ortho/para ratio?
5. Describe the mechanism of Friedel craft alkylation and asylation reaction.

Chapter: 8

Alkyl Halides

Objectives:

- Keep in mind how alkyl halides are classified and named.
- Estimate alkyl halide solubility and relative boiling points. talk about the common applications for alkyl halides.
- Alkyl halides, also known as haloalkanes, are made via a variety of mechanisms; discuss these processes and the various reactions that result.
- Alkyl halide structures can be connected to many reaction types.
- Use stereochemistry in order to understand the reaction process.
- Find the rate law for the SN1, SN2, E1, and E2 reactions, then forecast the mechanism using the rate equation or reaction data.

8.1 Introduction:

Alkyl halide (haloalkane) is created when a aliphatic hydrocarbon has one or more hydrogen atoms replaced by halogen atoms. On the sp3 hybridized carbon atom of an alkyl group, halogen atom(s) are bonded to form haloalkanes. Lots of halogen-containing

Naturally occurringorganic compound, some of which have therapeutic value. In daily life as well as industry, many groups of compounds have extensive applications. They find application as starting materials for the synthesis of a diverse array of organic compounds and as solvents for comparatively non-polar substances. Typhoid disease can be effectively treated with the antibiotic chloramphenicol, which contains chlorine and is generated by soil bacteria. The key preparation techniques, chemical and physical characteristics, and applications of alkyl halide will all be covered in this unit.

8.2 Classification:

8.2.1 Classification based on the number of halogen atoms:

1. **Monohalogen compounds:** Monohalogen compounds are those that have just one halogen in their molecule.

$CH_3-CH_2-CH_2-Cl$
chloro propane

$CH_3-CH_2-CH-CH_3$
          |
          Cl
chloro butane
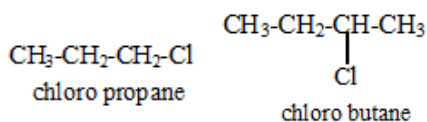
2. **Dihalogen compounds:** Dihalogen compounds are compounds that have two halogens in their structure.

CH_2—CH_2—CH_2
  | |
  Cl   Cl
dichloro propane
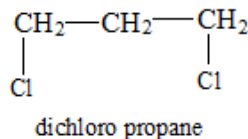
3. **Polyhalogen compounds:** Compounds which have more than three halogen atoms in their molecule.

CH_2—CH—CH_2
  | | |
  Cl   Cl   Cl
trichloro propane

CH_2—CH—CH—CH_2
  | | | |
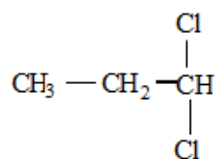 Cl   Cl   Cl   Cl
tetrachloro butane
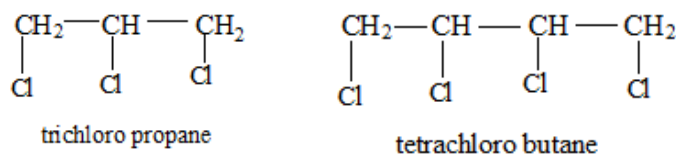
8.2.2 Classification based on the position of halogen atoms:

**1. Vicinal dihalide:** Vicinal dihalides are compounds that have two halogens on adjacent carbons.

CH_2—CH—CH_3
  | |
  Cl   Cl
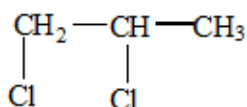
2. Geminal dihalide: Gem dihalides are compounds that have two halogen are present at on same carbon atom in molecule.

$$CH_3 — CH_2 — \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{CH}}$$
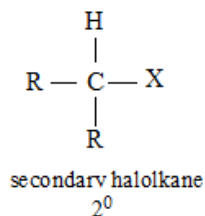
8.2.3 Classification based on nature of carbon atom attached to halogen atom: Alkyl halides are divided into three categories based on the kind of carbon that is joined to the halogen atom.
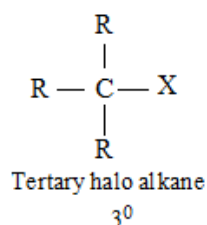
1. Primary alkyl halide: Halogen attached to 1° carbon atom.
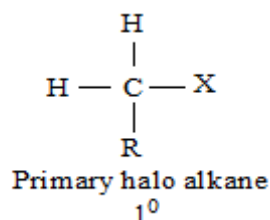
$$H — \overset{\displaystyle H}{\underset{\displaystyle R}{C}} — X$$

Primary halo alkane
1^0

2. Secondary alkyl halide: Halogen attached to 2^0 carbon atom.

$$R — \overset{\displaystyle H}{\underset{\displaystyle R}{C}} — X$$

secondarv halolkane
2^0

3. Tertiary alkyl halide: Halogen attached to 3^0 carbon atom.

$$R — \overset{\displaystyle R}{\underset{\displaystyle R}{C}} — X$$

Tertary halo alkane
3^0

Here R = Alkyl group CH_3, C_2H_5, C_3H_7 etc.

X = Halogen atom (Cl, Br, I etc.)

8.3 Nomenclature: There are two ways to give the nomenclature to alkyl halides

8.3.1 Common System: The alkyl group that is bonded to the halogen atom in this system is given the name first. An relevant word such as fluoride, bromide, or chloride follows this. Examples:

S.No.	Compound	Common name
1.	CH_3-Cl	Methyl chloride
2.	CH_3-CH_2-Cl	Ethyl chloride
3.	CH_3-CH_2-CH_2-Cl	n-propyl chloride

4.	CH_3——CH——CH_3
	           |
	           Cl
		iso-propyl chloride

5.	CH_3-CH_2-CH_2-CH_2-Cl	n-butyl chloride

6.	CH_3-CH_2-CH-CH_3
	               |
	              Cl
		Sec-butyl chloride

7.	CH_3-CH-CH_2-CH_2Cl
	        |
	       CH_3
		Iso-butylchloride

8.3.2 IUPAC System:
Rules are as follow:

1. Choose the carbon chain with the halogen atom that is the longest.
2. Assign the lowest possible number to the carbon that is carrying the halogen atom in the chain.
3. Use a number to represent the halogen atom's location together with the fluoro, chloro, and bromo symbols.
4. List more substitutes and use numbers to denote their positions.
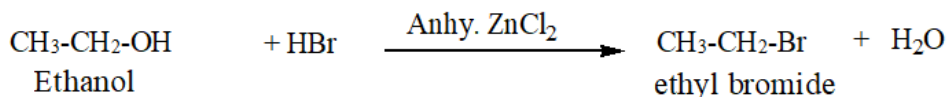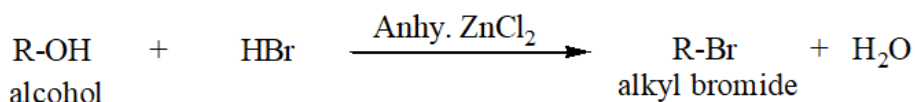
Example:

S.No.	Compound	Common name
1.	CH_3-Cl	1-Chloro methane
2.	CH_3-CH_2-Cl	1-Chloro ethane
3.	CH_3-CH_2-CH_2-Cl	1-Chloro propane

4.	CH_3—CH—CH_3
	        |
	        Cl
		2- Chloro propane

5.	CH_3-CH_2-CH_2-CH_2-Cl	1- Chloro butane

6.	CH_3-CH_2-CH-CH_3
	           |
	          Cl
		2-Chloro butane

7.	CH_3-CH-CH_2-CH_2Cl
	     |
	    CH_3
		3-Methyl-1chlorobutane

8.4 Formation of Alkyl halides: The following methods can be used to prepare alkyl halides:

8.4.1 Halogenation of Alkanes: When alkanes react with Cl_2 or Br_2 at 400°C or in the presence of UV light, they produce polyhalogen derivatives as well as alkyl halides.

$$CH_4 + Cl_2 \xrightarrow{\text{Sun light or UV light}} CH_3-Cl$$

8.4.2 From Alkenes: Alkyl halides are produced by adding halogen acids to alkenes. The Markownikoff's rule governs the addition of hydrogen halides to unsymmetrical alkenes.

$$CH_2{=}CH_2 \;+\; HBr \longrightarrow CH_3\text{-}CH_2\text{-Br}$$
Ethene   1-bromo ethane

$$CH_3\text{-CH}{=}CH_2 \;+\; HBr \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-Br}$$
Propene   1- bromo- propane

CH_3-CH=CH_2 + HBr →

        CH_3-CH_2-CH_3.   80% (major)
             |
            Br
       2 - bromo- propane

        CH_3-CH_2-CH_2-Br   20% (minor)
       1- bromo- propane

Markownikoff's rule: Addition of HX to unsymmetrical alkenes, the nehative part of reagent goes to carbon atom containing least no. off H-atom across the C=C.

Note: In presence of peroxide as a catalyst, HBr adds to unsymmetrical alkenes against to Markownikoff's rule which is called Anti-markownikoff's rule and also known as "Kharasch effect"

$CH_3-CH=CH_2 + HBr$ $\xrightarrow{peroxide}$

$CH_3-CH_2-CH_{;3}$.
  |
  Br   20% (minor)
2 - bromo- propane

$CH_3-CH_2-CH_2-Br$ 80% (major)
1- bromo- propane

Propene
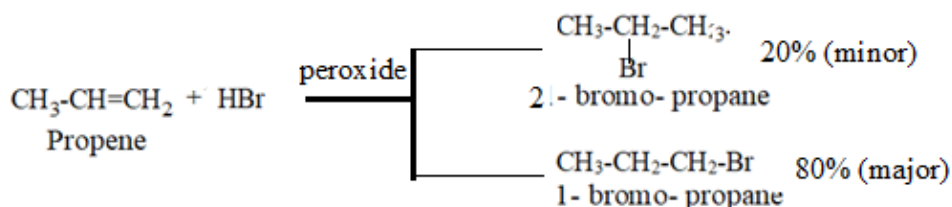
8.4.3 From Alcohol:

i. Reaction with Hydrogen halide: In the presence of anhydrous $ZnCl_2$, any alcohol reacting with hydrogen halide produces an alkyl halide in proportion.

$R-OH$ $+$ HBr $\xrightarrow{\text{Anhy. } ZnCl_2}$ $R-Br$ $+$ H_2O
alcohol   alkyl bromide

CH_3-CH_2-OH $+ HBr$ $\xrightarrow{\text{Anhy. } ZnCl_2}$ CH_3-CH_2-Br $+$ H_2O
Ethanol   ethyl bromide

ii. Reaction with PCl$_5$ (Phosphorus pentachloride): Alcohol eliminates phosphoryl chloride (POCl$_3$) when it reacts with PCl5 to produce alkyl halide.

$R-OH$ $+$ PCl_5 $\longrightarrow$ $R-Cl$ $+$ $POCl_3$ $+$ HCl
alcohol   alkyl chloride

CH_3-CH_2-OH $\longrightarrow$ CH_3-CH_2-Cl $+ POCl_3 + HCl$
Ethanol   Ethyl chloride
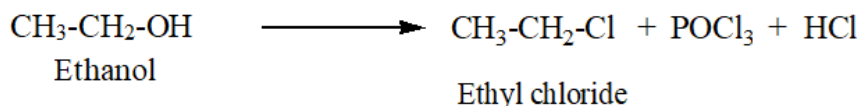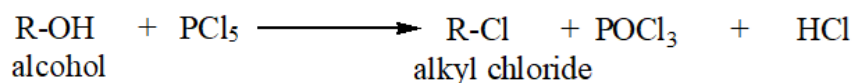
iii. Reaction with PCl$_3$ (Phosphorus trichloride): Alcohol removes H_3PO_4 when it reacts with PCl$_3$ to produce an alkyl halide.

$$3\ R\text{-}OH\ +\ PCl_3 \longrightarrow 3\ R\text{-}Cl\ +\ H_3PO_4$$
alcohol alkyl chloride

$$3\ CH_3\text{-}CH_2\text{-}OH \longrightarrow 3\ CH_3\text{-}CH_2\text{-}Cl\ +\ H_3PO_4$$
Ethyl chloride
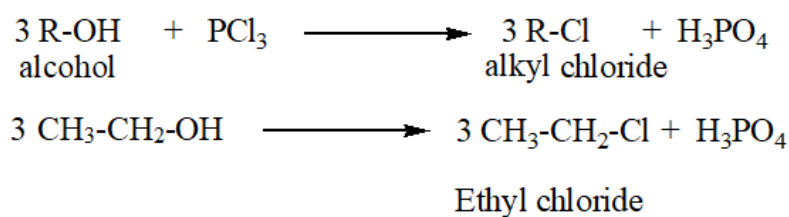
iv. Reaction with SOCl₂ (Thionyl chloride): Alcohol removes HCl and CO₂ when it reacts with SOCl₂ to produce an alkyl halide.

$$R\text{-}OH\ +\ SOCl_2 \longrightarrow R\text{-}Cl\ +\ SO2\ +\ HCl$$
alcohol alkyl chloride

$$CH_3\text{-}CH_2\text{-}OH\ +\ SOCl_2 \longrightarrow CH_3\text{-}CH_2\text{-}Cl\ +\ SO2\ +\ HCl$$
Ethanol Ethyl chloride
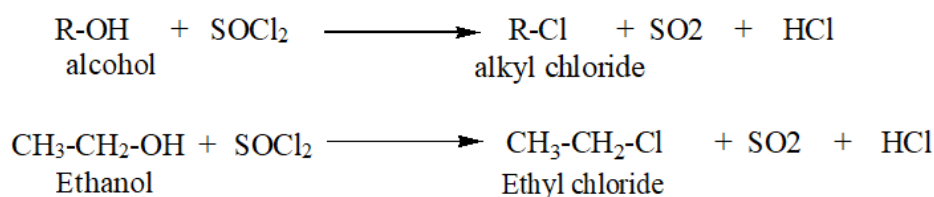
8.4.4 From halogen exchange reaction: When making alkyl iodides, this process is quite useful. Alkyl bromide is form when alkyl bromide or chloride heated in acetone along with a concentration of sodium iodide.

$$CH_3\text{-}CH_2\text{-}Br\ +\ Na \xrightarrow{Acetone/C_2H_5I} CH_3\text{-}CH_2\text{-}I\ +\ NaBr$$
Ethyl bromide Ethyl iodide
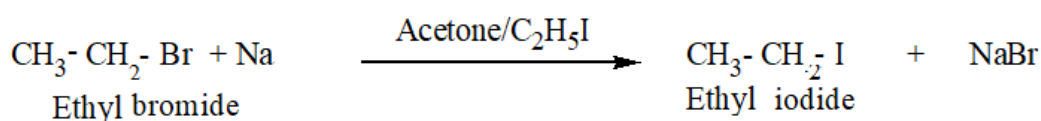
Alkyl fluorides can also be made by treating inorganic fluorides to alkyl chloride or bromide.

$$2CH_3\text{-}Cl\ +\ Hg_2F_2 \longrightarrow 2CH_3\text{-}F\ +\ Hg_2Cl_2$$
Methyl chloride Methyl fluoride
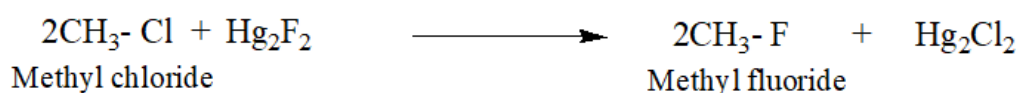
8.5 Physical Properties of Alkyl halides:

1. The lower alkyl halides like CH_3F, CH_3Cl, CH_3Br and C_2H_5Cl are gases at room temperature and other alkyl halides upto C-18 are present in liquid state.

2. Liquid alkyl halides having higher boiling point.

3. Haloalkanes are polar in nature but not immiscible in water because haloalkanes does not have ability to form hydrogen bond with water molecule.

4. In comparison to their parent hydrocarbons, haloalkanes have greater melting and boiling temperatures. This is because halo compounds have-

(i)   Larger molecular masses than parent hydrocarbons, which results in larger van der Waals forces of attraction

(ii)   Intermolecular dipole-dipole interaction, as the following example illustrates:
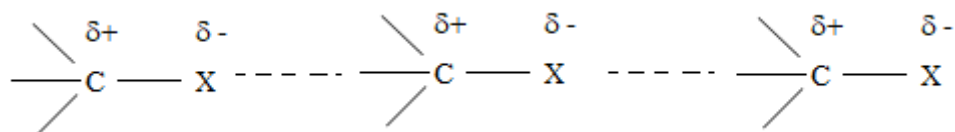
5. For a particular alkyl halide as the size of halogen atom increases (from fluoro to iodo) there boiling point increases.

8.6 Chemical reaction of Alkyl halides:

8.6.1 Formation of alcohols or Hydrolysis:

a. When alkyl halides are boiled with aqueous NaOH or KOH they are hydrolysed to give alcohols.

$$\underset{\text{alkyl halide}}{R-X} + NaOH(aq.) \xrightarrow{\Delta} \underset{\text{alcohol}}{R\text{-}OH} + NaX$$

$$\underset{\text{Ethyl chloride}}{CH_3\text{-}CH_2\text{-}Cl} + NaOH(aq.) \xrightarrow{\Delta} \underset{\text{Ethyl alcohol}}{CH_3\text{-}CH_2\text{-}OH} + NaCl$$
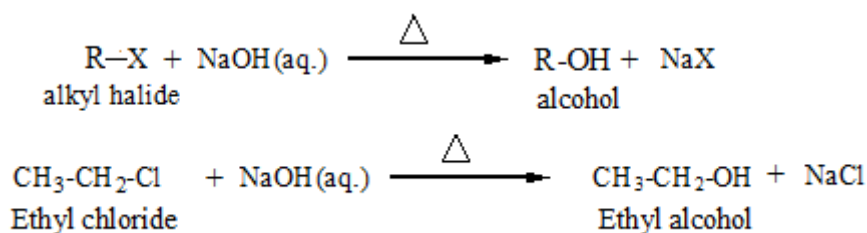
b. Alkyl halides reacts with moist Ag_2O gives corresponding alcohols.

$$\underset{\text{alkyl halide}}{2\ R-X} + NaOH(aq.) \longrightarrow \underset{\text{alcohol}}{2\ R\text{-}OH} + 2\ AgX \downarrow$$

$$\underset{\text{Ethyl bromide}}{2\ CH_3\text{-}CH_2\text{-}Br} + Ag_2O + H_2O \longrightarrow \underset{\text{Ethyl alcohol}}{2\ CH_3\text{-}CH_2\text{-}OH} + 2\ AgBr \downarrow$$
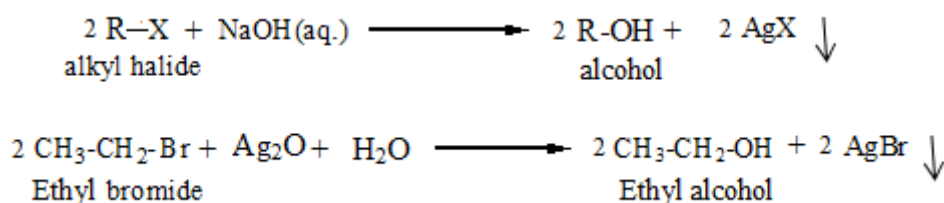
8.6.2 Williamson ether synthesis: When alkyl halides are heated with Sodium alkoxides gives corresponding ethers. This reaction known as Williamson ether synthesis.

$$R\text{-}Br + R^1\text{-}O^- Na^+ \xrightarrow{\text{Dry ether}} R\text{-}O\text{-}R^1 + NaBr$$

Alkyl bromide   Sodium alkoxide   Ether

$$CH_3\text{-}Br + CH_3\text{-}O^- Na^+ \xrightarrow{\text{Dry ether}} CH_3\text{-}O\text{-}CH_3 + NaBr$$

methyl bromide   Sodium methoxide   Dimethyl ether

$$\underset{\text{Isopropyl bromide}}{CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}Br} + \underset{\text{Sodium ethoxide}}{C_2H_5\text{-}O^- Na^+} \xrightarrow{\text{Dry ether}} \underset{\text{ethyl isopropyl ether}}{CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}O\text{-}C_2H_5} + NaBr$$
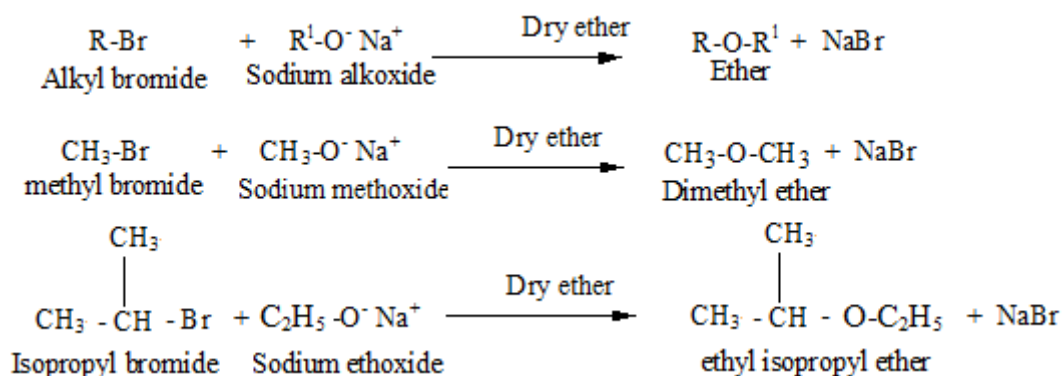
8.6.3 Formation of alkane nitrile or alkyl cyanides: When alkyl halides are heated with aq. Alcoholic KCN, alkyl cynides are formed as major product.

$$R\text{-}X + KCN(aq.) \xrightarrow{\Delta} R\text{-}CN + KX$$

$$\underset{\text{Ethyl chloride}}{CH_3\text{-}CH_2\text{-}Cl} + KCN(aq.) \xrightarrow{\Delta} \underset{\text{ethyl cyanide}}{CH_3\text{-}CH_2\text{-}CN} + KCl$$
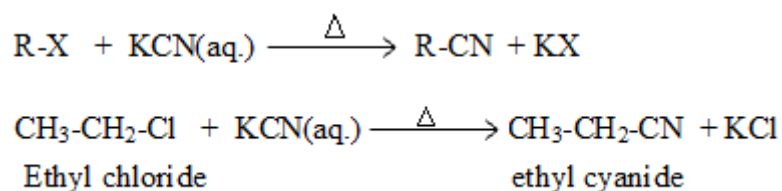
Note: KCN is an ionic compound. The lone pair electrons of the carbon atom involved in the nucleophilic attack.

8.6.4 Formation of alkane isonitrile and alkyl isocynide: When alkyl halide are warmed with alcoholic silver cyanide gives respective alkyl isocyanides.

$$R\text{-}X + \underset{\text{silver cyanide}}{AgCN} \xrightarrow{\Delta} \underset{\text{alkyl isonitrile}}{R\text{-}NC} + AgX$$

$$\underset{\text{Ethyl chloride}}{CH_3\text{-}CH_2\text{-}Br} + AgCN \xrightarrow{\Delta} \underset{\text{propane isonitrile}}{CH_3\text{-}CH_2\text{-}NC} + AgBr$$
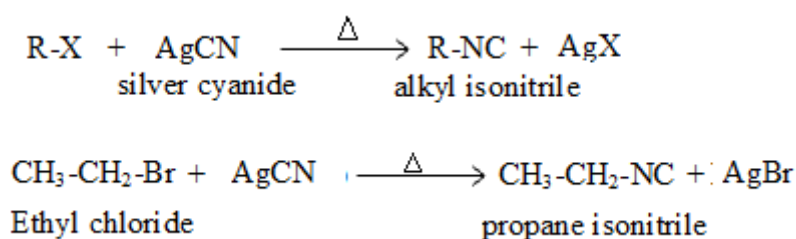
Note: AgCN is covalent in nature. Only nitrogen atom has lone pair electrons involve in nucleophilic attack.

8.6.5 Formation of nitroalkane: When alkyl halides are warmed with alcoholic silver nitrite $(AgNO_2)$ gives respective nitroalkane.

$$R\text{-}X \ + \ AgNO_2 \ \xrightarrow{\Delta} \ R\text{-}NO_2 \ + \ AgX$$

silver nitrite   nitroalkane

$$CH_3\text{-}CH_2\text{-}Br \ + \ AgNO_2 \ \xrightarrow{\Delta} \ CH_3\text{-}CH_2\text{-}NO_2 \ + \ AgBr$$

Ethyl chloride   nitro ethane
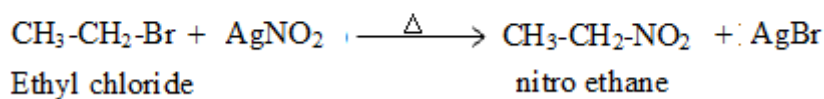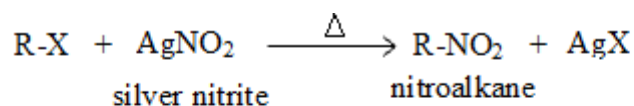
8.6.6 Formation of alkyl nitriles: When alkyl halides are warmed with alcoholic potassium nitrite (KNO_2) gives respective alkyl nitrite.

$$R\text{-}X \ + \ KNO_2 \ \xrightarrow{\Delta} \ R\text{-}O\text{-}N\text{=}O \ + \ AgX$$

Alkyl nitrite

$$CH_3\text{-}CH_2\text{-}Br \ + \ KNO_2 \ \xrightarrow{\Delta} \ CH_3\text{-}CH_2\text{-}ONO \ + \ AgBr$$

Ethyl chloride   ethyl nitrite
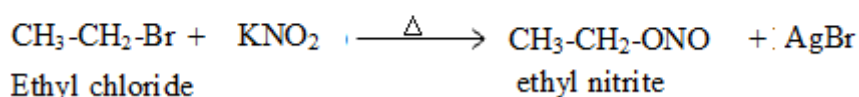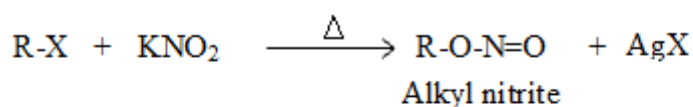
Note: KNO_2 is ionic in nature. The electron of oxygen atom involved in nuclephilic attack. $AgNO_2$ is covalent in nature. The lone pair electrons of less electronegative nitrogen atom involved in nucleophilic attack.

8.7 Nucleophilic substitution reaction types: Haloalkanes undergo nucleophilic substitution reaction proceeds through different mechanism namely SN^1 & SN^2.

8.7.1 Substitution Nucleophilic unimolecular Reaction (SN^1 Reaction):

Tertiary alkyl halides undergo substitution by SN1 mechanism. When tertiary alkyl halide is warmed with aqueous NaOH or KOH gives tertiary alcohol, where the rate of reaction depends only on the concentration of alkylhalide, but not on $Conc^n$ of nucleophile (NaOH).

Example: When a tertiary butyl bromide is wamed with aqueous NaOH or KOH, it undergoes nucleophilic substitution reaction gives t-butyl alcohol.

$$\underset{\text{tert-butyl bromide}}{CH_3\text{---}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{---}Br} \ + \ NaOH\ (aq.) \ \xrightarrow{\Delta} \ \underset{\text{tert-butanol}}{CH_3\text{---}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{---}OH} \ + \ NaBr$$
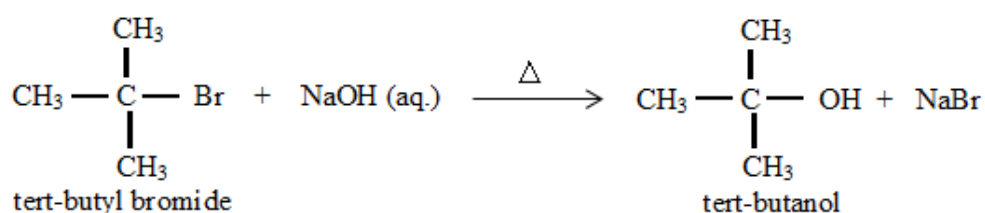
The rate of the reaction is given by

Rate α [ter. Butyl bromide]$^1\times$[NaOH]^0

Rate $= K$ [ter. Butyl bromide]$^1\times$[NaOH]^0

Order $= 1+0=1$

Mechanism: The mechanism involves two steps.

Step 1: In the first step t-butyl bromide undergoes slow dissociation forming tertiary butyl carbonium ion and bromide (Br⁻) ion.

First step is slow step, which determine rate of reaction.
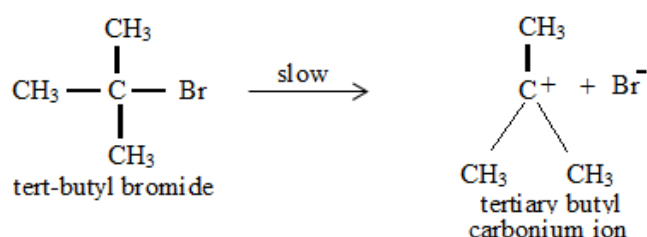
Step 2: The nucleophilic OH⁻ can attack the planar carbonium ion from either side or direction forming two enantiomers with inversion and retention of configuration. Enatiomers with inverted configuration is predominant product.
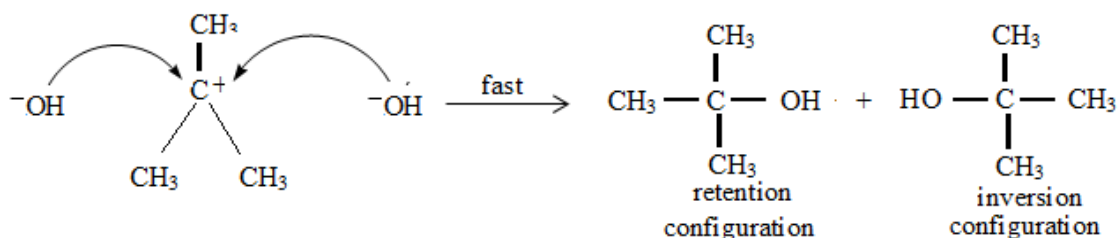
The mechanism above makes it evident that only one reactant—butyl bromide—occurs in the slowest stage; as a result, the rate of reaction is dependent on its concentration, designating it as a first-order reaction. The uni-molecular nucleophilic substitution (SN^1) reaction is the name given to this process.

Mathematically:

$$\frac{dx}{dt} = K\left[\text{Alkyl halide}\right]$$

Factors affecting the SN^1 reaction:

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1. Structure of alkyl halide: The rate of SN^1 reaction depends on the stability of carbocation, higher is the rate of SN^1 reaction. The stability of the carbocation are in the order

$$\text{Benzyl} > \text{Allyl} > 3^0 > 2^0 > 1^0 > {}^+CH_3$$
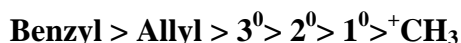
2. Nature of the leaving group: Better the leaving group, easier is the formation of carbocation, higher the rate of reaction.

$$\text{R-I} > \text{R-Br} > \text{R-Cl}$$

3. Nature of the Nucleophile: Weaker nucleophile can favour the SN^1 reaction.

4. Concentration of nucleophile: Lower concentration of the nucleophile favour the SN^1 reaction. (since nucleophile not take part in the slow step reaction)

5. Nature of solvent: The more polar solvent favour the SN^1 reaction. Greater the polarity of the solvent, greater is the ionising power of the solvent. More easily cation formed.

Order of reactivity in case of $H_2O > CH_3OH > C_2H_5OH > CH_3COOH$

8.7.2 Substitution Nucleophilic Bimolecular Reaction (SN^2 Reaction):

Primary alkyl halides often follow this kind of one-step process. Due to the repulsion between nucleophilic and halogen, in this kind of mechanism, Nu-attacks the carbon connected to the halogen atom from the other side of the halogen carrying carbon atom. When a primary alkyl halide is warmed with aq. NaOH or KOH gives primary alcohol.

$$\text{R-X} + \text{NaOH} \xrightarrow{\text{heat}} \text{R-OH} + \text{NaX}$$
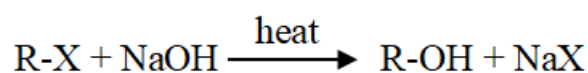
In this reaction rate of reaction depends on the concentration of both alkyl halide and aq. NaOH or KOH.

So the rate of reaction is given by:

Rate α $[\text{R-X}]^1 \times [\text{NaOH}]^1$

Rate $= K [\text{R-X}]^1 \times [\text{NaOH}]^1$

Order $= 1+1=2$

Mathematically:

$$\frac{dx}{dt} = K \left[\text{Alkyl halide} \right] \left[\text{KOH} \right]$$

Hence it is Bimolecular reaction or 2nd order reaction. Example when methyl bromide is warmed with NaOH gives methyl alcohol. The reaction follows SN^2 mechanism, which occurs in a single step.

$$CH_3\text{-}Br + NaOH \xrightarrow{\text{heat}} CH_3\text{-}OH + NaBr$$
$$\text{methyl bromide} \qquad\qquad \text{methyl alcohol}$$
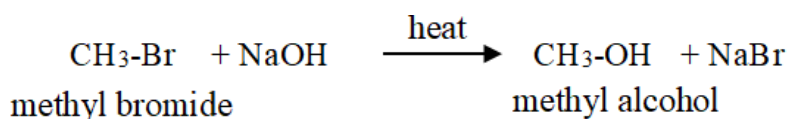
Mechanism: The nucleophile OH- attacks the primary-carbonation from the opposite side of the outgoing nucleophile (Br⁻) forming a transition state that is the new bond between the carbon and nucleophile is slowly formed, simultaneously the C-Br bond becomes gradually weakened. The half bonded state is known as " transition state". As the transition state is unstable it decomposes giving an invert product

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$
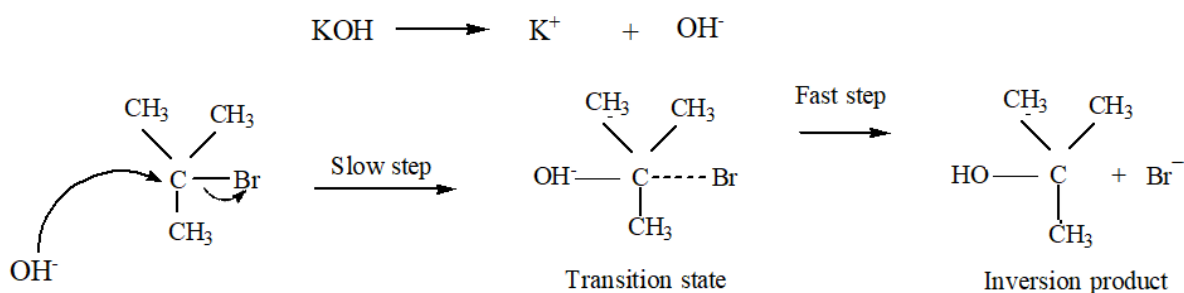
Formation of KBr:

$$K^+ + Br^- \longrightarrow KBr$$
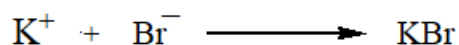
The halide ion leaves the transition state rapidly and the product has inverted configuration (walden incersion). The reaction occurs in single step in which the slow step involves both alkyl halide and NaOH. Hence the rate of reaction depends on the concentration of both primary alkyl halide and NaOH. It is a bimolecular reaction or 2nd order reaction.

Factor affecting SN^2 reaction:

1. Structure of alkyl halide (steric effect): Less bulkier group, more is the reactivity of the alkyl halide towards SN^2 reaction.

$$CH_3\text{-}X > 1^0 > 2^0 > 3^0$$
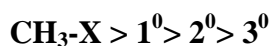
2. Nature of the leaving group: Rate of SN^2 reaction depends on the basicity of the leaving group, weaker the base best is the leaving group.

$$I^- > Br^- > OH^- > CH_3COO^- > C_2H_5O^-$$

3. Nature of the Nucleophile: Higher the electron donating tendency higher the reactivity of SN^2 reaction that is the stronger nucleophile favour the SN^2 reaction.

$$CN^- > I^- > C_2H_5O^- > OH^- > C_6H_5\text{-}O^- > Cl^- > CH_3COO^-$$
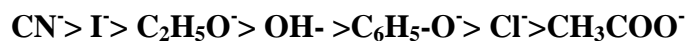
4. Nature of solvent: Lesser the polarity of solvent higher is the reactivity.

8.7.3 Difference between SN^1 and SN^2 mechanism:

S.No.	Factors	SN^1	SN^2
1	Reaction kinetics	First order reaction	Second order reaction
2	Nature of alkyl halide	3^0 alkyl halide more reactive	1^0 alkyl halide more reactive
3	Nature of nucleophile	Weaker and stronger nucleophile favours SN^1	Stronger nucleophile favour SN^2
4	Concentration of nucleophile	Lower concentration of nucleophile favours SN^1	Higher concentration of nucleophile favours SN^2
5	Reactive intermediate	Carbocation	Transition state
6	Nature of solvent	Polar solvent favours SN^1	Non polar solvent favours SN^2
7	Stereochemistry	Retention of configuration of product	Inversion of configuration of product

Energy profile diagram SN^1 and SN^2 reaction:
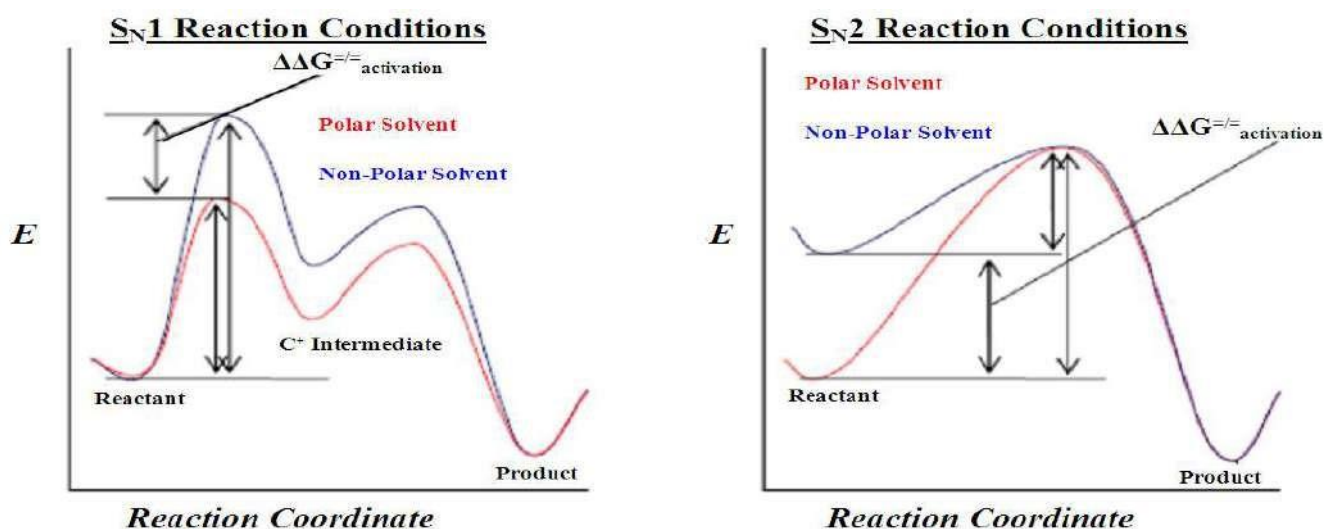
8.8 Elimination reactions:

The reaction in which the atoms or groups are lost from the adjacent carbon atoms results in the formation of C=C are called 1,2-elimination reaction or β-elimination reaction.

When alkyl halide containing β-hydrogen atom, when treated with alcoholic KOH dehydrohalogenation takes place to give alkene.
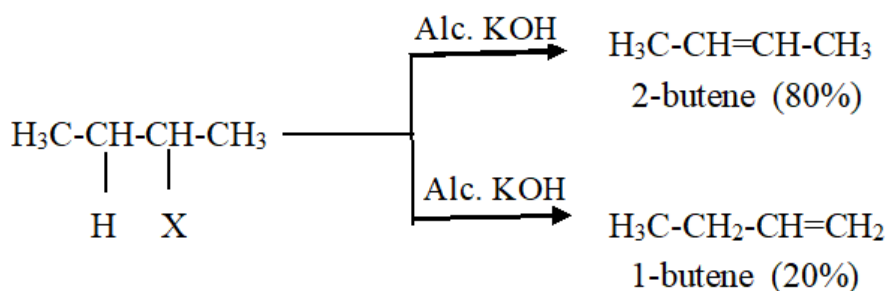
Saytzeff's rule: In the dehydrohalogenation reaction, the preferred product is the more substituted alkene. Alkene formed has greater number of alkyl groups attached to the doubly bonded carbon atom.

Example: Two alkenes are possible when 2-bromo butane is heated with alcoholic KOH.
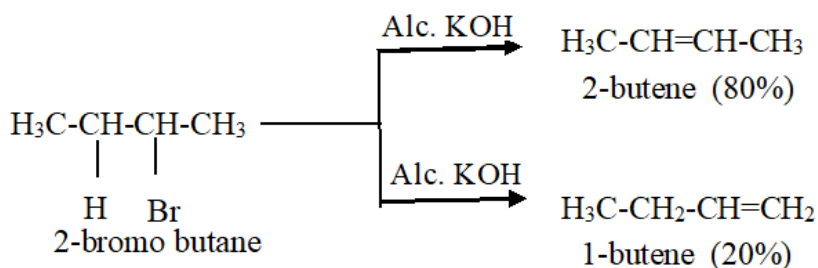
2-Butene is more substituted alkene than 1-Butene, hence 2-Butene is the major product.

Types of elimination reaction: Elimination reactions are two types:

1. E^1 Elimination Reaction   2. E^2 Elimination Reaction

8.8.1 E^1 Elimination Reaction or Uni-molecular Elimination Reaction:

These kinds of mechanisms, which are typically two steps in nature, are seen in tert. alkyl halides.

Step I: The first step is the slowest. Known as the rate-determining step, this process involves the hetrolytic fission of the C-X bond to produce an intermediate carbonium ion.

Step II: This one is quicker. In this step, the alkene is formed when the Nu-eliminates a β-hydrogen from the carbonium ion.

Mechanism:

$$KOH \longrightarrow K^+ + OH^-$$
$$Nu^-$$

Step I:

tert. butyl bromide 3^0 butyl carbonium ion
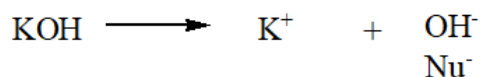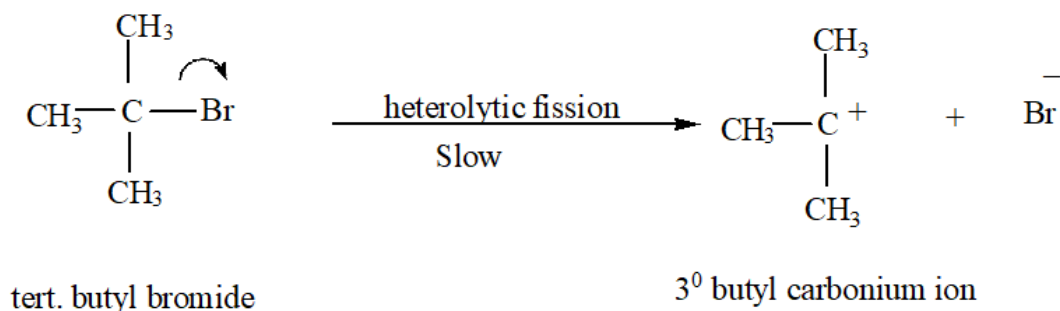
Step II:
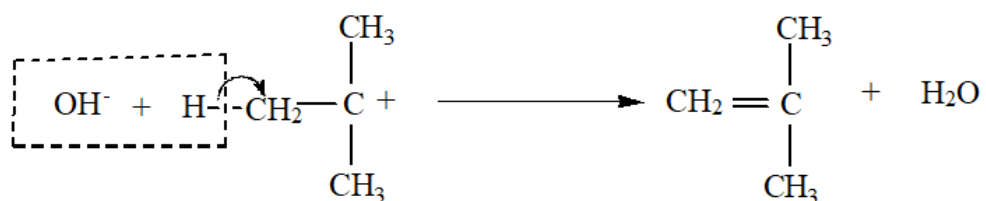
8.8.2 E2 Elimination (Bi-molecular Elimination Reaction):

The E2 mechanism is a bimolecular reaction and coordinated process. The rate law for the rate determining step depends on both the alkyl halide and the base since the base removes a hydrogen atom at the same time the C—X bond is broken to generate a halide ion: Rate = k [alkyl halide] [base]

The likelihood of the E2 mechanism functioningincreases with base strength. The reaction of 1-bromopropane with sodium ethoxide serves as an illustration of the E2 process.

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$

Attacking of Nu⁻:

Transition state

Fast step

$$Br^- + H_2O + \quad \underset{H}{\overset{H}{C}} = \underset{H}{\overset{H}{C}}$$
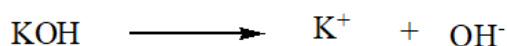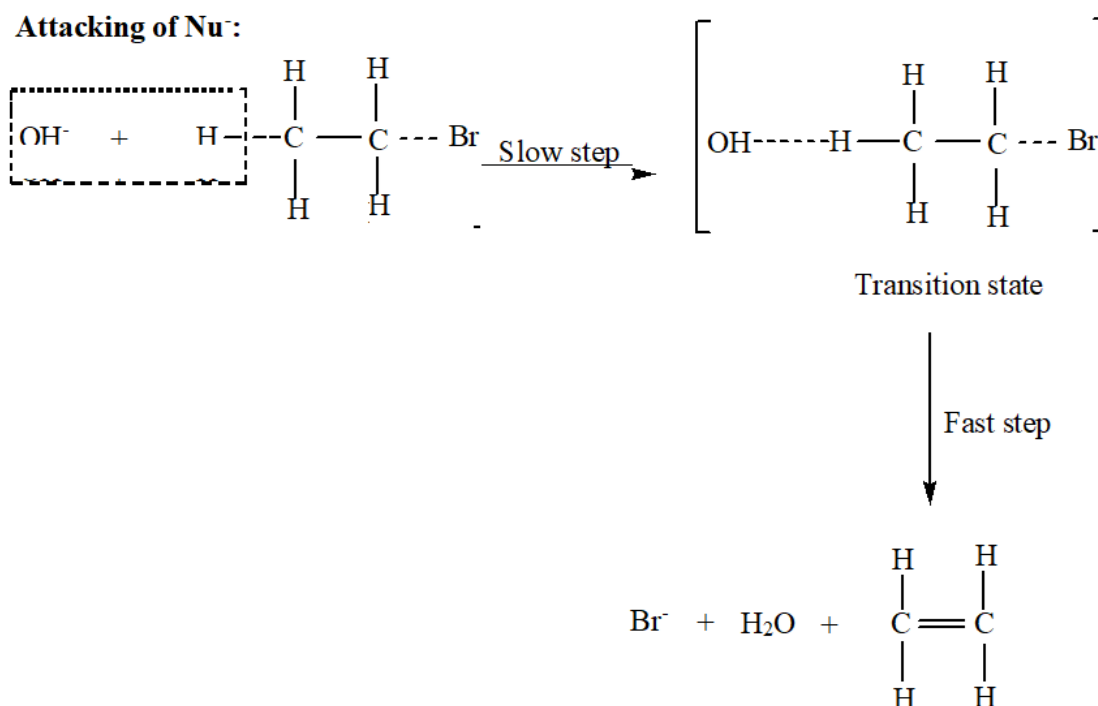
This step is the slow step and rate-determining step. It involves two reactant molecules, hence it is second order reaction.

SUMMARY:

Alkyl halides can be categorized as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds based on the number of halogen atoms they include in their structures. Alkenes can be halogenated using free radicals, phosphorus halides, thionyl chloride, or halogen acids. Alcohols' –OH group can also be replaced with a halogen using any of these methods to create alkyl halides.

Due to strong dipole-dipole and van der Waals forces of attraction, the boiling temperatures of organohalogen compounds are somewhat higher than those of the equivalent hydrocarbons. In organic solvents, they dissolve entirely, but just somewhat in water. Apart from nucleophilic substitution reactions, alkyl halides also experience β- elimination reactions. One carbon loses its halogen, and a neighboring carbon loses its proton. The two carbons from which the atoms are removed from a double bond. An alkene is thus result of an elimination reaction. Dehydro-halogenation is the process of taking out a proton and halide ion.

Keywords:

Substitution reaction: A chemical reaction in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms.

Nucleophile: A species (an atom or molecule) that donates a pair of electrons to form a chemical bond with an electron-deficient species, often resulting in the displacement of a leaving group.

Leaving group: An atom or group of atoms that departs with a pair of electrons in a substitution or elimination reactions to form a stable compound.

Stereochemistry: The study of the spatial arrangement of atoms or groups in molecules and the effect of this arrangement on chemical reactions.

Regioselectivity: The preference of a reaction for one direction of bond formation or bond cleavage over all other possible directions.

MCQ:

1. Among the following reagents, which one can not be used to convert an alcohol into an alkyl chloride?

(A)PCl_5 (B) $SOCl_2$ (C) NaCl   (D)$HCl + ZnCl_2$

Answer: (C)

2. Towards SN^1 mechanism, which compound responds most quickly?

(A) Methyl chloride   (B) isopropyl chloride

(C) ethylene chloride   (D) 3-butyl chloride

Answer: (D)

3.When alcoholic KOH is added to 1-butane, the following product is formed:

(A) 1-butene   (B)2-butene   (C) 1-butanol   (D). 2-butanol

Answer (D)

4. Alkyl halides experience the following reactions:

(A)electron-halide substitution reactions   (B) electron-halide addition reactions

(C)Addition reactions involving nucleophiles   (D) Nucleophilic substitution reactions

 Answer (D)

Short Answer Questions:

1. Sort following group of substances by increasing boiling point.

Bromomethane, Dibromomethane, Chloromethane, and Bromoform

2. What does happen when alcoholic KOH is used to treat with n-butyl chloride?

3. What is the main byproduct of the 2-bromobutane elimination reactions?

4. Nucleophilic substitution reactions: what are they? Describe the SN1 and SN2 reactions mechanisms in terms of aliphatic molecules.

5. Detailed notes on the E1 and E2 dehydrohalogenation mechanisms should be made.

Chapter: 9

Aryl Halides

Objectives:

- Based on their stated structure, name the aryl halide using the IUPAC system of nomenclature.
- Explain the chemical processes that lead to the creation of aryl halides.
- Recognize aryl halide-related reactions
- DDT and BHC synthesis.
- Comparative relativities between vinyl and aryl halides and alkyl halides.

9.1 Introduction: Monohalogen derivatives of aromatic hydrocarbons are called aryl halides. In aryl halides, halogen is bonded directly to a carbon of the Benzene ring.

9.2 Classification of Aryl halides:

Compounds with a minimum of one benzene ring and one halogen atom are known as aryl halides. These are listed in the following order:

Nuclear Halogen Compounds: In these compounds, halogen atoms are directly bonded to the benzene ring. For instance,
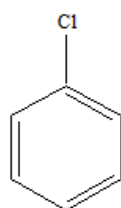
Chlorobenzene
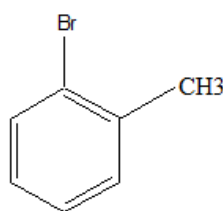
o-bromotoluene

Side-chain halogen Compounds: These compounds have halogen bonded to their side chains. The side chain could contain more than one halogen.
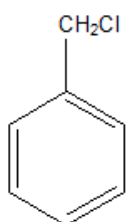
Benzyl chloride
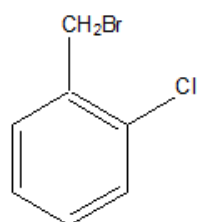
o-Chloro benzyl bromide
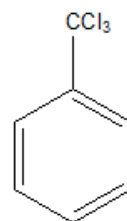
Benzotrichloride

9.3 Nomenclature of aryl halides:

According to the IUPAC and common system, aryl halides are also known as haloarenes. Aryl halide nomenclature is governed by certain principles as follows:

If a single halogen group is directly attached to the benzene ring, it is written as a prefix and counted as one position, with the benzene ring following as the main ring. Think of aryl chloride or chlorobenzene. Benzene is comparable in all six positions. So, by adding the halogen to any of the six positions could represent monohalogen compounds.

Chlorobenzene
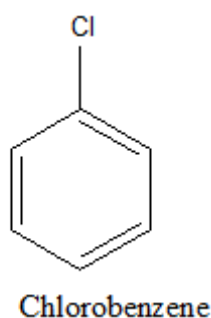
The prefixes o- (ortho), m-(meta), and p-(para) are used in a common system for dihalogen derivatives that include the same type of halogen. The two groups are orthogonal to one another if their positions are adjacent. In the event that there is a single position gap, the groups are considered meta, and in the event of a two position gap, the groups are considered para. In the IUPAC nomenclature of dihalogen derivatives, on the other hand, the location of halogen is assigned using the numerical prefixes 1,2, 1,3, and 1.

o-(ortho)
(1,2 dibromo benzene)

m-(meta)
(1,3dibromobenzene)

p-(para)
(1,4dibromobenzene)
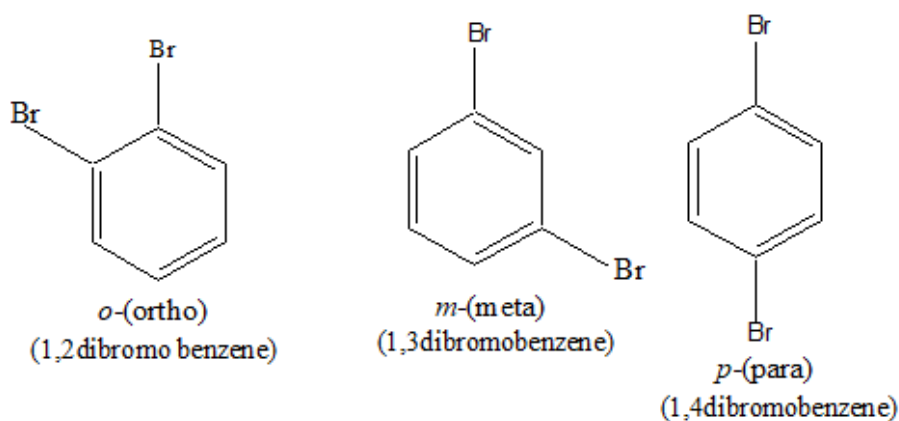
When two distinct halogen groups are joined to the benzene ring, the halogens should be numbered alphabetically and written similarly. For example: When two halogen groups, such as bromo and fluoro, are attached to a benzene ring, the bromo group will connect first and the fluoro group will follow.

1-Bromo3-fluoro
benzene
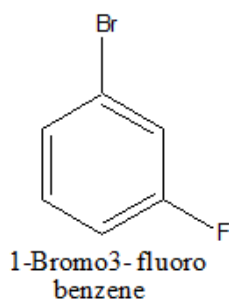
The number system is used for trihalogen compound naming. Group position is assigned number 1, and subsequent group numbers are assigned correspondingly. This is accomplished by moving in a clockwise direction.

1,2,3 Tribromobenzene

1,2,4 Tribromobenzene

1,3,5 tribromobenzene
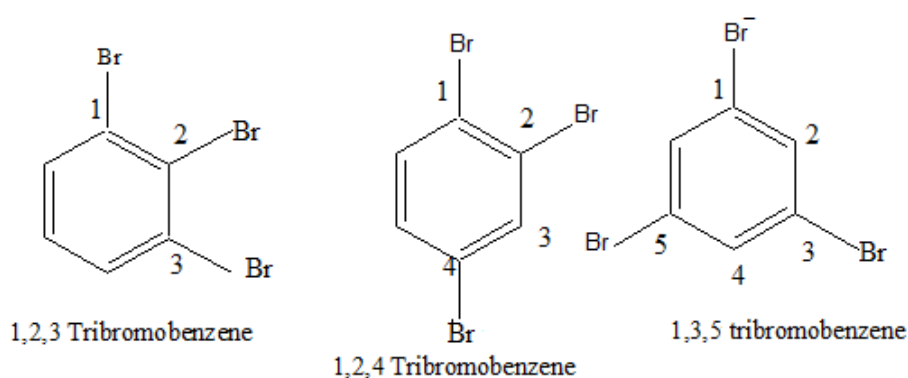
The names of side chain halogen compounds are as follows:

Benzyl Chloride

o-Bromo benzyl chloride

Benzal Chloride

Benzo Trichloride
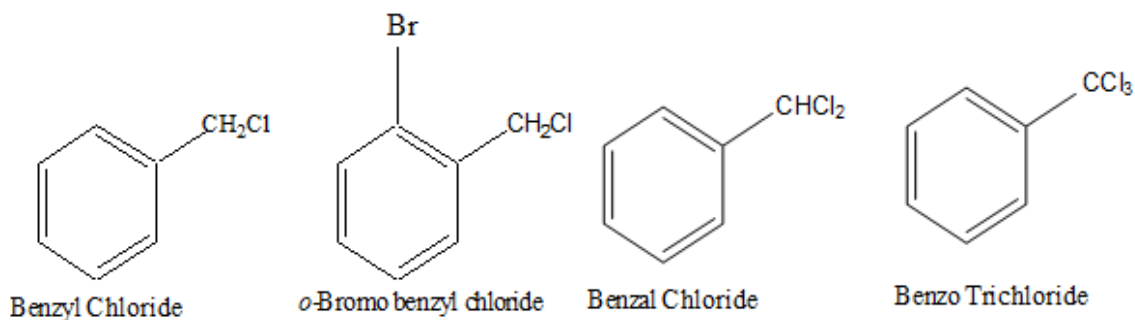
9.4 Methods of preparation of aryl halides:

9.4.1 Nuclear halogen in aromatic hydrocarbons is easily replaced by chlorine or bromine through direct halogenation in the presence of a halogen carrier like metallic Fe or lewis acids as chlorides or bromides of Fe, Sb and Al at ordinary temperature in absence of light. Depending on the ratio of halogen to hydrocarbon, mono-, di-, tri chloro or bromo derivatives are produced. Additional hydrogenation results in the formation of o- and p-dichlorobenzene.

The deactivating effect of the halogen atom on the aromatic ring causes this reaction to halt at the mono-substituted stage.

benzene   + Cl_2 $\xrightarrow{Fe}$ chlorobenzene   +   HCl
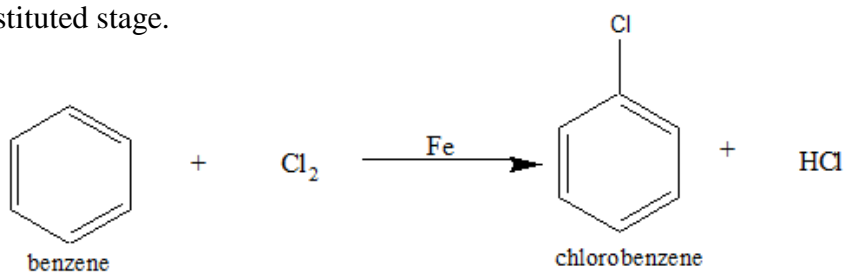
Nonetheless, excessive usage of chlorine results in further substitution, which produces a combination of o- and p-dichlorobenzene.

o-dichlorobenzene   p-dichlorobenzene

o-chloro toluene   p-chloro toluene

o-bromo toluene   p-bromo toluene
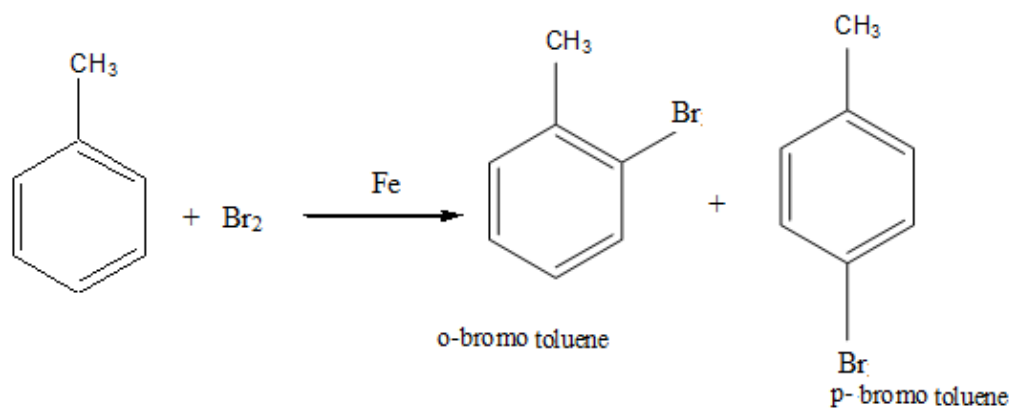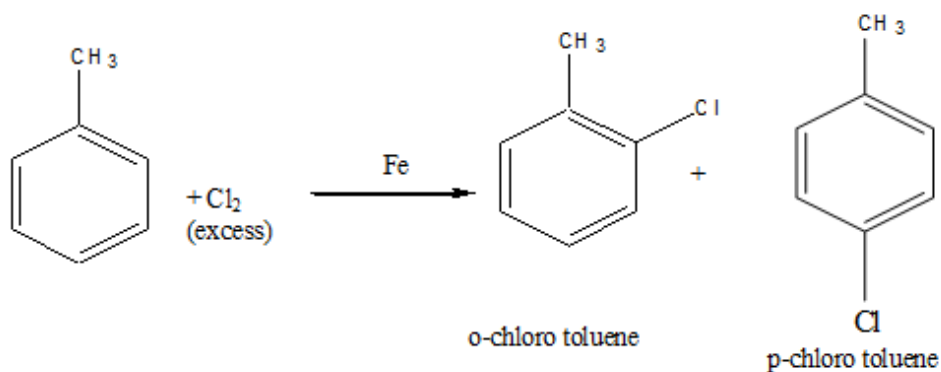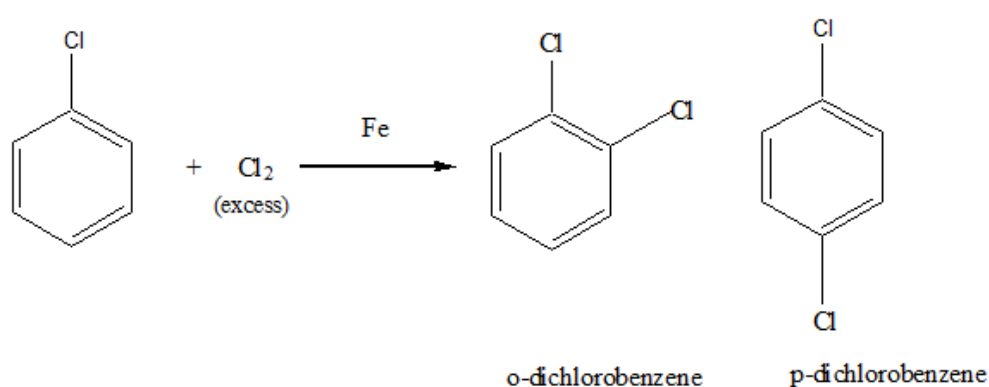
High temperatures are necessary for the halogen to enter the meta position in aromatic compounds that include highly deactivating groups, such as $-NO_2$, $-COOH$, etc.
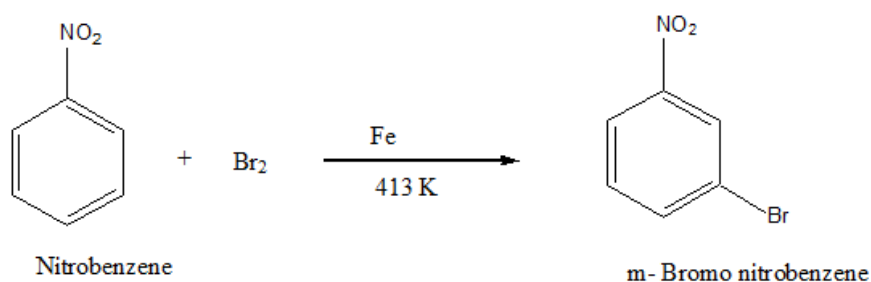
9.4.2 Sandmeyer's reaction/ Decomposition of aryl Diazonium salts: Aryl amines when reacted with acidic sodium nitrite at low temperature (0-5^{0}C), it formed aryl diazonium salts which in presence of acidic cuprous chloride converted into aryl halide. This reaction is known as Sandmeyer reaction, helpful method to synthesized aryl halides, especially those which cannot synthesized by direct halogenation.
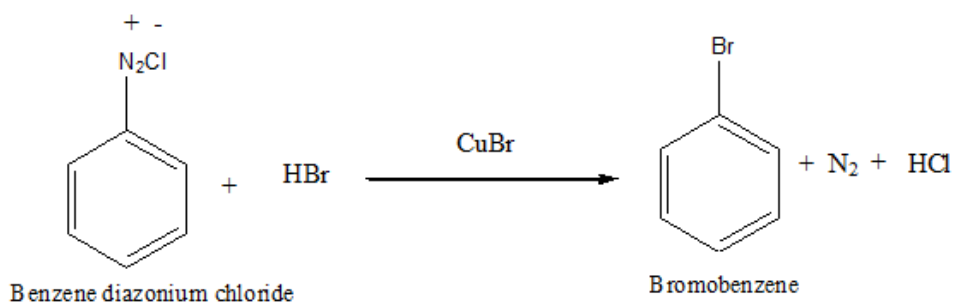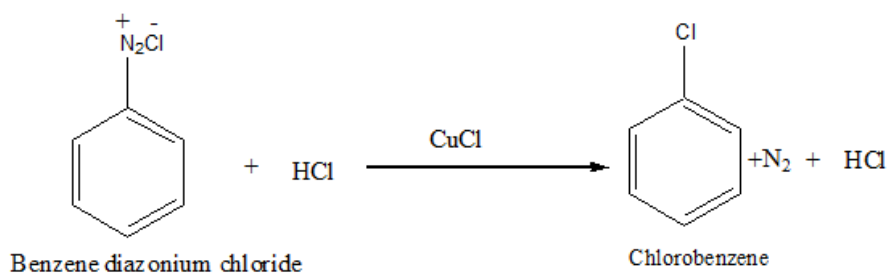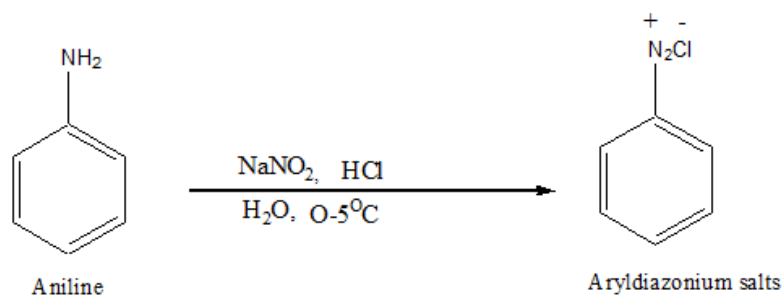
9.4.3 Gattermann Reaction: When diazonium salt formed in sandmeyer reaction heated with copper powder and form halobenzene, this reaction is known as Gattermann reaction.
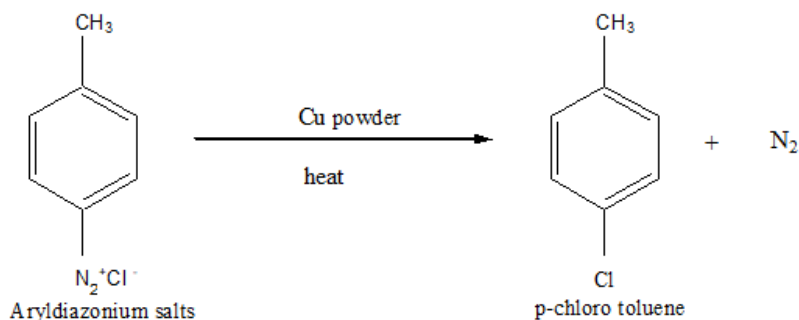
9.4.4 Schiemann reaction: Neither the Sandmeyer nor the Gattermann reactions can be used to prepare fluorobenzene. Balz-Schiemann reaction is used for the synthesis of fluorobenzene. In this reaction benzene diazonium chloride is treated with Fluoroboric acid to prepare fluoroborate Diazomium salt,which when heated, yields fluorobenzene.
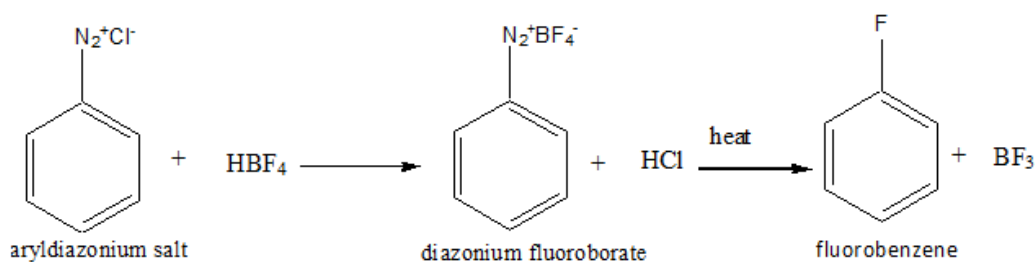
From phenols: Phenols react with PCl_5 and form aryl chloride.
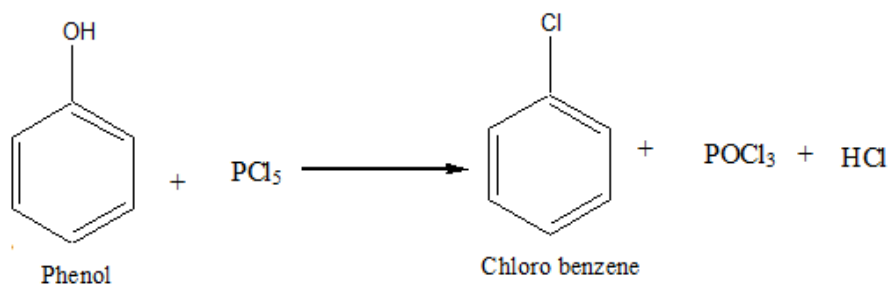
9.4.5 Hunsdiecker reaction: When Silver salt of benzoic acid is heated with Cl_2 form chlorobenzene.
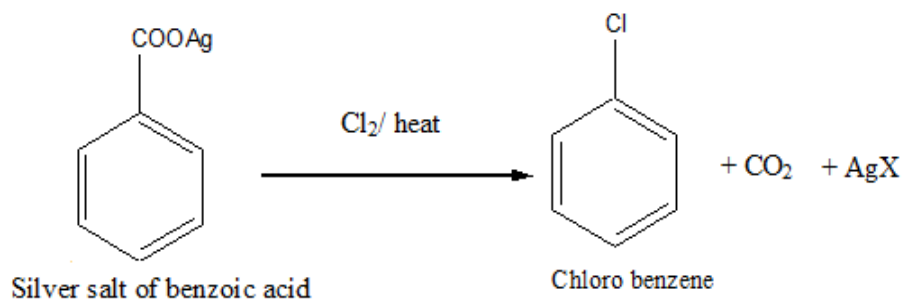
9.5 Physical properties:

1. Aryl halides are heavier than water. Melting point and boiling point order of different aryl halides is as follows:

Aryl Iodides > Aryl Bromides > Aryl Chlorides > Aryl Fluorides

2. Among ortho, meta and para isomeric aryl halides, difference in melting point is higher than the boiling point difference. For example: Boiling point of o-, m- ans p-dichlorobenzene is 180º, 174ºand 175º respectively while melting point are 17º, 25º and 55º respectively.

9.6 Chemical reactions of Aryl halides:

Reactions of aryl halides are due to halogen atom, give nucleophilic substitution reaction and due to aromatic ring, show Electrophilic substitution reaction.

9.6.1 Nucleophilic substitution reactions: Nucleophilic substitution reactions tend to be rather unreactive towards aryl halides. For instance, at room temperature, chlorobenzene is virtually inert to aqueous sodium hydroxide. More than 300ºC is needed for the reaction to occur at a suitable rate.
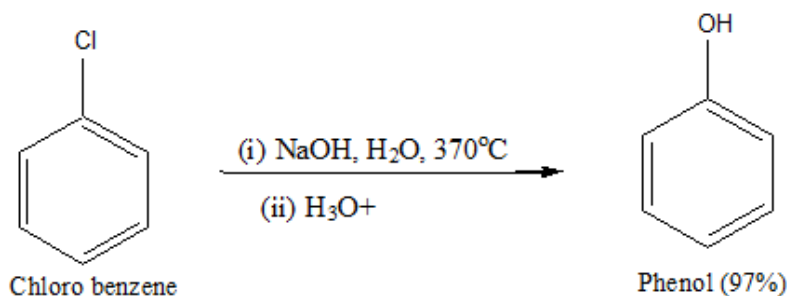
Reactivity of aryl halides towards nucleophilic substitution reaction is lesser than alkyl halide. Reason behind this lack of reactivity is as follows:

In the aryl halides carbon-chloride σ bond found. Nonetheless, a pair of electrons in the p-orbital of chlorine is parallel to the delocalized p-orbitals of the benzene nucleus. Chlorine's p-orbital may potentially overlap with the delocalized p-orbitals of the benzene nucleus. As a result, there is a stronger bond between carbon and chlorine.
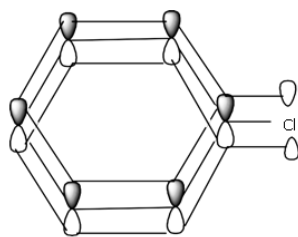
In aryl halides, the C-Cl bond has a partial double bond character due to the delocalized π MO.
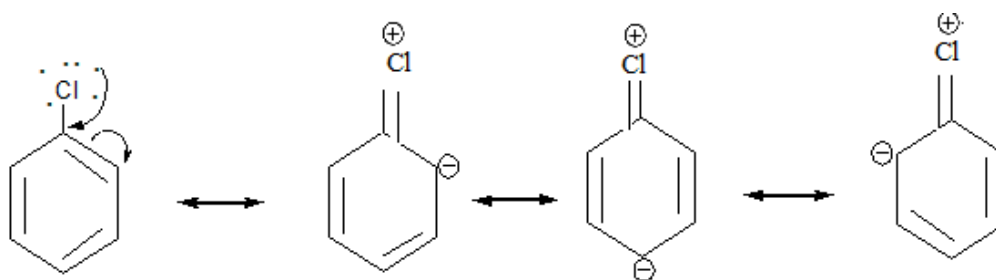

Second reason for lesser reactivity of aryl halide is π electron density in aromatic ring, due to this nucleophile does not allow to attack benzene ring easily.

During the nucleophilic substitution reaction aryl carbocation is form which is highly unstable due to higher energy.
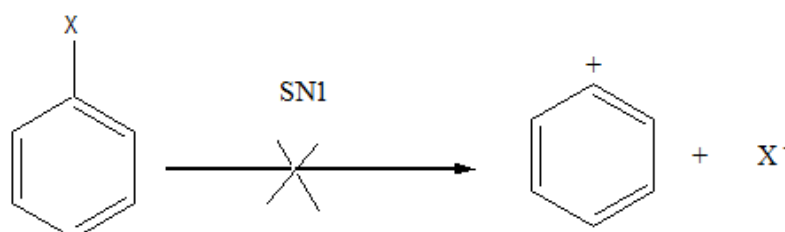
Additionally, alkyl halides are unable to proceed through the SN2-type process because the aromatic ring prevents the nucleophile from approaching the carbon on the side opposite the bond to the leaving group. It is not feasible to reverse the configuration.
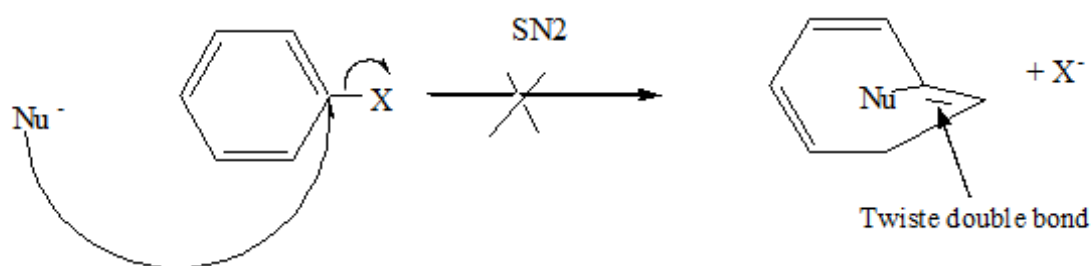
9.6.2 Mechanism Nucleophilic substitution reaction:

There are two types of mechanism as follows:

I. Addition/elimination mechanism
II. Elimination/addition mechanism

I. Addition/elimination mechanism

This is two step reaction.

Step 1: Nucleophile attacks at the similar position where the leaving group attached, this is known as ipso attack.
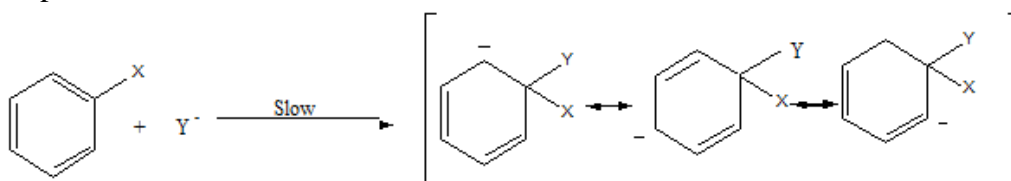
**Step 2:** The leaving group separated, causing the benzene ring's aromaticity to regenerate.

Example:

4-Nitrophenol
(p-nitrophenol)

1-Chloro-4-nitrobenzene
(p-nitrochlorobenzene
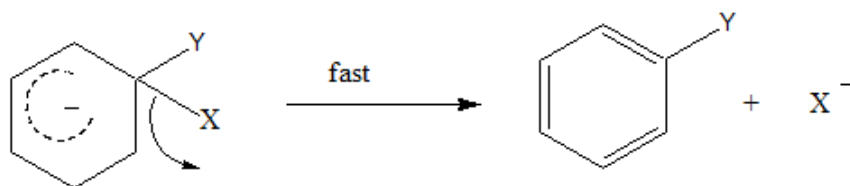
4-Nitroaniline
(p-nitroaniline)
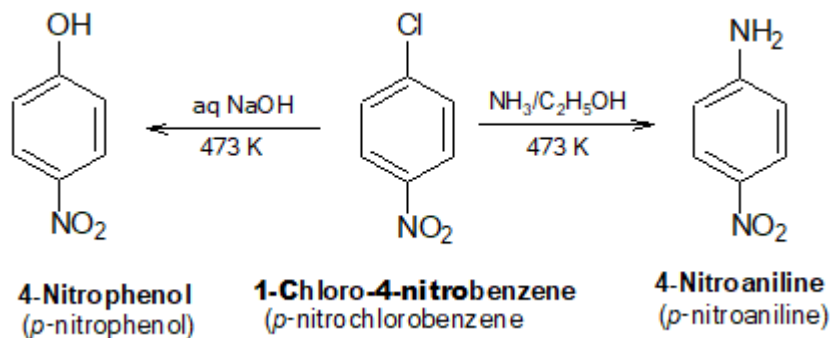
II. Elimination /addition mechanism/ Benzyne Mechanism:

The benzyne mechanism is used to carry out the elimination/addition process. When the benzyne intermediate is in the transition state, the benzene ring contains a triple bond. The benzoyne intermediate is extremely reactive and goes through a nucleophilic substitution process quickly.

Only in the presence of extremely strong bases, such as alkali metal amide and organolithium reagents, or somewhat weaker bases under intense circumstances, do aryl halides undergo substitution by the benzyne mechanism.
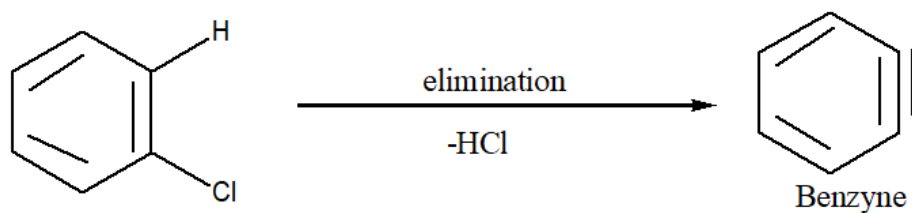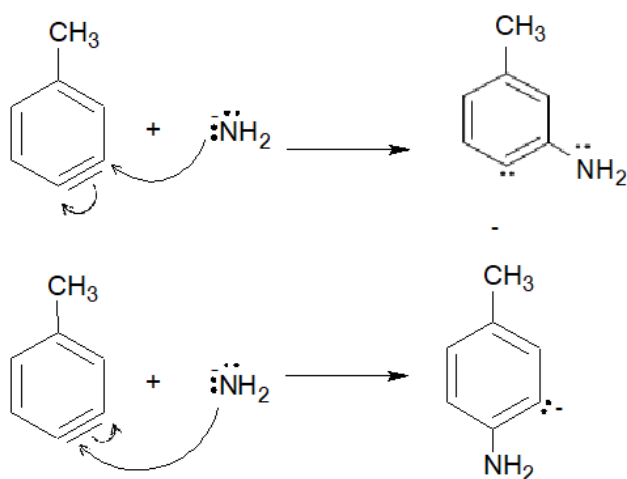

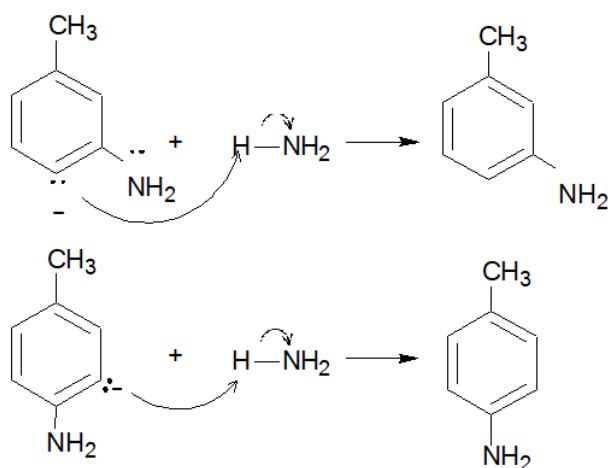Benzyne mechanism completed in following steps:

Step I: Benzene ring undergoes dehydrohalogenation anf form benzyne intermediate.
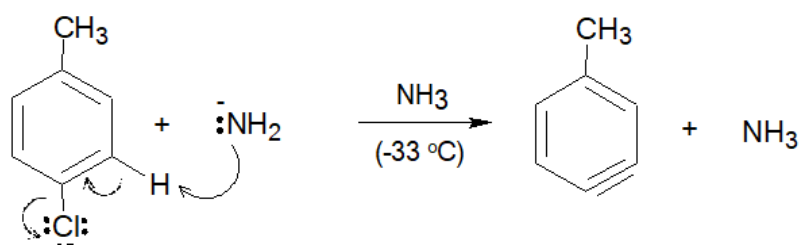
Step II: Amide ion as a nucleophile attack on both the carbon atom triple bond and form two carbanion intermediate.


Step III: Carbanions abstract protons from ammonia to give final product.

### 9.6.3 Electrophilic substitution reaction of Aryl halides:

Due to their weak deactivators, aryl halides are less reactive than benzene when it comes to the electrophilic aromatic substitution. However, they are still reactive. The intermediate cations are less stable than those formed when benzene is substituted because of the halogen's electronegativity, which is the cause of the weak deactivation. Halides are groups that direct either o- or p-.
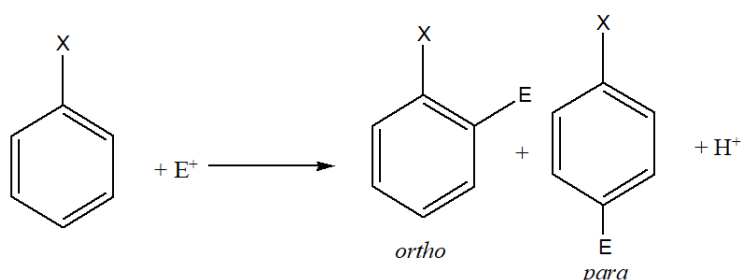

By utilizing unshared electron pairs to create resonance and delocalize the positive charge, a chlorine ortho or para can be applied to the site of electrophilic attack to stabilize the carbocation intermediate. An intermediate carbocation produced on a meta attack cannot be stabilized in this way.


cation intermediate
on *meta* attack

cation intermediate
formed on *ortho* attack

cation intermediate
on *para* attack
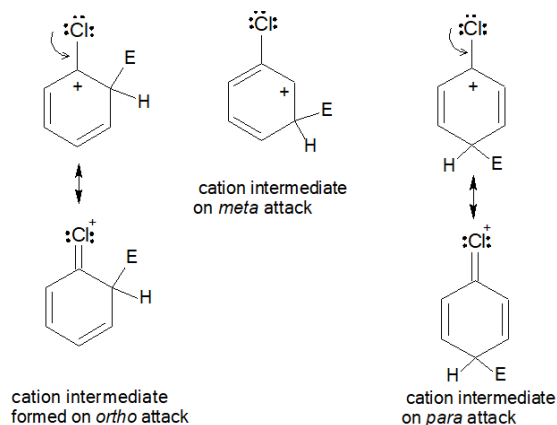
Following reaction are example of electrophilic addition reactions of benzene:

$Cl_2/FeCl_3$

HNO_3/H_2SO_4

H_2SO_4

$CH_3Cl/AlCl_3$
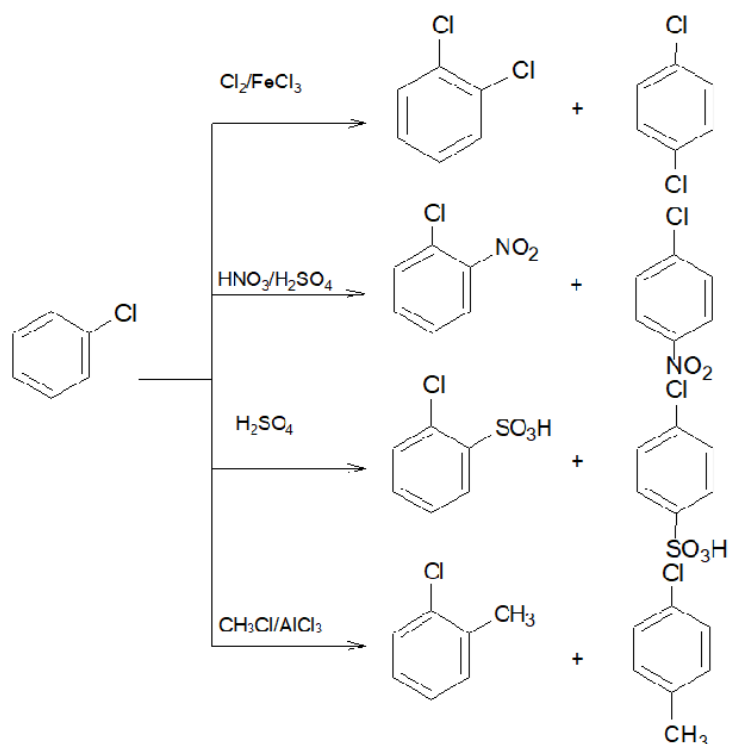
9.6.4 Wurtz-Fittig reaction: An alkyl benzene is produced when aryl halide is treated with an ethereal alkyl halide solution in the presence of sodium.

$$-Cl + 2Na + Cl\text{-}CH_3 \xrightarrow[\text{ether}]{\text{Dry}} -CH_3 + NaCl$$
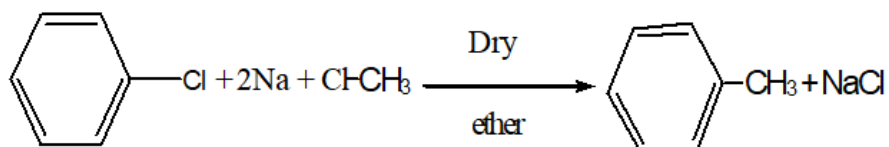
when aryl halide reacted with sodium that form diaryl compounds, this type of reactions are known as Fitting reaction.

$$-Cl + 2Na + Cl- \xrightarrow{\text{ether}} \text{di phenyl}$$
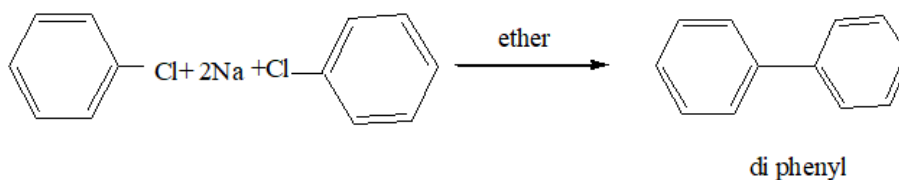
9.6.5 Reduction: In the presence of alkali, Aryl halide are undergoes reduction by Nickel-Aluminium alloy in alkali or sodium amulgum and aqueous alcohol.
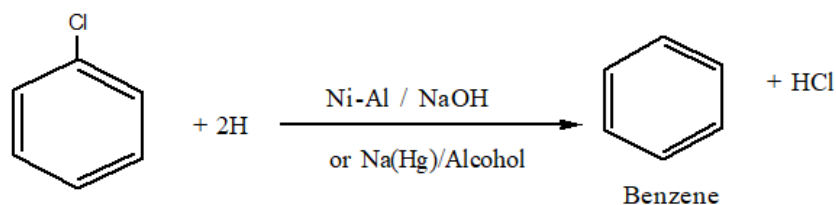
9.6.6 Grignard reagent formation: Aryl halides and iodides react to form Grignard reagent when they are treated with magnesium turnings in dry ether. Only in reactions when dry tetra hydro furan (THF) is used as the solvent does aryl chloride yield Grignard reagent.
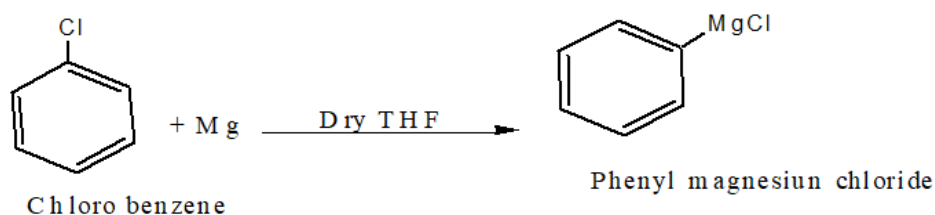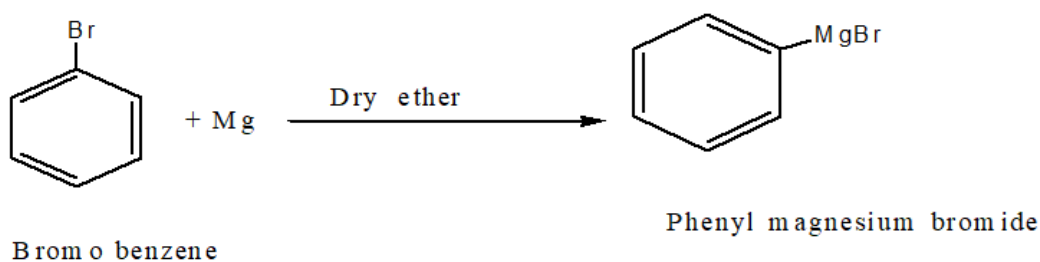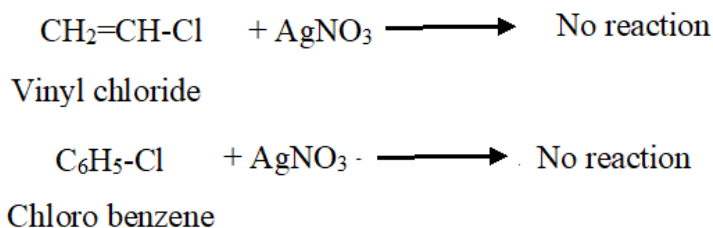

9.7.7 Reactivity and relative strength of C-X bond in alkyl, allyl, benzyl, vinyl and aryl halides:

In the alkyl, allyl and benzyl halides the hydrogen atom is attached to sp^3 hybridised carbon atom. The C-X bond has less s-character, longer bond length and weaker bond than that in vinyl and aryl and benzyl halides readily undergo nucleophilic substitution gives a precipitate of silver halide with alcoholic $AgNO_3$.
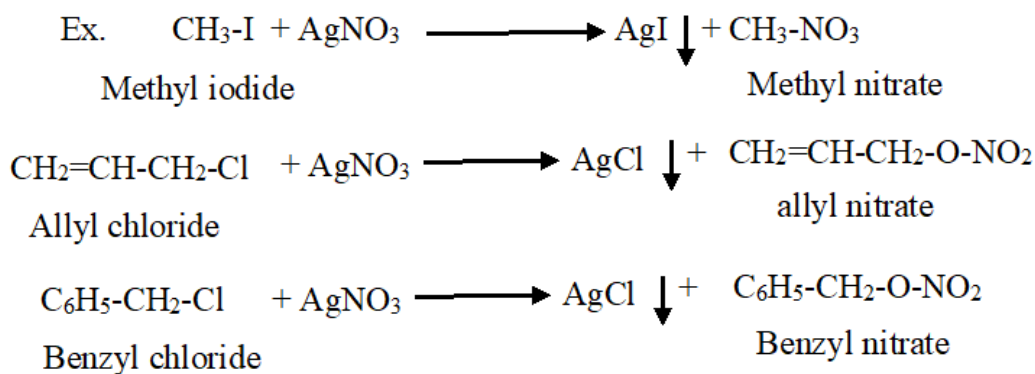
In vinyl and aryl halides, the halogen atom is attached to sp2 hybridised carbon atom. The C-X bond has more s-charater, shorter bond length and stronger than that in alkyl, allyl and benzyl halides. The C-X bond has double bond character due to resonance, it cannot break easily. Hence vinyl and aryl halides donot give a precipitate of silver halide with alcoholic $AgNO_3$.

$$CH_2=CH-Cl \quad + AgNO_3 \longrightarrow \quad No\ reaction$$
Vinyl chloride

$$C_6H_5-Cl \quad + AgNO_3 \longrightarrow \quad No\ reaction$$
Chloro benzene

Summary:

Nucleophilic aromatic substitution reactions occur when an alkyl halide has substituents that remove electrons at both the ortho and para positions. A nucleophilic attack on the aromatic ring produces a resonance-stabilized anionic intermediate, which is the first step in these reactions. A substituent product is created when the intermediate halide ion is lost.

When the nucleophile is an unusually strong base (such as an amide ion, NH_2^-), and there are no strong electron absorbing groups present, the benzyne mechanism is used. Many of the electrophilic aromatic substitution processes that benzene can experience, such as Friedel-Crafts alkylation or acylation, nitration, sulfonation, and further halogenation, can also occur with alkyl halides.

Keywords:
Aryl halide: A compound containing a halogen atom (fluorine, chlorine, bromine, or iodine) bonded to an aromatic ring, such as benzene or other aromatic hydrocarbons.
Halogen: Any of the five elements fluorine, chlorine, bromine, iodine, and astatine, which form a group in the periodic table and readily react with alkali metals to form salts.
Synthesis: The formation of a compound from simpler substances through a chemical reaction.
Reactivity: The tendency of a chemical substance to undergo a chemical reaction, either by itself or with other substances.

MCQ:

1. Compared to alkyl halides, aryl halides are less reactive to nucleophilic substitution because of the following:

(A) Inductive effect   (B) Electromeric effect

(C) Resonance stabilization   (D) Stereoisomerism.   Answer (C)

2. Which reagent can be used to distinguish between chlorobenzene and allyl chloride?

(A)H_2/Ni   (B)Zn/HCl   (C)Br_2 in CCl_4(D) NH_2NH_2.

Answer (B)

3. Alkyl halides experience the following reactions:

(A) Electrophilic substitution reaction   (B) Electrophilic addition reaction

(C) Nucleophilic addition reaction   (D) Nucleophilic substitution reaction.

Answer (C)

4. Which reagent is appropriate for the following conversion?

(A) HNO_3+H_2SO_4 (B)$NaNO_2$

(C) H_2SO_4 (D)NO_3.

Answer (A)

Short Answer Questions:

1. Define aryl halides. Give two example.

2. Explain williamson's ether synthesis with example.

3. How can you convert aniline to chlorobenzene?

4. Why chlorobenzene does not give precipitate even on prolonged heating with alc. $AgNO_3$?

Chapter: 10

Alcohols

Objectives

- Understand the classification of alcohols into primary, secondary, and tertiary categories.
- Analyse how the structure of alcohols influences their physical and chemical properties, such as solubility, boiling points, and hydrogen bonding.
- Explore the various methods used to synthesize alcohols, including hydrogenation, hydration, reduction, and Grignard reactions.
- By the end of the chapter, students should possess a solid understanding of the fundamental concepts related to alcohols, enabling them to apply this knowledge in both theoretical and practical contexts within the realm of organic chemistry.

10.1. About Alcohols

Alcohols are chemical molecules in which the carbon atoms of aliphatic compounds are linked to one or more hydroxy (-OH) groups. They are extensively distributed in nature and have a wide range of industrial and medicinal uses. As an example, two significant alcohols for industry are methanol and ethanol. Alcoholic drinks, cosmetics, and medication preparations all contain ethyl alcohol, sometimes known as grain alcohol. Wood alcohol, or methyl alcohol, has two uses: as a solvent and as fuel. One common usage of isopropyl alcohol is as a cleanser for the skin after injections and small cuts.
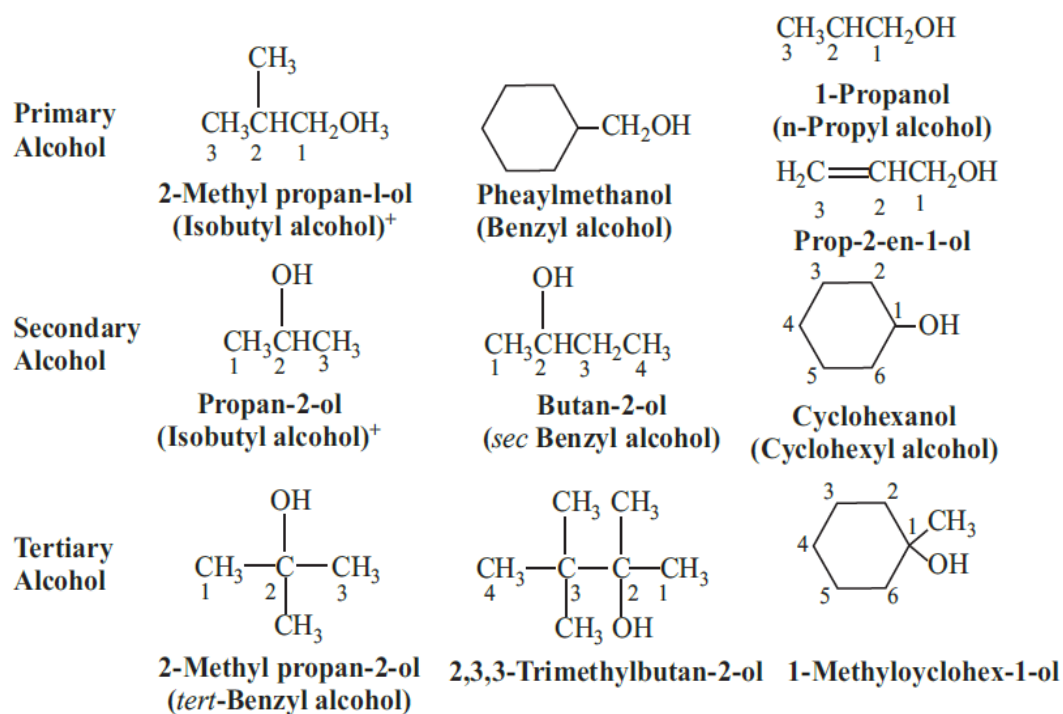

| Ethyl alcohol | Methyl alcohol | Isopropy alcohol |
| **Ethanol** | **Methanol** | **Propan-2-ol** |
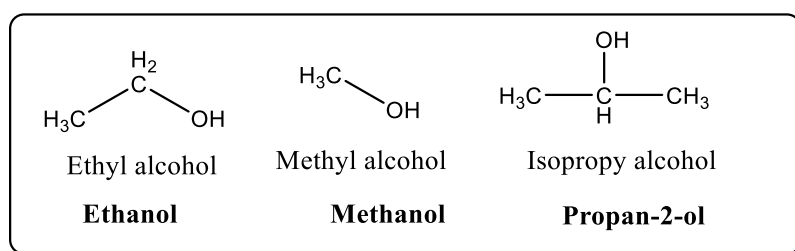
10.2. Classification of Alcohols

Primary (1º), secondary (2º), and tertiary (3º) alcohols are categorized according to how many alkyl groups are attached to the carbon atom that contains the hydroxy group—one, two, or three, respectively**.**
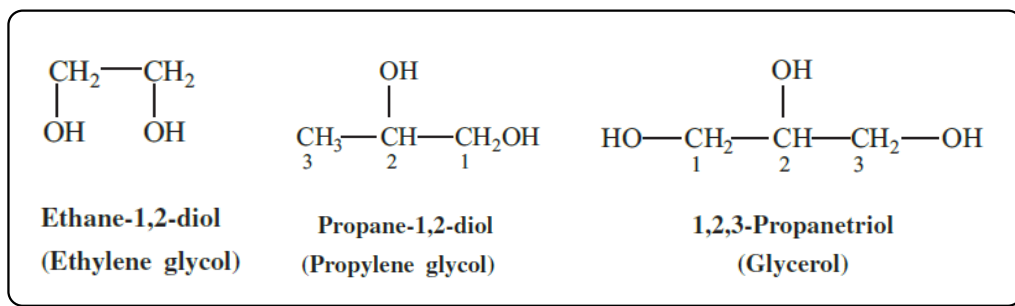
primary alcohol $1°$ secondary alcohol $2°$ tertiary alcohol $3°$
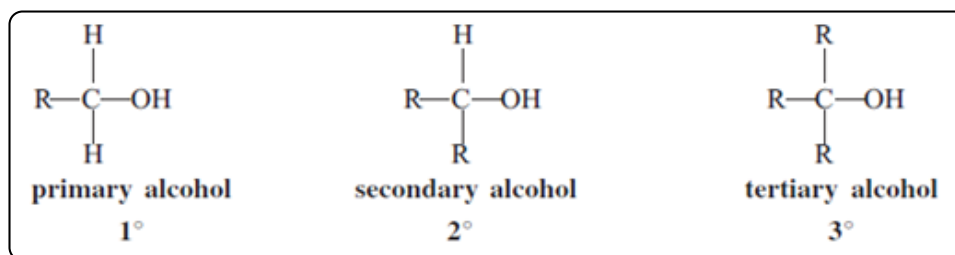
10.3. Nomenclature of 'Alcohols'

In the common word, alcohols are named as alkylalcohols. 'IUPAC system' the name of saturated alcohols are derives from corresponding alkanes by replacing by 'ol'. The IUPAC names of a few members are this class are given below (The names given in the brackets are common name).

Primary Alcohol

$CH_3CHCH_2OH_3$ (with CH_3 branch)
3 2 1
2-Methyl propan-l-ol
(Isobutyl alcohol)+

—CH_2OH
Pheaylmethanol
(Benzyl alcohol)

CH_3CHCH_2OH
3 2 1
1-Propanol
(n-Propyl alcohol)

$H_2C=CHCH_2OH$
3 2 1
Prop-2-en-1-ol

Secondary Alcohol

CH_3CHCH_3 (OH)
1 2 3
Propan-2-ol
(Isobutyl alcohol)+

$CH_3CHCH_2CH_3$ (OH)
1 2 3 4
Butan-2-ol
(sec Benzyl alcohol)

Cyclohexanol
(Cyclohexyl alcohol)

Tertiary Alcohol

$CH_3—C—CH_3$ (OH, CH_3)
1 2 3
2-Methyl propan-2-ol
(tert-Benzyl alcohol)

$CH_3—C—C—CH_3$ (CH_3 CH_3, CH_3 OH)
4 3 2 1
2,3,3-Trimethylbutan-2-ol

1-Methyloyclohex-1-ol

In all these examples all molecules have one –OH group and all these are named as *monohydric* alcohols. In the IUPAC system, di-hydric alcohols are named as *alkanediols* and *tri-hydric* alcohol are named as *alkanetriols*. **The term glycol in generally used for 1,2-diol or vicinal diol**Some example of *di-hydric* alcohols is as follows-

Ethane-1,2-diol
(Ethylene glycol)

Propane-1,2-diol
(Propylene glycol)

1,2,3-Propanetriol
(Glycerol)

## 10.4 General method for preparation of alcohols:

Alcohols are obtained by the following general ways:

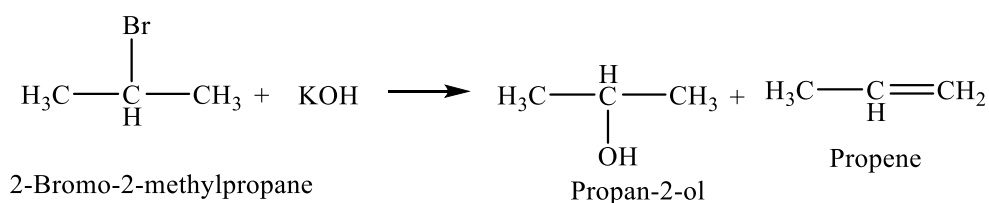**(i)**   **By the 'Hydrolysis'**of halo-alkanes

 The halogen containing alkanes when heated with alkali hydroxide in aqueous solution or moist silver oxide they provide the corresponding alcohols with same carbon atoms.

$$CH_3CH_2Cl + NaOH(aq.) \longrightarrow CH_3CH_2OH + NaCl$$

Chloroethane   **Ethanol**

2-Bromobutane

Butan-2-ol
(90%)
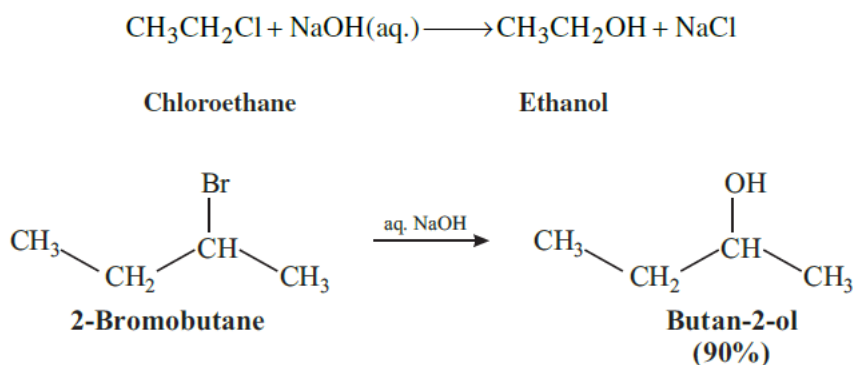
In this reaction only primary alkyl-halide gives better yield of alcohols. The tertiary alkyl halides, during this reaction provide, mainly alkenes through dehydrogenation.

2-Bromo-2-methylpropane

2-methylprop-1-ene
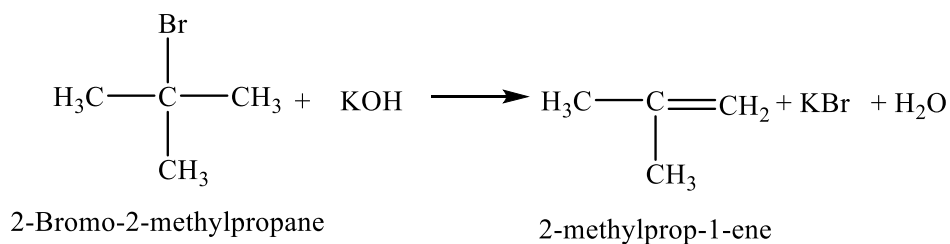
Another side the secondary alkyl-halides contribute a mixture of 'Alcohols and Alkene'

2-Bromo-2-methylpropane

Propan-2-ol

Propene

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(ii)   Hydration of Alkenes

The hydration of alkenes can be accomplished indirectly by first adding H_2SO_4 to produce alkyl hydrogen sulfate. Subsequent hydrolysis with hot water then yields alcohols. For example,

$$H_2C{=}CH_2 + H_2SO_4 \longrightarrow \quad \xrightarrow[\;-H_2SO_4\;]{\;H_2O\;} \quad H_3C{-}CH_2{-}OH$$

Ethene   Ethanol

Ethyl hydrogen sulfate
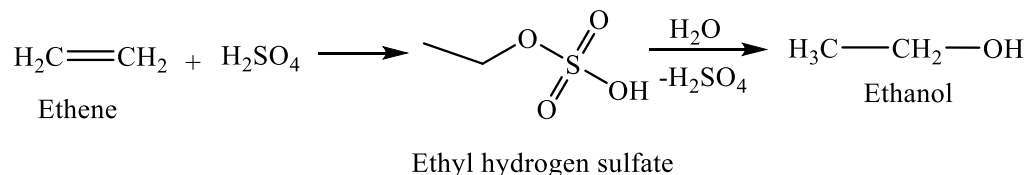
Certain secondary reactive alkenes can directly undergo hydration in the presence of mineral acids, which serve as catalysts.

2 Methylpropene   2-Methylpropanol
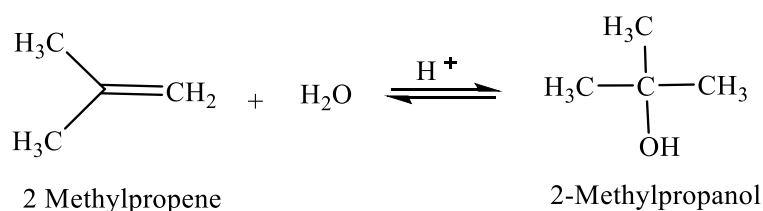
(iii)   Using Grignard Reagents.

Grignard reagents react with both Ketone and aldehydes, yielding products that decompose when treated with dilute HCl or dilute H_2SO_4, resulting in the formation of primary, secondary, and tertiary alcohols.

Formaldehyde (methanal) provides '*primary alcohol*.'

Propyl magnesium   Methanal   Butan-1-ol
bromide   (Primary alcohol)
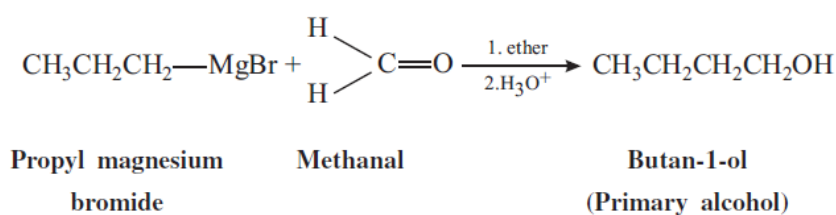
Although, all other aldehydes give '*secondary alcohols*'.

Ethyl magnesium   Ethanal   Butan-2-ol
bromide   (Acetaldehyde)   (Secondary alcohol)
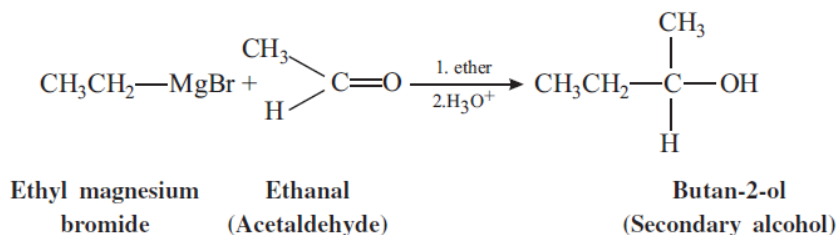
and ketones furnish '*tertiary alcohols*'.

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CH₃CH₂—MgBr + (CH₃)(CH₃)C=O $\xrightarrow[\text{2.H}_3\text{O}^+]{\text{1. ether}}$ CH₃CH₂—C(CH₃)(CH₃)—OH

Ethyl magnesium bromide   **Propanone**   **2-Methylbutan-2-ol**
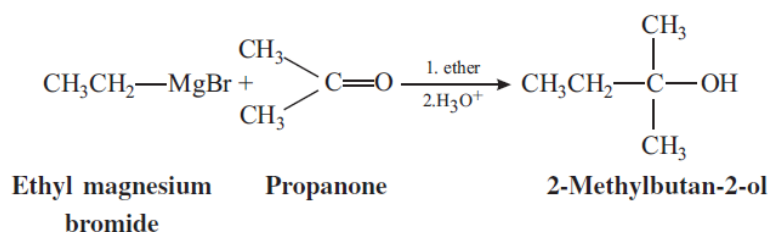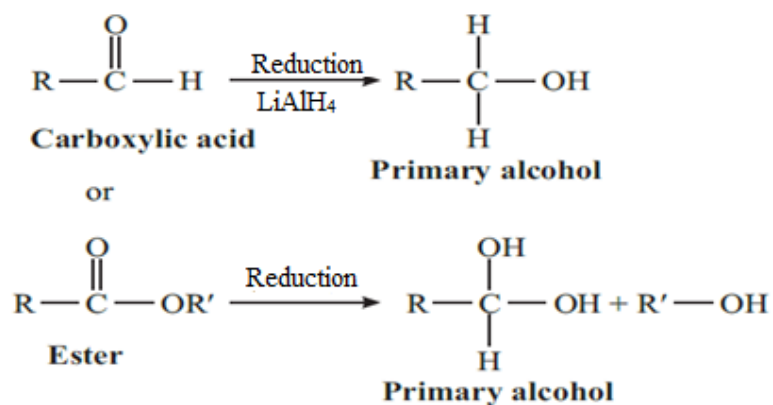
(iv)   Synthesis of alcoholsby Reduction

Carbonyl compounds (aldehydes and ketones) and other C=O group containing derivatives such as carboxylic acids and esters undergoes to form alcohol. Aldehydes during the reduction afford'*primary alcohols*' and ketonesgive'*secondary alcohols*'. Various reducing agents and catalyst are employed (NaBH₄, LiAlH₄Na/C₂H₅OH or H₂ with Ni, Pt, Pd catalyst).

R—C(=O)—H $\xrightarrow[\text{H}_2\text{/Pd}]{\text{Reduction}}$ R—C(H)(H)—OH

Aldehyde   **Primary alcohol**

R—C(=O)—R′ $\xrightarrow[\text{NaBH}_4]{\text{Reduction}}$ R—C(OH)(H)—R′

Ketone   **Secondary alcohol**
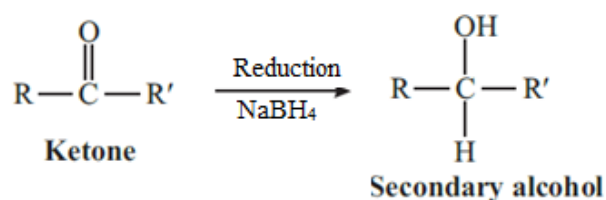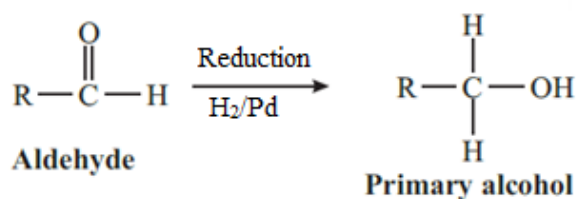
Carboxylic acids and esters reduce to primary alcohols as

R—C(=O)—H $\xrightarrow[\text{LiAlH}_4]{\text{Reduction}}$ R—C(H)(H)—OH

Carboxylic acid   **Primary alcohol**

or

R—C(=O)—OR′ $\xrightarrow{\text{Reduction}}$ R—C(OH)(H)—OH + R′—OH

Ester   **Primary alcohol**

10.5. Structure and physical properties of Alcohols

Alcohols bear a structural resemblance to water, which an alkyl group in place of one of the hydrogen atoms in a water molecule. The structures of both water and methanol is illustrate below in figure-10.1. Although they both comprise oxygen atoms, the bond angle in methanol [108.9°] is significantly greater than the bond angle that exists in water [104.5°] due to the larger methyl group in methanol than in hydrogen atoms.
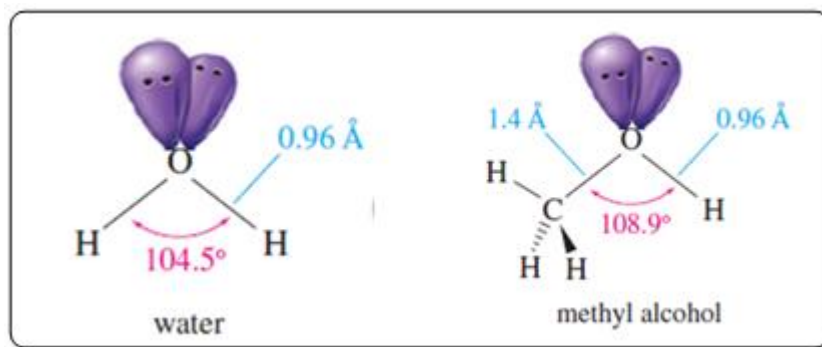
Figure-10.1 Structures of Water and Methanol

As we can see the higher electronegativity of oxygen atom than that of hydrogen atom is the origin of the polarity of the O-H bond in alcohols. A small positive charge is carried by hydrogen and a slight negative charge is carried by oxygen. Nonetheless, the higher boiling temperatures of alcohols relative to hydrocarbons or haloalkanes cannot be entirely explained by this bond polarity alone.

Hydrogen bonding is usually responsible for alcohols' higher boiling points. The given figure-10.2 provides an example of how alcohol molecules form hydrogen bonds.
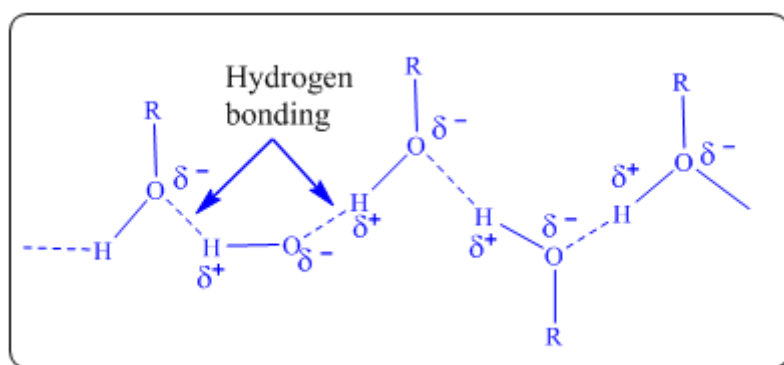
Figure-10.2 Hydrogen bonding in Alcohols

The negatively (-ve) polarized oxygen atom of one alcohol molecule attracts the positively (+ve) polarized hydrogen atom of another molecule, leading to association or cohesion among alcohol molecules. This attraction must be overcome for a molecule to transition from the liquid to the

vapor phase. Consequently, more heat energy is needed to break these hydrogen bonds, resulting in higher boiling points for alcohols compared to alkanes and halo-alkanes of similar molecular mass. Due to hydrogen bond formation the alcohols are miscible in water. The complete miscibility is exhibited by lower alcohols, whose solubility decrease with increasing size of the hydrocarbon portion of the molecule.
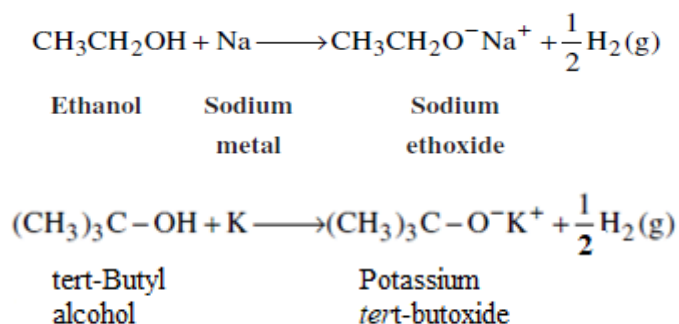
10.6. Chemical reaction of Alcohols

The functional group in alcohols is the -OH group. Consequently, the reactions of an alcohol's -OH group are typically involved in its chemical characteristics. These are responsive to both '**substitution and elimination**' reactions. The carbon chain that is joined to the -OH group determines the chemical reactivity of alcohols. The chemical reactions of alcohol mainly divided in following three categories.

- Reactions participating breaking of O-H Bond.
- Reactions participatingbreaking of C-O Bond.
- Reactions participatingboth alkyl and OH bond.

10.6.1.Reactions participating breaking of O-H Bond

Alcohols are very weak acids (Ka= 10^{-16}- 10^{-18}) even feeble than water (Ka=10^{-16}- 10^{-18}). Alcohols typically don't exhibit acidic properties to the same extent as acids. However, under certain conditions, they can undergo acidic reactions.

The hydrogen atom attached to the oxygen in the alcohol group (-OH) can be removed in the presence of a strong base, resulting in the formation of an alkoxide ion:

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2(g)$$

| Ethanol | Sodium metal | Sodium ethoxide |

$$(CH_3)_3C-OH + K \longrightarrow (CH_3)_3C-O^-K^+ + \frac{1}{2}H_2(g)$$

tert-Butyl alcohol

Potassium *tert*-butoxide

This alkoxide ion can then act as a nucleophile in various reactions. However, compared to true acids like hydrochloric acid (HCl) or sulfuric acid (H_2SO_4), alcohols have a significantly weaker tendency to donate protons.

The acidic strength of alcohols decreases with increasing number of alkyl groups on alcohols this is due the positive inductive effect of alkyl groups.

Primary alcohol > Secondary alcohol> Tertiary alcohols

**(i)   Etherification reaction of alcohols**

Etherification is a common reaction where an alcohol reacts with carboxylic acids in presence acid catalyst, typically sulfuric acid (H_2SO_4). In the present reaction a water molecule is eliminated by by combined of –OH from –COOH and H from –OH.
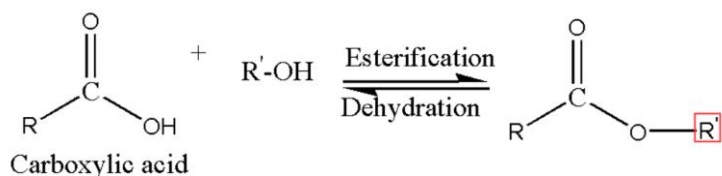
This reaction as shown in above equation is reversible

(ii)   Reaction with (RMgX) Grignard Reagent

When an alcohol reacts with a Grignard reagent, produces the alkanes. In this reaction the alkyl part of Grignard Reagent by taking hydrogen from alcohols convert to corresponding alkanes.
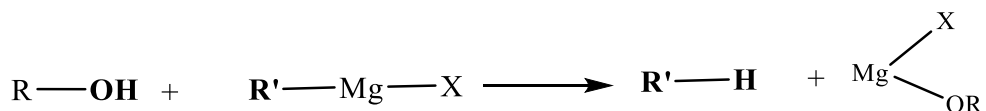
10.6.2. Reactions participating breaking of C-O Bond

Reaction with HX (**Lucas Test**): This test is used to distinguish between primary, secondary and tertiary alcohols. It is done by using a solution of anhy. $ZnCl_2$ in HCl [**Lucas reagent**]

10.6.3. Reactions participating both alkyl and OH bond.

(i) Oxidation of alcohols:

Alcohols experience oxidation to form carbonyl compounds. Specifically, primary alcohols oxidize to yield aldehydes or carboxylic acids, while secondary alcohols yield ketones. Tertiary alcohols, on the

other hand, typically do not undergo oxidation. Common oxidizing agents used for this purpose include potassium permanganate ($KMnO_4$), chromium trioxide (CrO_3), sodium dichromate ($Na_2Cr_2O_7$), or potassium dichromate ($K_2Cr_2O_7$).

$$CH_3CH_2CH_2OH \xrightarrow[H_2O]{K_2Cr_2O_7, H_2SO_4} CH_3CH_2CHO$$

Propan-1-ol   Propanal

$$\downarrow \text{further Oxidatipn}$$

$$CH_3CH_2COOH$$

Propanioc acid
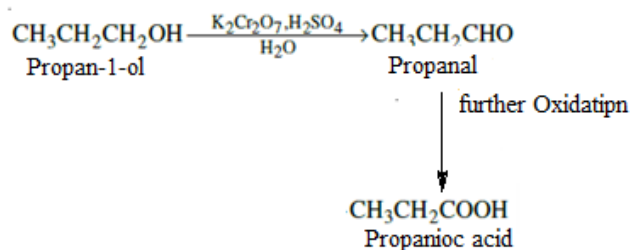
The aldehydes resulting from the oxidation of primary alcohols undergo further oxidation to form carboxylic acids, as demonstrated previously.

By utilizing 'pyridiniumchlorochromate'(**PCC**), oxidation can be moderated, leading to the formation of aldehydes as the primary products. PCC serves as a mild reagent for this purpose.

$$CH_3(CH_2)_8CH_2OH \xrightarrow{PCC} CH_3(CH_2)_8CHO$$

Decanol   **Decanal**
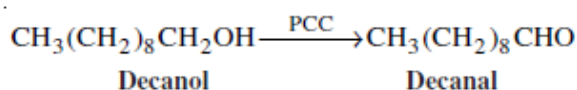
As demonstrated below, secondary alcohols can oxidize to ketones.

Propan-2-ol   **Propan-2-one**
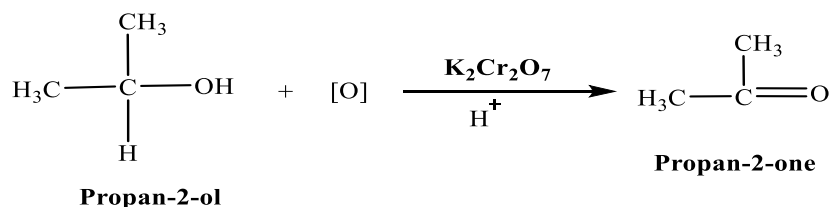
Tertiary alcohols generally do not undertake oxidation under standard conditions. This is because they lack a hydrogen atom attached to the carbon atom bearing the hydroxyl group, which is essential for oxidation to occur via typical oxidation mechanisms. However in acidic conditions, they first convert to alkenes and alkenes then undergoes oxidation to ketone, which finally oxidized carboxylic acid with to lesser no of carbon atoms.

2-methylprop-1-ene

$$CH_3COOH$$
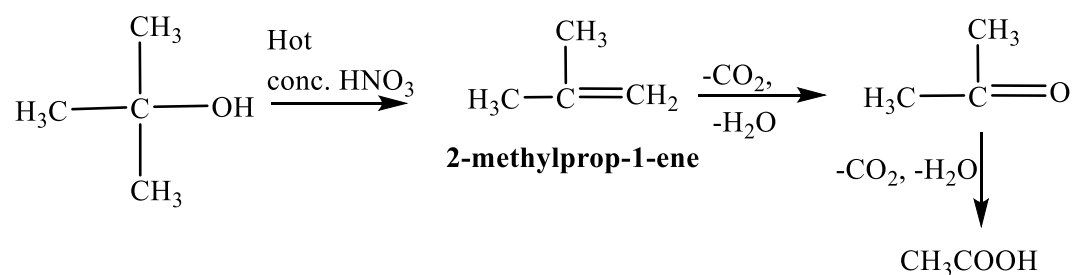
(ii)Oppenauer-Oxidation; The process known as oxidation involves selectively oxidizing secondary alcohols to produce ketones. The name Rupert Viktor Oppenauer is honoured in this reaction. Where there is more [Al(i-Pro)$_3$] than acetone, an oxidation process occurs.
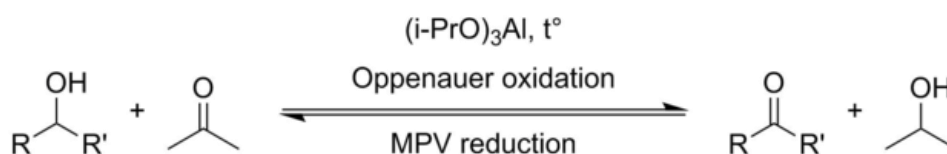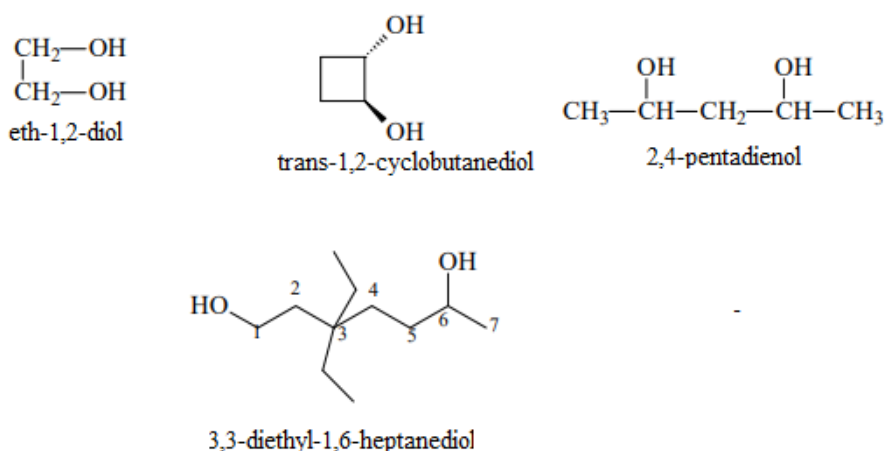

The Oppenauer Oxidation is a process catalyzed by aluminumalkoxides, aimed at oxidizing secondary alcohols into their respective ketones. It serves as the reverse reaction to the Meerwein-Ponndorf-Verley(MRV) reduction. Notably, it is highly effective for oxidizing allylic alcohols to α,β-unsaturated ketones.

10.7. Di-hydric Alcohols

These compounds feature two hydroxyl (–OH) groups within a molecule, serving as dihydroxy constituents of alkanes. Their general formula is $CnH_{2n}+2O_2$. The primary and pivotal dihydric alcohol is ethylene glycol.

In naming polyhydric alcohols, the name of the alkane remains unchanged, retaining the -e ending, while adding a di- or tri- 'prefix' to the -ol 'suffix'. Consequently, dihydric alcohols are termed alkane diols, and trihydric alcohols are termed alkane triols.
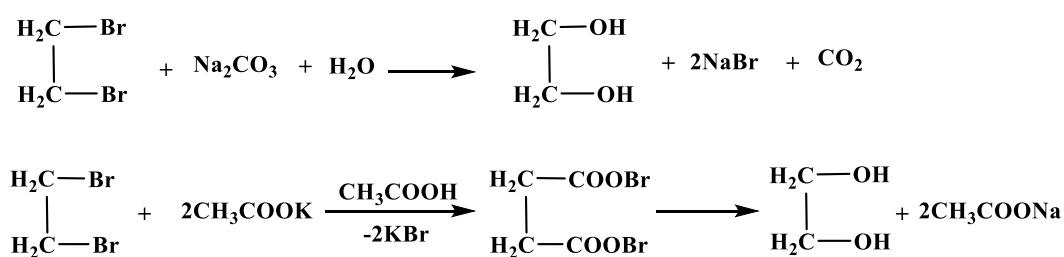

eth-1,2-diol

trans-1,2-cyclobutanediol

2,4-pentadienol

3,3-diethyl-1,6-heptanediol

10.7.1. Preparation Methods

(i) From Ethylene

syn hydroxilation

anti hydroxilation

(ii) From di-bromo ethane

$$H_2C-Br \mid H_2C-Br + Na_2CO_3 + H_2O \longrightarrow H_2C-OH \mid H_2C-OH + 2NaBr + CO_2$$

$$H_2C-Br \mid H_2C-Br + 2CH_3COOK \xrightarrow[-2KBr]{CH_3COOH} H_2C-COOBr \mid H_2C-COOBr \longrightarrow H_2C-OH \mid H_2C-OH + 2CH_3COONa$$
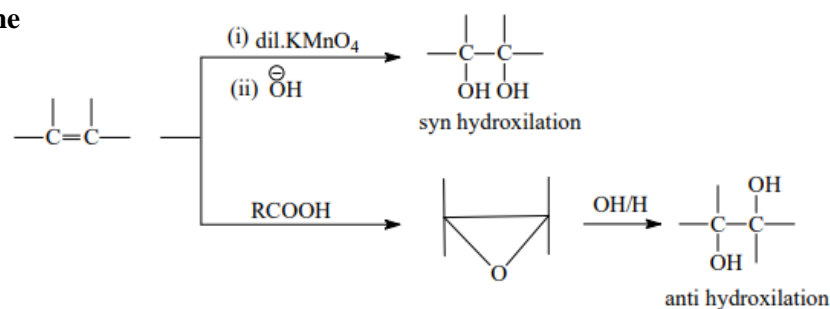
10.7. 2. Chemical Reactions

Since the glycerol molecule is composed of two linked groups of primary alcohols, its chemical reactions are the same as those of primary alcohols twice over, i.e.
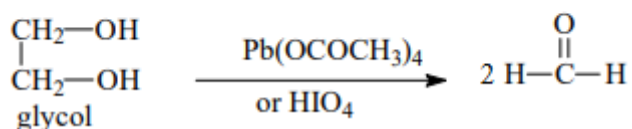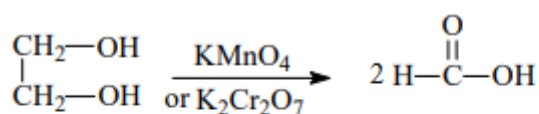
(i)   Reaction with sodium

$$CH_2-OH \mid CH_2-OH + Na \xrightarrow{50\,^0C} CH_2-ONa^+ \mid CH_2-OH + 1/2H_2$$

$$CH_2-ONa^+ \mid CH_2-OH + Na \xrightarrow{160\,^0C} CH_2-ONa^+ \mid CH_2-ONa^+ + 1/2H_2$$

(ii)   Reaction with HCl

$$CH_2-OH \mid CH_2-OH + HCl \xrightarrow{160\,°C} CH_2-Cl \mid CH_2-OH + H_2O$$

$$CH_2-Cl \mid CH_2-OH + HCl \xrightarrow{200\,°C} CH_2-Cl \mid CH_2-Cl + H_2O$$
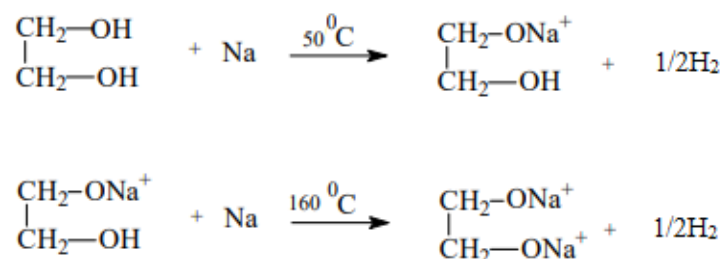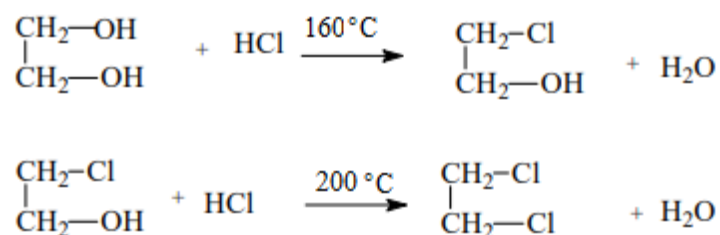
(iii)   Reaction with carboxylic acid

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} + CH_3COOH \longrightarrow \begin{array}{l} CH_2\text{–}OCOCH_3 \\ | \\ CH_2\text{—}OH \end{array} + H_2O$$

glycol monoacetate

$$\begin{array}{l} CH_2\text{–}OCOCH_3 \\ | \\ CH_2\text{—}OH \end{array} + CH_3COOH \xrightarrow[\text{in excess}]{H_2SO_4} \begin{array}{l} CH_2\text{–}OCOCH_3 \\ | \\ CH_2\text{—}OCOCH_3 \end{array}$$

glycol diacetate

(iv)   Oxidation Reaction

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} \xrightarrow[\text{or } K_2Cr_2O_7]{KMnO_4} 2\ H\text{—}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{—}OH$$

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \\ \text{glycol} \end{array} \xrightarrow[\text{or } HIO_4]{Pb(OCOCH_3)_4} 2\ H\text{—}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{—}H$$
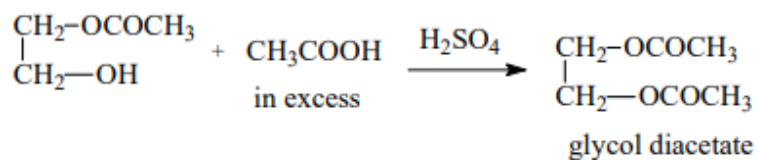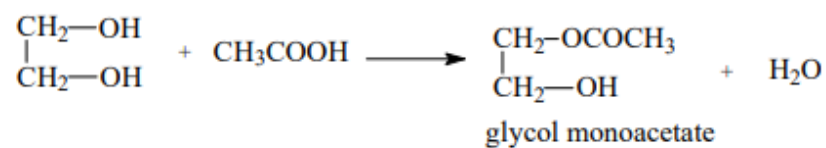
(v)   Oxidation with HNO$_3$
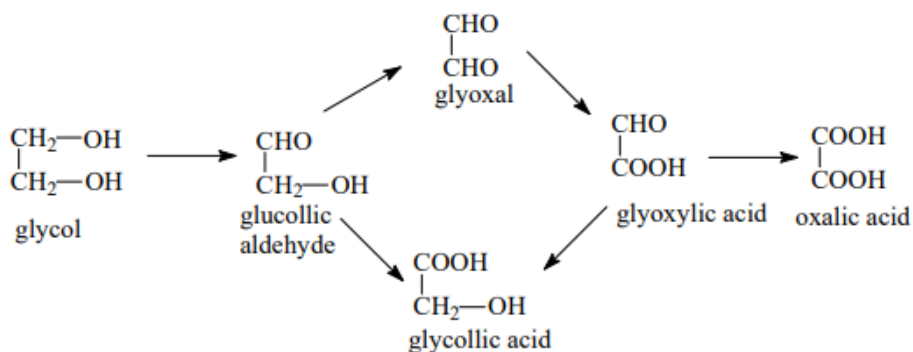
(vi)   Pinacol – pinacolone rearrangement

This transformation involves the conversion of 1, 2 diols in 'ketones' on action with H$_2$SO$_4$.A reaction between molecules is the pinacol-pinacolone rearrangement. German scientist Wilhelm Fitting developed it in 1860, making it one among the oldest rearrangements in recorded history. Carbonyl compounds are produced in large quantities using the pinacol-pinacolone rearrangement.
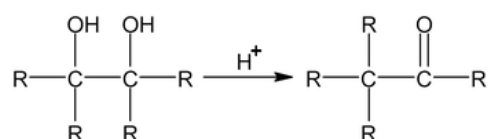
Mechanism
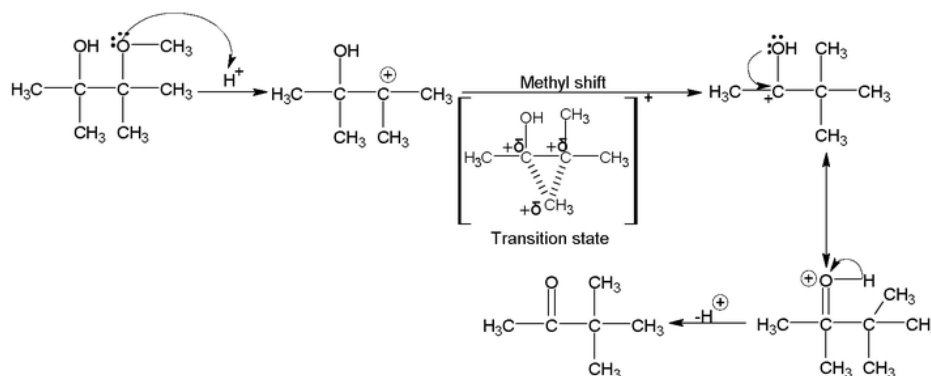
10.7. 3. Uses of ethylene glycol include:

- Antifreeze: Prevents water from freezing in car radiators, particularly in cold regions.
- Industrial applications: Its high viscosity makes it suitable for use in hydraulic brakes, printing ink balls, pen inks, and organic solvents.
- Manufacturing: Utilized in the production of Dacron, dioxane, and other compounds.
- Solvent and preservative: Functions as both a solvent and a preservative.
- Cooling agent: Employed as a cooling agent in aircraft.
- Polymer production: Large quantities are converted into polymers like polyethylene glycol, which find applications in manufacturing Dacron fibers, photographic films, and cassette tapes.

10.8. Tri-hydric Alcohol

Being a triol, glycerol possesses three hydroxyl (–OH) groups. The addition of a third –OH group to the diol molecule elevates its boiling point by approximately 10°C, enhances viscosity, and imparts a sweeter taste to the alcohol. Glycerol is a notable example of such a triol.
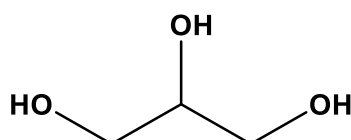
In IUPAC nomenclature, it is designated as 'prop-1, 2, 3-triol'. Conceptually, it can be viewed as a derivative of propane, where three hydrogen atoms from distinct carbon atoms
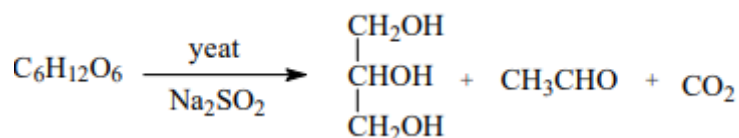
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are substituted with three hydroxyl groups. In industrial contexts, it is commonly referred to as glycerine. Glycerol occurs naturally as glycosides in nearly all animal and vegetable oils and fats.

10.8.1. Preparation Methods

(i) Hydrolysis; upon the hydrolysis of fats and oils, glycerol and higher fatty acids are produced.
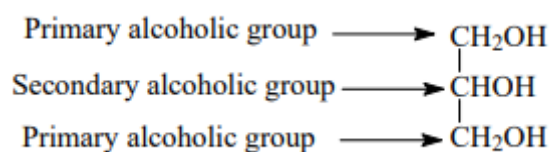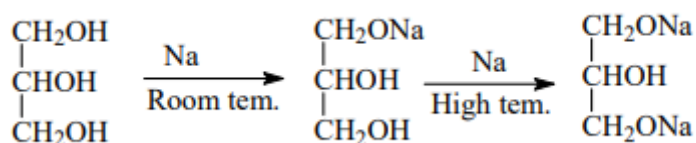
$$
\begin{array}{l}
CH_2OOCR \\
| \\
CHOOCR \quad + \quad 3\,H_2O \\
| \\
CH_2OOCR
\end{array}
\longrightarrow
\begin{array}{l}
CH_2OH \\
| \\
CHOH \quad + \quad 3\,RCOOH \\
| \\
CH_2OH
\end{array}
$$

(ii) **Fermentation reaction;**

$$
C_6H_{12}O_6 \xrightarrow[Na_2SO_2]{yeat}
\begin{array}{l}
CH_2OH \\
| \\
CHOH \quad + \quad CH_3CHO \quad + \quad CO_2 \\
| \\
CH_2OH
\end{array}
$$

10.8.2. Chemical Reactions

Glycerol comprises two primary – OH groups and another one secondary – OH group. Thus, it shows features of both these types alcohol

$$
\begin{array}{ll}
\text{Primary alcoholic group} \longrightarrow & CH_2OH \\
 & | \\
\text{Secondary alcoholic group} \longrightarrow & CHOH \\
 & | \\
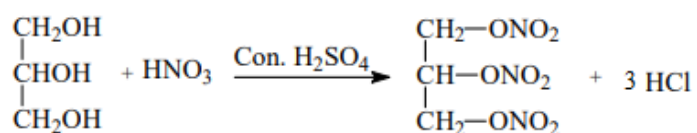\text{Primary alcoholic group} \longrightarrow & CH_2OH
\end{array}
$$

(i)   When reacting with sodium, only the primary alcoholic groups are sequentially attacked, while the secondary alcoholic group remains unreactive. At room temperature, sodium forms monosodium glycerolate, and at higher temperatures, it yields disodium glycerolate.

$$
\begin{array}{l}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\xrightarrow[\text{Room tem.}]{Na}
\begin{array}{l}
CH_2ONa \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\xrightarrow[\text{High tem.}]{Na}
\begin{array}{l}
CH_2ONa \\
| \\
CHOH \\
| \\
CH_2ONa
\end{array}
$$

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(ii) Upon heating glycerol with an ample quantity of HI, the initial formation of allyl iodide occurs, which subsequently undergoes reduction to propene. Propene, in the presence of an excess of HI, further reacts to produce iso-propyl iodide.

$$
\begin{array}{c}
CH_2 \\
\parallel \\
CH \\
\mid \\
CH_2I
\end{array}
+ HI \longrightarrow
\begin{array}{c}
CH_3 \\
\mid \\
CHI \\
\mid \\
CH_2I
\end{array}
\xrightarrow{-I_2}
\begin{array}{c}
CH_3 \\
\mid \\
CH \\
\parallel \\
CH_2
\end{array}
+ HI \longrightarrow
\begin{array}{c}
CH_3 \\
\mid \\
CHI \\
\mid \\
CH_3
\end{array}
$$
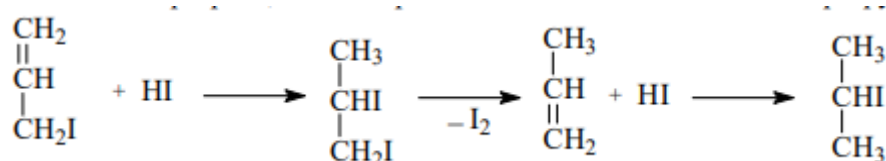
(iii) When one part of glycerol is carefully added in a thin stream to three parts of concentrated HNO_3 and five parts of conc. sulfuric acid, nitroglycerin (glyceryl tri-nitrate) is produced.

$$
\begin{array}{c}
CH_2OH \\
\mid \\
CHOH \\
\mid \\
CH_2OH
\end{array}
+ HNO_3 \xrightarrow{\text{Con. } H_2SO_4}
\begin{array}{c}
CH_2-ONO_2 \\
\mid \\
CH-ONO_2 \\
\mid \\
CH_2-ONO_2
\end{array}
+ 3\ HCl
$$

The yellow, oily liquid glyceryl tri-nitrate is well-known for being poisonous and having a tendency to give headaches. When exposed to abrupt shock or quick heating, it behaves explosively. But as it becomes absorbed on kieselguhr, it changes into a less dangerous explosive form. This altered type is known by its renowned name, **dynamite**. Alfred Nobel made the initial discovery of dynamite in 1867.

10.8.3. Uses of Glycerol

- Sweetening Agent: Glycerol finds application as a 'Sweetening agent' in confectionery, beverages, and Medicines due to its non-toxic nature.
- Antifreeze: It serves as an anti-freeze in 'Automobile Radiators'.
- Soap Production: Glycerol is utilized in the preparation of high-quality soap.
- Personal Care Products: It contributes to the formulation of hand lotions, shaving creams, toothpaste, and cosmetics.
- Lubrication: Glycerol functions as a lubricant in watches.
- Preservative: It is employed as a preservative.

Summary:

This unit covers the classification of alcohols based on the number of hydroxyl groups present, including monohydric, dihydric, trihydric, and polyhydric alcohols. It explains the

naming of alcohols according to IUPAC conventions and various methods of alcohol preparation, such as hydrolysis of halogeno-alkanes, hydration of alkenes, and reduction of aldehydes and ketones using Grignard reagents, $LiAlH_4$, $NaBH_4$, and fermentation of carbohydrates. Additionally, it discusses the amphoteric nature of alcohols, highlighting their ability to act as acids or bases. Special focus is given to the properties, reactions, and applications of dihydric alcohol glycol and trihydric alcohol glycerol.

Keywords:

- **Primary- alcohol**: an alcohol in which there is just one other carbon atom connected to the carbon atom bound to the –OH group.
- **Secondary -alcohol**: An alcohol in which two additional carbon atoms are joined to the carbon atom linked to the –OH group.
- **Tertiary- alcohol**: Three more carbon atoms are joined to the carbon atom that is connected to the –OH group in an alcohol.
- **Glycerol:** A three-carbon alcohol ($C_3H_8O_3$) also known as glycerin or glycerine, commonly used in cosmetics, pharmaceuticals, and food production.
- **Industrial applications**: The use of alcohols in various manufacturing processes and industries, such as pharmaceuticals, cosmetics, fuels, and solvents.

MCQ

1. Which of the following best describes the classification of alcohols based on the number of hydroxyl groups present?

(A) Monohydric, dihydric, trihydric   (B) Primary, secondary, tertiary

(C) Alkanols, alkenols, alkynols   (D) Saturated, unsaturated, aromatic

Answer: (A)

2. How are alcohols named according to IUPAC conventions?

(A) By replacing the ending -e in the corresponding alkane with -ol

(B) By adding the prefix di- or tri- to the alkane name

(C) By replacing the -OH group with –ane

(D) By changing the alkane name to an alkene nam

Answer: (A)

3. Which of the following functional groups characterizes alcohols?

A) –OH   B) -COOH   C) -NH$_2$ D) -CO

Answer: A)

4. Which method is commonly used for the preparation of alcohols from alkenes?

A) Hydrolysis of halogenoalkanes   B) Fermentation of carbohydrates

C) Reduction of aldehydes and ketones   D) Hydration of alkenes

Answer: D)

Short Answer Question

1. Explain the basic properties of alcohols.
2. How we can differentiate the primary, secondary and tertiary alcohols.
3. How does the boiling point of alcohols compare to that of alkanes with the same molecular weight?
4. Discuss the two synthetic methods of alcohols.
5. Write to note on oxidation of alcohols.

Chapter: 11

Phenols

Objective:

- This unit's goals include studying the phenol's structure and bonding, as well as its physical and chemical characteristics, such as its acidic nature.

- Students will also learn about the general procedures used to prepare phenols, as well as how acidic they tend to be in comparison to alcohols, how different chemical reactions work, especially their distinct electrophilic substitution reactions, and become familiar with some well-known named reactions involving phenols.

11.1. About the Phenols

The term "phenol" specifically refers to a compound in which a hydroxyl group is directly attached to a benzene ring.Phenols have a very different chemistry from alcohols, even though they both have the same functional group—that is, an aliphatic carbon to which the -OH group is connected.The chemical formula for 'hydroxybenzene', or phenol, is C_6H_5OH. This is the most basic type of phenol. By itself, phenol has antibacterial properties. Mouthwashes, deodorant soaps, and medicated skin cleansers all include hexachlorophene, another phenolic derivative.In nature, phenols are abundantly distributed.Aspirin and other organic molecules are synthesized with the help of phenols, which are also used to make dyes. Phenol is also used in the production of Bakelite, a very versatile polymer.

A sp^2-hybridized aromatic carbon atom and a hydrogen atom are connected by σ bonds to form the -OH group. The high electro-negativity of the oxygen atom causes both the C-O and O-H bonds to exhibit polarity. There is a conjugation between the aromatic ring and an unshared electron pair on the oxygen.

Thus, phenols have a shorter carbon-oxygen bond distance, a more basic hydroxyl oxygen, and an acidic hydroxyl proton (-OH) than simple alcohols. Hence, phenols are acidic in nature and due to its acidic nature they are also known as "**Carbolic acids**"

Structure of phenol
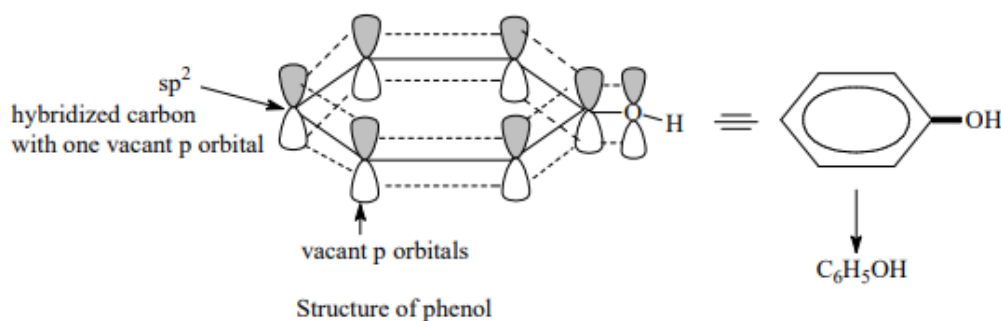
The electronic structure of phenol can be depicted as a resonance hybrid, formed by a combination of various canonical forms. The +M effect of OH enhances the electron density in benzene ring activated the electrophilic substitutions on *ortho*and *para* position.
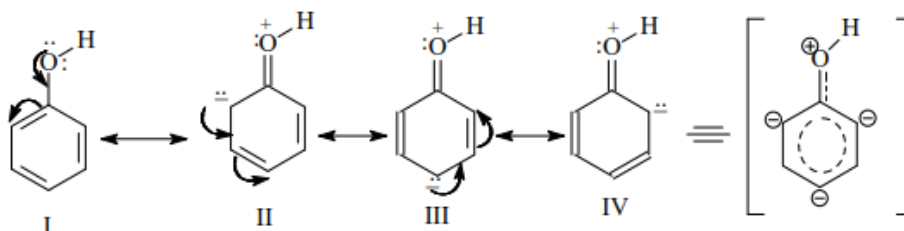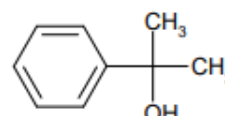

It's important to clarify that aromatic compounds where the -OH group isn't directly bonded to the benzene ring aren't classified as phenols but rather as aromatic alcohols. These can be seen as aryl derivatives of aliphatic alcohols.
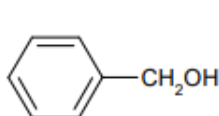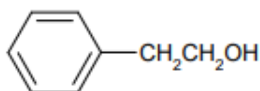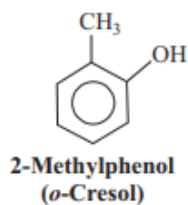

Benzyl alcohol   2-Phenylethanol   2-Phenylpropanol

11.2. Nomenclature of Phenols

The examples of some phenolic compounds are given

2-Methylphenol
(*o*-Cresol)
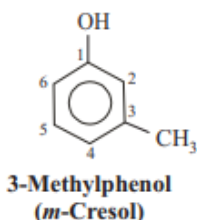
3-Methylphenol
(*m*-Cresol)
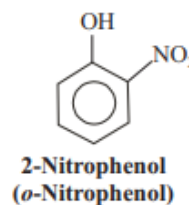
2-Nitrophenol
(*o*-Nitrophenol)
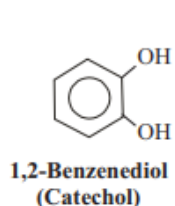
1,2-Benzenediol
(Catechol)
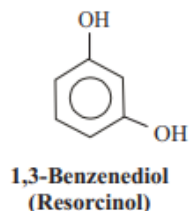
1,3-Benzenediol
(Resorcinol)
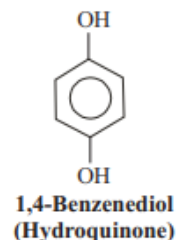
1,4-Benzenediol
(Hydroquinone)

2,6-Dibromophenol

1-Naphthol
(α-Naphthol)

120
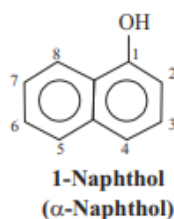
Note that "phenol" serves as the parent name, with other substituents in the compound being assigned specific numbers based on their positions on the aromatic ring. Following convention, the common names of these compounds are provided in brackets alongside their corresponding IUPAC names.

11.3. Preparative methods of Phenols

We can classify methods of preparing phenols into two categories: laboratory based synthetic procedures and industrial based synthetic procedures.
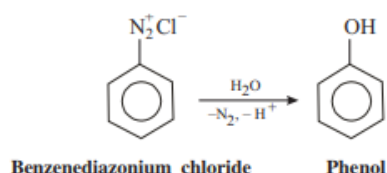
11.3.1. Laboratory based synthetic procedures

(i)   From Arene-diazonium Salts

This is the main strategy for making phenols and usually calls for mild reaction environment. Arene-diazonium salts, also known as aromatic **Diazonium Salt**s, are derived from the diazotization process of primary aromatic amines, as illustrated below.


Benzenamine
(Aniline)
(an aromatic amine)   **Benzenediazonium chloride**
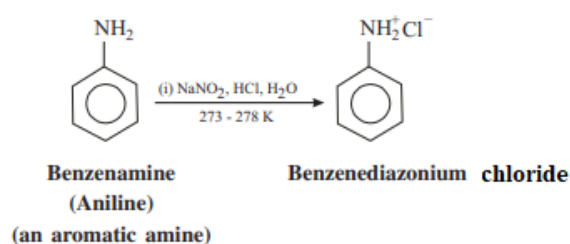
The arenediazonium salt on hydrolysis yields phenol.

Benzenediazonium chloride   **Phenol**

(ii)   From Sodium Benzene-sulphonate

This method, initially developed in Germany in 1890, marked the first commercial synthesis of phenol. It's also applicable in laboratory settings.


Sodium benzenesulphonate   **Sodium phenoxide**

Phenol

121
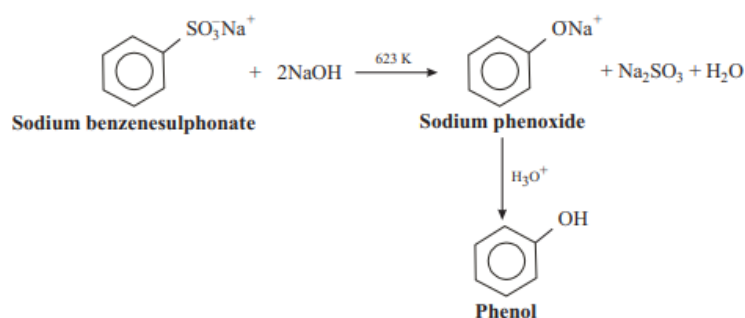
It involves fusing **sodium benzene-sulfonate** with sodium hydroxide to produce sodium phenoxide, which upon acidification, yields phenol.

## 11.3.2 Industrial based synthetic procedures

(i)   Dow Process

In this procedure, chlorobenzene undergoes heating with aqueous sodium hydroxide under pressure. Upon acidification of the resulting sodium phenoxide, phenol is obtained.
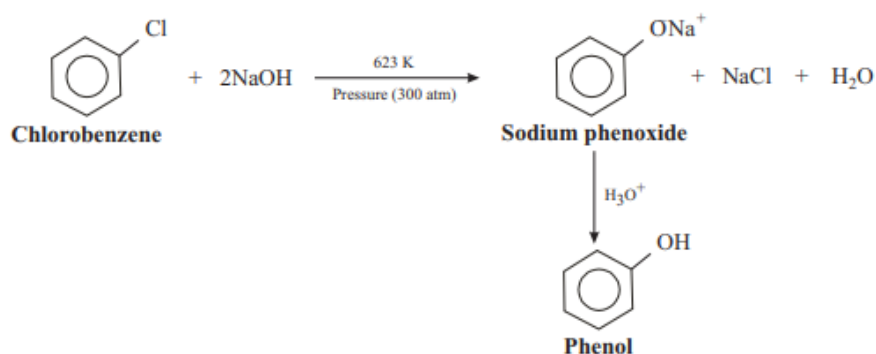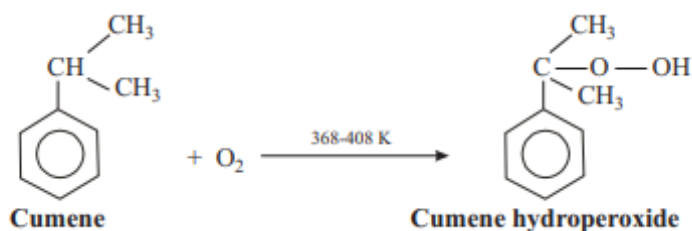

(ii)   Synthesis usingCumeneHydroperoxide

Commercially, phenol can be synthesized from **cumene**, which is derived from petroleum via the '**Friedel-Crafts Reactio**n' as outlined below.
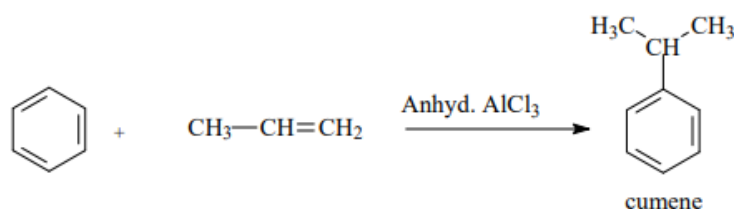
In the next step the cumenehydroperoxide is obtained by air oxidation of Cumene.

In the last stage, treating cumenehydroperoxide with 10% sulfuric acid results in the hydrolytic rearrangement, yielding phenol and acetone
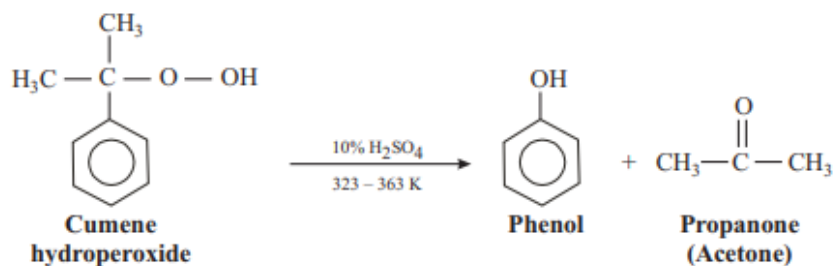
Here, in this reaction the additional obtained product propanone (acetone) is very important to us.

11.4. Properties of Phenols

Like alcohols, phenols possess a H atom bonded to the electronegative oxygen (O) atom. Consequently, phenols demonstrate intermolecular '**hydrogen bonding**', resulting in higher boiling points contrast to hydrocarbons of comparable Molecular Weight.

b.p. – 454.7 K
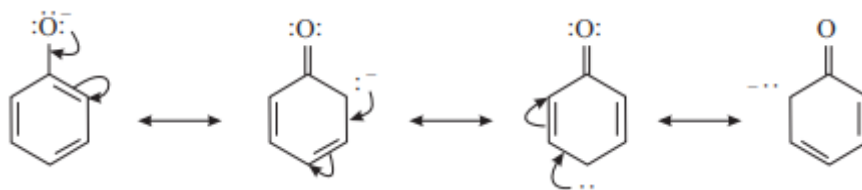Phenol

b.p. = 383.6 K
Methylbenzene]
(Toluene)
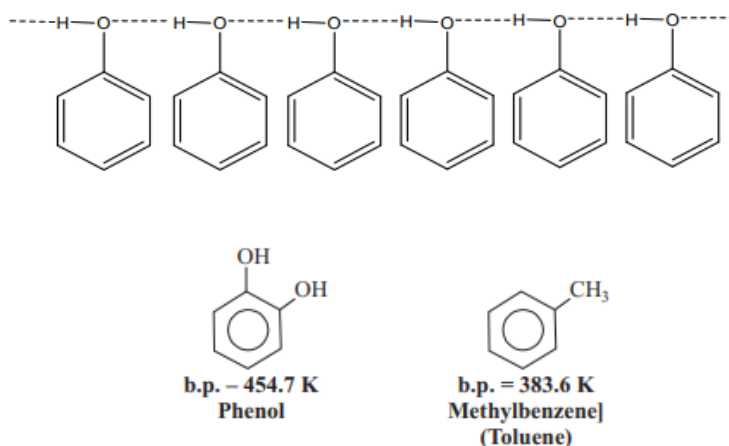
11.4.1. Acidic Properties of Phenols

Phenols are significantly more acidic than alcohols. They ionize in aqueous solutions, providing bases with H^+ ions. Nevertheless, they don't react with bicarbonates or carbonates.The increased acidity of phenols results from the resonance stabilization of the phenoxide ion formed upon hydrogen ion release. The dispersion of the negative charge across the benzene ring stabilizes the phenoxide ion, a stabilization not achievable with alkoxide ions.

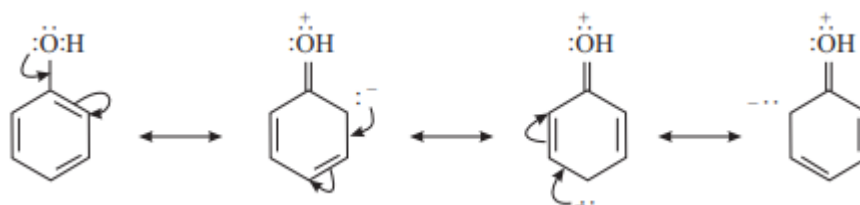
phenol

phenoxide ion

123
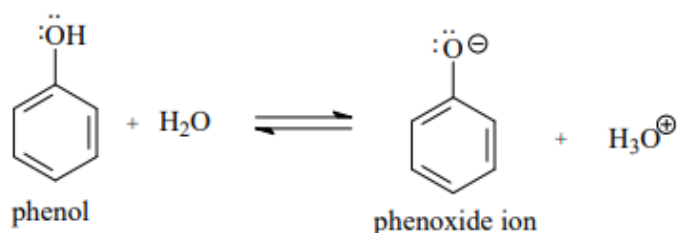
Phenol exhibits weaker acidity compared to carboxylic acids, with the equilibrium strongly favoring the reactants.

The phenoxide ion's resonance stabilization is the cause of phenols' higher acidity. The phenoxide ion's resonance forms are shown as.


The dispersion (delocalization) of the negative charge across the benzene ring stabilizes the phenoxide ion. Such stabilization is not achievable with alkoxide ions in case of alcohols. Due the +M effect the phenol itself also shows similar resonance as we discuss the starting in this chapter. The resonance structures of phenols involve the separation of charge and due to this the resonance patterns of phenol are less stable than those of phenoxide ions.

Electron-donating substituents like methyl groups diminish the acidity of phenol, resulting in 'alkyl-phenols' having higher pKa values compared to phenol itself. Conversely, electron-withdrawing substituent's enhance acidity, leading to phenols containing these substituent's (such as -Cl, -NO$_2$, etc.) exhibiting lower pKa values than phenol. Remarkably, 2,4,6-trinitrophenol (picric acid) is more acidic than numerous carboxylic acids.
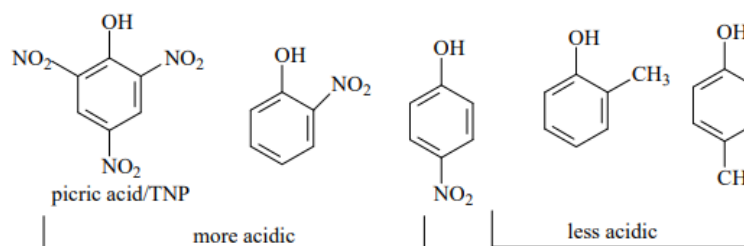
Additionally, phenols may have feeble fundamental behavior. They can be protonated to create 'phenyloxonium ion's, just as alcohols.

Phenyloxonium ion
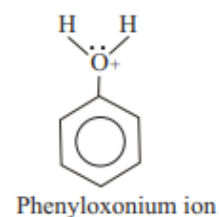
11.4.2. Other properties of phenols are as

- Phenols are only weakly soluble in water, but they dissolve well in ether and other organic solvents.
- Pure phenol has a disinfectant-like smell.
- Crystalline and white substance.
- It must be handled carefully since it instantly results in white blisters on the skin.\

11.5. Chemical Reactions of Phenols

Because of its strong activating properties, the hydroxyl group makes it easier for phenols to participate quickly in electrophilic substitution processes. During these reactions, one of the hydrogen atoms in the benzene ring is displaced by an electrophile, a molecule that seeks for electrons. The ortho and para positions in phenol are electron-rich, which means that replacement mostly takes place at these locations. The two main examples of these reactions are nitration and halogenation. Let's examine their workings in more detail.

(i) **Halogenation**: In an aqueous solution, phenol and bromine react to produce 2,4,6-tribromophenol with a yield of almost 100%.


By conducting bromination under low temperature and employing a less polar solvent like carbon disulfide, the reaction can be selectively directed towards monobromination, predominantly yielding 4-bromophenol. A minor quantity of 2-bromophenol is also produced as a byproduct.

(ii) Nitration; When phenol is nitrated using diluted nitric acid, it yields a mixture of 2-nitro and 4-nitrophenols.
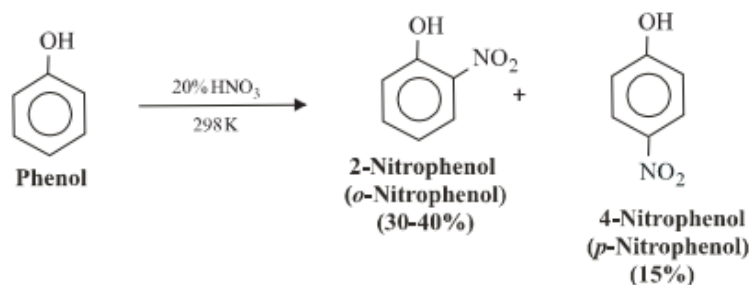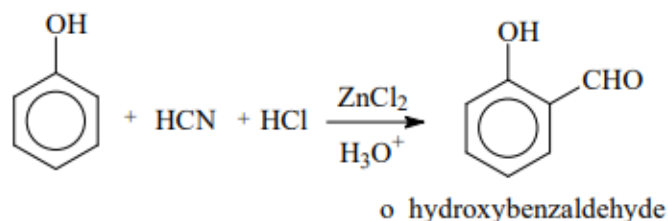
Using concentrate HNO_3 tri-nitro phenols are formed.


2, 4, 6-trinitrophenol
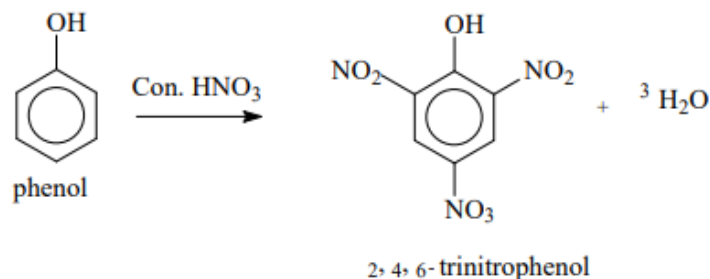
(iii) Gatter-mann Reaction;

In this reaction phenol undergoes formylation, resulting in the formation of salicylaldehyde in presence of HCN, HCl and $ZnCl_2$. The reaction is valuable for introduction of –CHO group on aromatic compounds.

o hydroxybenzaldehyde

**(iv) Reimer Tiemann Reaction**; The important method for the formylation of phenols. In this reaction, phenol is treated with chloroform ($CHCl_3$) and a strong base, typically sodium hydroxide (NaOH), in the presence of a trace amount of a weak acid, such as hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). The reaction proceeds as follows:

o hydroxybenzaldehyde   p hydroxybenzaldehyde
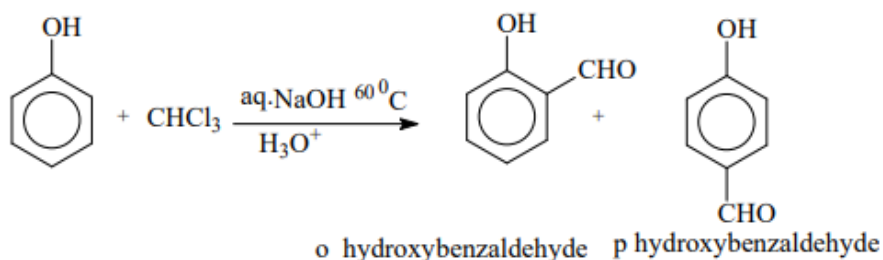
Mechanism; In presence of NaOH the $CHCl_3$ produce CCl_2 as a electrophile and undergoes further reaction as
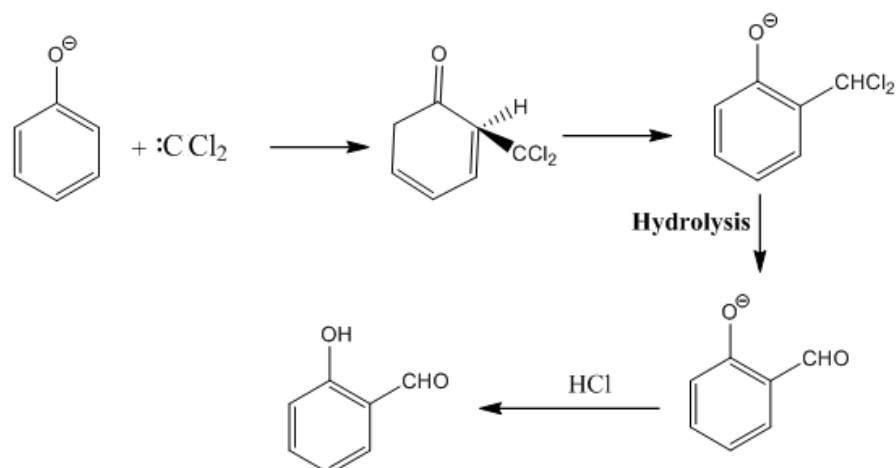
Salicylic acid is produced by substituting carbon tetrachloride for chloroform. Due to greater thermodynamic stability, an *ortho-* and *para*-isomer mixture is produced, with the ortho isomer predominating. The *para*-isomer is the main product if one of the ortho locations is occupied.

o hydroxybenzoic acid   p hydroxybenzoic acid
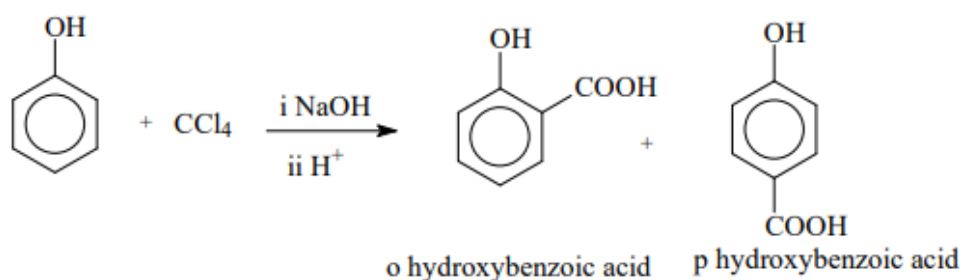
Commercial edible product vanillin is generated as the main product when anisole is treated **with CHCl₃ in the presence of alkali.**

anisol

vanillin
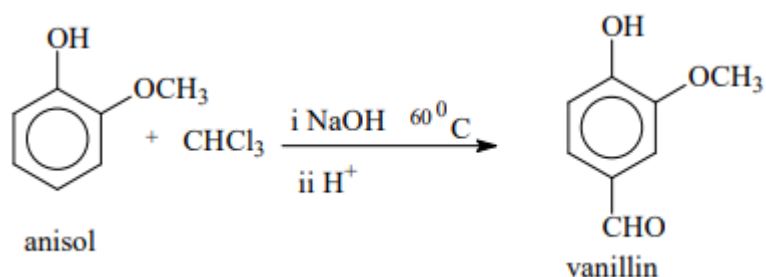
(v)Houben –Hoesch reaction

The Houben-Hoesch reaction involves the acylation of reactive polyhydric phenols where –OH groups are positioned '*meta*' to each other.

127

OH
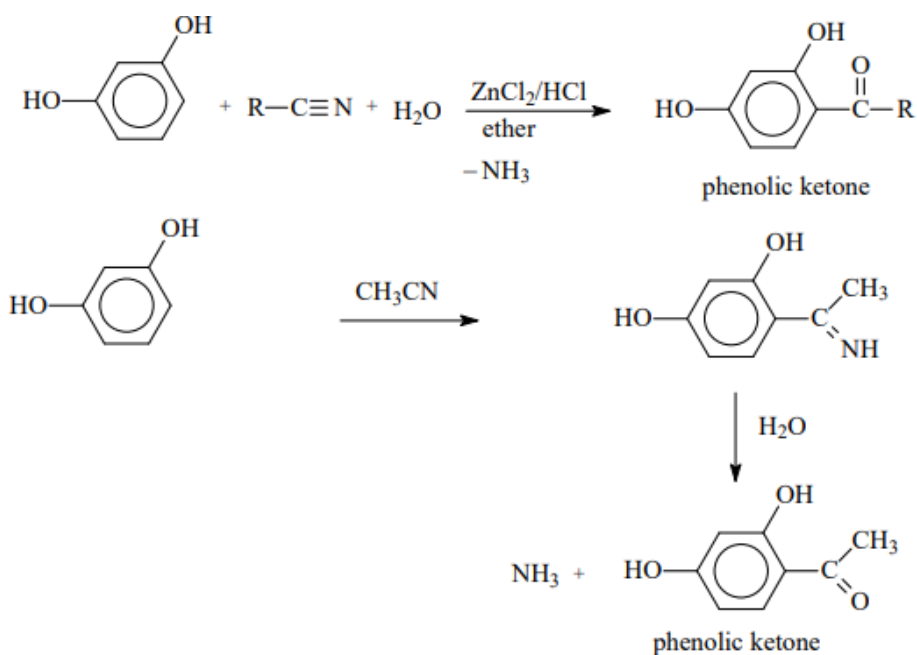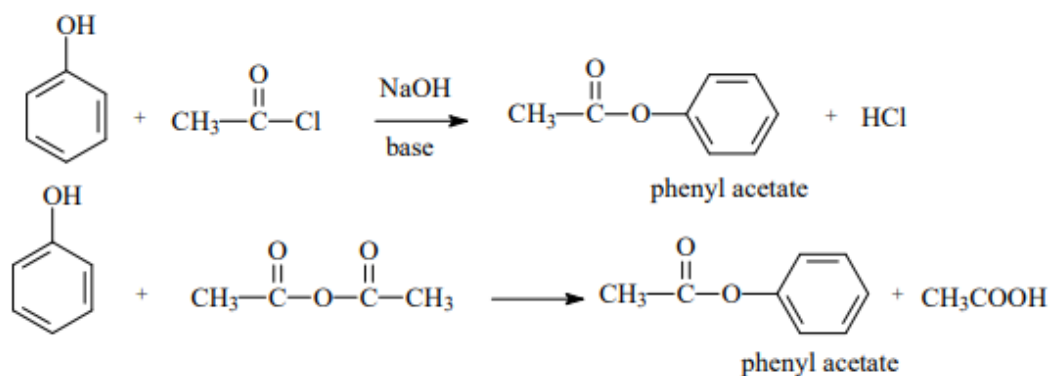
HO— ... + R—C≡N + H₂O $\xrightarrow[\text{ether}]{\text{ZnCl}_2/\text{HCl}}$ HO— ... —C—R

−NH₃

phenolic ketone

OH

HO— ... $\xrightarrow{\text{CH}_3\text{CN}}$ HO— ... C—CH₃, NH

H₂O

NH₃ + HO— ... C—CH₃

phenolic ketone

This process is accomplished by treating the phenols with alkyl cyanides in the presence of zinc chloride ($ZnCl_2$) and hydrochloric acid (HCl). As a result, the reaction yields phenolic ketones as the final product.

(vi) Schotten-Baumann Reaction; is a chemical process wherein phenols react with benzoyl chloride in the presence of a base, typically sodium hydroxide. This reaction facilitates the conversion of phenols into esters. It's a significant method for the synthesis of phenyl esters, often used in organic chemistry for various applications.

OH

... + CH₃—C—Cl $\xrightarrow[\text{base}]{\text{NaOH}}$ CH₃—C—O— ... + HCl

phenyl acetate

OH

... + CH₃—C—O—C—CH₃ $\longrightarrow$ CH₃—C—O— ... + CH₃COOH

phenyl acetate

Summary

This chapter focuses on exploring the properties, structure, physical characteristics, and chemical behaviors of phenols, with an emphasis on distinguishing them from alcohols. It delves into the acidic nature of phenols compared to alcohols and carboxylic acids. Detailed discussions are provided on chemical reactions stemming from both the –OH group and the

aromatic ring, which predominantly exhibit electrophilic tendencies. Additionally, the unit elaborates on significant named reactions involving phenols.

Keywords:

- **Hydroxyl (-OH) group**: When oxygen atom bonded to a hydrogen atom, characteristic of alcohols and phenols.
- **Acidic**: Having properties resembling an acid, such as the ability to donate a proton (H+) to a base.
- **Solubility**: The aptitude of a substance to dissolve in a solvent to form a 'Homogeneous solution'.
- **Phenoxide ion**: The conjugate base of phenol, formed by deprotonating the hydroxyl group to yield a negatively charged species.
- **Hydrogen bonding**: attraction between a hydrogen atom bonded to an electronegative atom and another electronegative atom

MCQ

1. Which of the following statements about phenols is correct?

(A) Phenols are more acidic than alcohols

(B) Phenols do not react with strong bases

(C) Phenols cannot undergo electrophilic aromatic substitution reactions

(D) Phenols have higher boiling points than alcohols

Answer: (a)

2. Phenols are soluble in:

    (A) Nonpolar solvents   (B) Strong acids   (C) Water   (D) Hydrocarbons

    Answer : (C)

3. Which functional group is present in a phenol molecule?

    (A) Alcohol   (B) Aldehyde   (C) Ketone   (D) Phenyl

    Answer: (A)

4. Phenols are generally:

    (A) Weak acids   (B) Weak bases

    (C) Non-reactive   (D) Strong acids

    Answer: (A)

5. Which of the following is not a property of phenols?
    (A) They can undergo oxidation reactions

(B) They can form hydrogen bonds with water

(C) They react with alkali metals to liberate hydrogen gas

(D) They are highly soluble in nonpolar solvents

 Answer: (D)

Short Answer Question

1.   Explain the acidic nature of phenols.

2.   Phenols are ortho and para directing groups explain this statement.

3.   Describe the Friedel crafts reaction for synthesis of phenols.

4.   Demonstrate the physical properties of phenols

5.   State the two characteristic reactions of phenols

Chapter: 12

Ethers

Objects

- This unit's goals are to introduce ethers to the students, provide their IUPAC designation, and identify ethers as either dialkyl ethers or alkoxyalkanes.

- Understanding the properties of ethers provides insights into their chemical reactivity, stability, and potential applications.

- Studying ether properties helps in understanding the behavior of this functional group in various chemical reactions, such as nucleophilic substitution and cleavage reactions.

12.1. About the Ethers

Ethers are chemical molecules in which two alkyl or aryl groups are joined by an oxygen atom. They can be written as ROR', where R and R' stand for aryl or alkyl groups, respectively. The ether is **symmetrical** if R and R' are the same, and **unsymmetrical** if they are not.Ethers frequently have the formula $CnH_{2n+2}O$.Diethyl ether ($C_2H_5OC_2H_5$) is an example of a symmetrical ether, while [$C_2H_5OCH_3$ and $C_2H_5OC_6H_5$] are '**unsymmetrical ethers**'. Diethyl ether is often referred to simply as "ether" due to its extensive use as a solvent in organic reactions and compound extraction. It has also served as an anesthetic for more than a century. Ethers stand out from other organic compounds because they do not have a continuous carbon chain.

Ethers are supposed of as alkyl equivalents of water.When the hydroxyl hydrogens of alcohols are replaced by hydrocarbon groups, the resulting compounds are called ethers. These compounds can be categorized into various types such as open-chain, cyclic, saturated, unsaturated, and aromatic. Additionally, the oxygen atom in ethers can be part of a ring structure, leading to a subclass known as cyclic ethers or epoxides.Epoxides are generated through the bonding of an oxygen atom to carbon atoms within a carbon chain, forming a three-membered ring. A cyclic ether tetrahydrofuran is a cyclic ether frequently employed as a solvent. Ethers, in general, find widespread used solvents in the vide organic reactions.
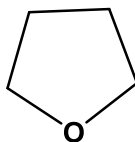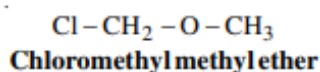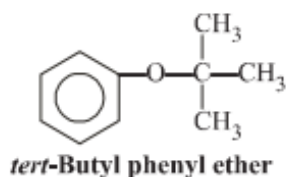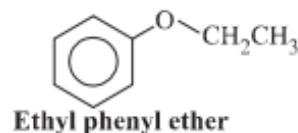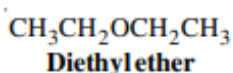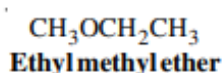
Tetrahydrofuran (THP)

The depicted symmetrical ether is diethyl ether, commonly known simply as ether due to its extensive utilization as a solvent in organic reactions and compound extraction. Additionally, it served as an 'anesthetic' for over a century.

12.2. Nomenclature of Ether

The two groups connected to the oxygen are named alphabetically to create common names for ethers, which are then followed by the term "ether." Below are some examples of common names for several ethers.

$CH_3OCH_2CH_3$
Ethyl methyl ether

$CH_3CH_2OCH_2CH_3$
Diethyl ether

Ethyl phenyl ether

tert-Butyl phenyl ether

$Cl-CH_2-O-CH_3$
Chloromethyl methyl ether

The smaller alkyl group is regarded as an alkoxy substituent on this alkane, whilst the bigger alkyl (or aryl) group functions as the root name comparable to the alkane in IUPAC nomenclature. For example, in ethyl methyl ether, where both methyl and ethyl groups are present, the ether is considered a derivative of ethane due to the bigger ethyl group.

$CH_3OCH_2CH_3$
Ethyl methyl ether
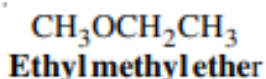
The component that remains, or in this case, the $-OCH_3$ part, is referred to as the methoxysubstituent's. Thus, methoxy-ethane is the name given to the ether above. Below are a few more instances of IUPAC names for ethers.

$CH_3CH_2OCH_2CH_3$
Ethoxy ethane

Ethoxybenzene

$CH_3O\overset{1}{C}H_2\overset{2}{C}H_2OCH_3$
1, 2-Dimethoxyethane
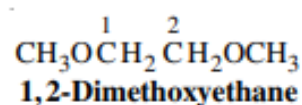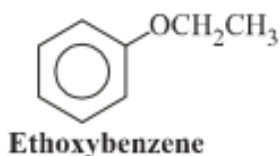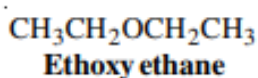
12.3. Methods for Preparation

(i) Williamson Synthesis; this method is crucial in laboratory settings for synthesizing both symmetrical and unsymmetrical ethers. It entails treating an alkyl halide with the sodium or potassium salt of an alcohol or phenol. Compared to the earlier procedures, this one delivers higher amounts of mixed ethers. The SN_2 mechanism governs the reaction. With this method, ethers with secondary or tertiary substituted alkyl groups can also be produced. The halide ion is nucleophilically replaced by an alkoxide ion throughout the process.

$$2\,CH_3CH_2OH + Na \longrightarrow CH_3CH_2ONa + H_2$$

$$CH_3CH_2ONa + R-X \longrightarrow CH_3CH_2-O-CH_2CH_3 + NaX$$
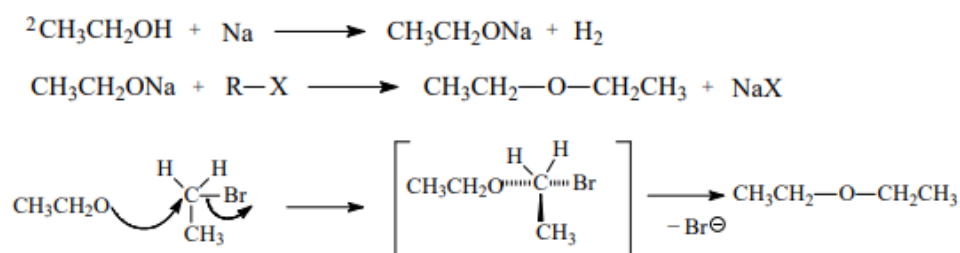
Satisfactory outcomes are achieved when employing a primary alkyl halide. However, when a tertiary alkyl halide is utilized, only an alkene is produced, and no ether forms.

For example, when CH_3ONa reacts with $(CH_3)_3C$-Br, the exclusive product obtained is 2-methylpropene.
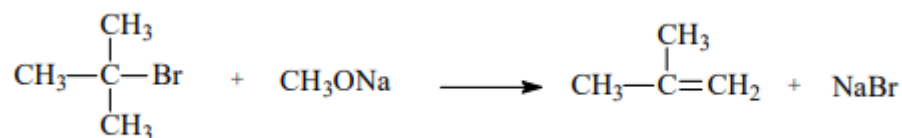
This occurs because alkoxides act not only as nucleophiles but also as strong bases. Consequently, they react with alkyl halides, resulting in elimination reactions.
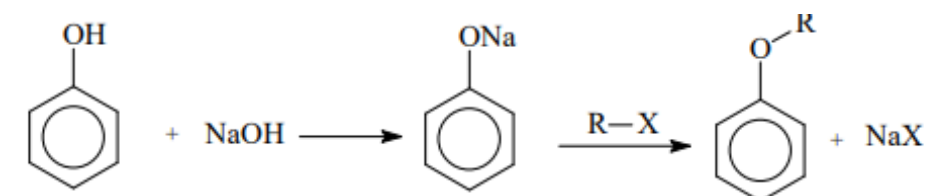
Tertiary alkyl halides undergo elimination reaction with sodium alkoxide to produce

(ii) Synthesis using 'Grignard reagent': This method is effective for synthesizing higher ethers from lower members. When lower halogenated ethers are heated with a Grignard

reagent, higher ethers are produced.

CH₃—O—CH₂Cl + BrMgCH₂CH₃ $\longrightarrow$ CH₃—O—CH₂CH₂CH₃ + Mg⟨Br Cl

monochlorodimethylether   methylpropylether

12.4. Structure and properties of Ethers

Alcohols and water have a similar geometry to ethers. As shown, the oxygen atom in ethers is sp^3 hybridized and has two lone pairs of electrons.

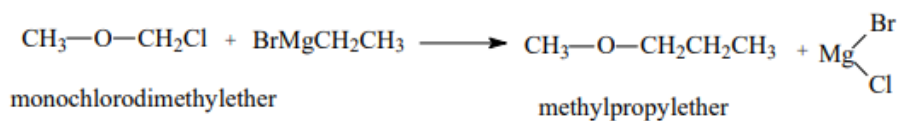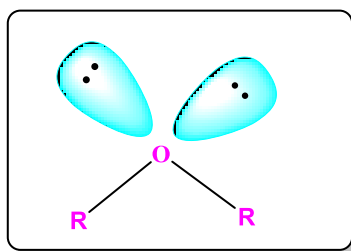The bent configuration of the ether molecule, along with its polar carbon-oxygen bond, generates a net dipole moment, making the ether molecule inherently polar (as illustrated in Figure). Consequently, ethers serve as effective polar solvents.
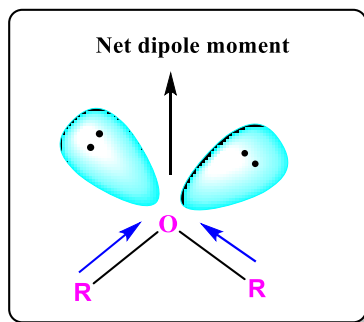
Because ethers lack a hydrogen atom attached to the oxygen atom, they are unable to engage in hydrogen bonding among their molecules. This deficiency in hydrogen bonding contributes to their lower boiling points when compared to alcohols with similar molecular masses.
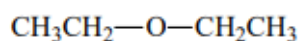
CH₃CH₂—O—CH₂CH₃
diethylether
ethoxyethane

b. p 35°C
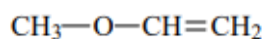
CH₃—O—CH=CH₂
methoxy ethene
methyl ethenyl ether

b. p 12°C
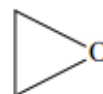
epoxide

b. p 11°C

Ethers that have three or more carbon atoms are soluble in water due to their capacity to create hydrogen bonds with water molecules.
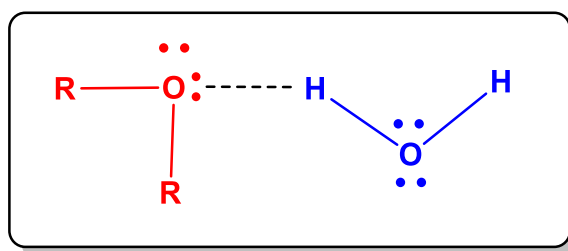
Solubility decreases as the number of carbon atoms increases. The growing hydrocarbon segment of the molecule reduces the likelihood of **hydrogen bond** formation. Ethers maintain appreciable solubility in organic solvents such as acetone, benzene and alcohol.

Water Solubility Order: Alcohols >Ethers>Alkanes

12.5. Chemical Properties of Ethers

Indeed, ethers are desirable solvents because of their well-known relative stability and inertness. Ethers, however, can have a range of reactions in specific situations, such as:

Ethers combine with Lewis acids, such as BF_3, $AlCl_3$, $FeCl_3$, *etc.*, because they are Lewis bases and formed a complex known as '*etherates*' . For example- ***Boron-trifluoro-etherate***
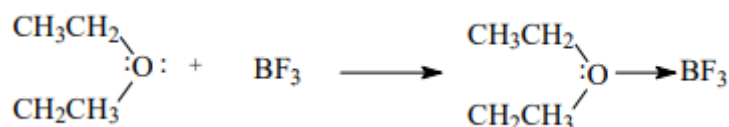
Another example they formed 'Grignard reagent etherate' as

Grignard reagent eterate
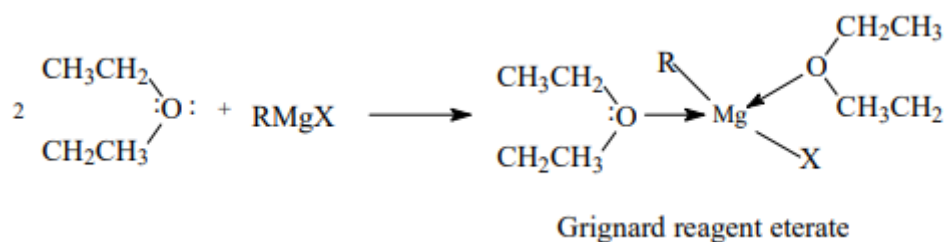
Grignard reagents dissolve in ether as a result of the etherate's production. For this reason, ethers are typically used to prepare Gilbert reagents. These, however, cannot be synthesized in benzene because the latter cannot form complexes with them due to the absence of a lone pair of electrons.

(i) Reaction with Hydroiodic acid (HI)

(a) With cold HI

$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5I + C_2H_5OH$
Diethyl ether   Ethyl iodide   Ethyl alcohol

(b) With hot HI

$R-O-R' + 2HI \longrightarrow RI + R'I + H_2O$

Phenol

$CH_3CH_2\text{-}I$

When phenyl ethers are mixed with aliphatic ethers, they respond differently. Phenyl ethers undergo cleavage reactions that produce phenols and alkyl halides. Because of the sp^2 carbon in the C-O bond, the reaction stops with the production of phenol, unlike with aliphatic ethers. This carbon structure prevents the SN^1 or SN^2 reactions that are required to produce an additional aryl halide molecule.

(ii) With H-Br

Ethers can function as bases in reactions with H-Br because the oxygen atom has lone pairs of electrons on it. Ethers are hence fundamental in nature. Even though bases usually don't affect ether stability, acidic environments can cause the ether oxygen to get protonated. Substitution reactions can then be carried out with this protonated oxygen.

Grignard reagent eterate

$H_2O + CH_3CH_2Br$

(iii) Zeisel Method

When the compound is heated with an excess of hydriodic acid, it undergoes a reaction to produce an alcohol and iodo-methane. The resulting iodo-methane is then distilled off and directed into an alcoholic solution of silver nitrate. In this solution, silver iodide precipitates out. This precipitate of silver iodide serves as the basis for detecting and estimating methoxy (–OCH$_3$) groups in an organic compound.

$$R\text{-}O\text{-}CH_3 + HI \rightarrow ROH + CH_3I$$

$$CH_3I + AgNO_3 \text{ (alc.)} \rightarrow AgI \downarrow + CH_3NO_3$$

The method, known as the Zeisel method, was pioneered by S. Zeisel in 1886.

Summary

Ethers, organic compounds characterized by an oxygen atom bridging two alkyl or aryl groups, possess distinct properties, nomenclature, and reactivity. Nomenclature follows a straightforward pattern, with the alkyl or aryl groups alphabetically listed before the word "ether." Despite their overall inertness, ethers undergo several notable reactions. Acidic conditions can induce cleavage, yielding alcohols and alkyl halides. Exposure to air and light may lead to peroxide formation, a potentially hazardous phenomenon. Ethers can also react with alkyl halides to form alkyl ethers via SN_2-type mechanisms. Furthermore, treatment with hydriodic acid results in the production of alcohols and alkyl iodides, with subsequent precipitation of silver iodide enabling the detection of methoxy groups in the Zeisel method. In essence, ethers offer versatility as solvents, display predictable nomenclature, and participate in various reactions, albeit with a generally lower reactivity compared to other functional groups.

Keywords:

- **Ether**: A class of organic compounds characterized by an oxygen atom bonded to two alkyl or aryl groups.
- **Diethyl ether**: A common ether compound with the formula $(C_2H_5)_2O$, historically used as a general anesthetic and solvent.
- **Ether linkages**: The oxygen-carbon-oxygen (C-O-C) bonds present in ether molecules.
- **Etherification**: The chemical reaction in which an alcohol reacts with an alkyl halide to form an ether and an inorganic salt.
- **Ether cleavage**: The breaking of ether linkages to yield smaller molecules, often achieved through acid-catalyzed or base-catalyzed hydrolysis.

MCQ

1. Which functional group characterizes ethers?

   (A) –OH   (B) –COOH   (C) -O-   (D) -NH$_2$

   Answer: (C)

2. How ethers are typically named?

    (A) By listing the alkyl or aryl groups alphabetically followed by the word "ether"

    (B) By using the IUPAC system for alcohols

    (C) By indicating the number of carbon atoms in the longest chain

    (D) By using the suffix "-ane"

    Answer: (A)

3. Under acidic conditions, ethers can undergo cleavage to yield:

    (A) Alcohols and alkyl halides   (B) Alcohols and ketones

    (C) Alkenes and water   (D) Aldehydes and carboxylic acids

    Answer: (A)

4. Which method is used for the detection of methoxy groups (-OCH3) in organic compounds using ethers?

    (A) Grignard reaction   (B) Friedel-Crafts acylation

    (C) Zeisel method   (D) Williamson ether synthesis

    Answer: C)

5. Which of the following is a potential hazard associated with ethers?

    (A) Formation of peroxides when exposed to air and light

    (B) Production of toxic gases when heated

    (C) Corrosive properties when in contact with skin

    (D) None of the above

    Answer: A)

Short Answer Questions

1. Talk about how ethers are polar and contrast that with alcohols' polar properties.
2. Review ether's various characteristics and applications.
3. Describe the general preparation techniques of ether.
4. Discuss the reaction of ethers with HI.
5. Write a note on nomenclature of ethers.

# Chapter: 13
Aldehydes and Ketones

Objectives
- Understanding the reactivity and properties of carbonyl compounds, such as aldehydes and ketones.
- Investigating the synthesis and transformation of carbonyl compounds in organic synthesis.
- Considering the polar nature of the carbonyl group, talk about trends in the physical properties of aldehydes and ketones.
- Applying the knowledge of carbonyl chemistry in designing and executing organic synthesis strategies.

13.1. About the carbonyl compounds

Aldehydes and ketones are examples of chemicals that contain a >C=O group and have the general formula $C_nH_{2n}O$. They are ingredients in textiles, polymers, and medications. They are also employed as solvents and reagents.

Aldehydes have one H atom bound to a carbonyl group, and the other group might be either alkyl /aryl or hydrogen. Ketones, on the other hand, have two alkyl or aryl groups bound to a carbonyl group. These two groups can either be the same in ketones, which would produce a symmetrical ketone, or they can differ, which would produce an unsymmetrical ketone.

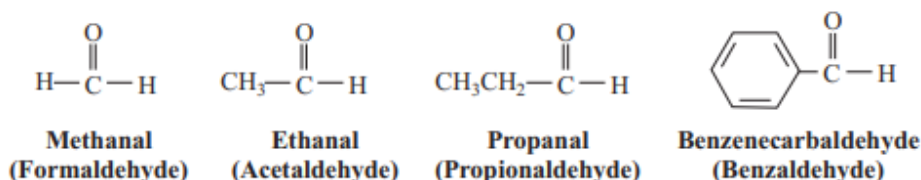**Carbonyl group**   **an aldehyde**   **a ketone**
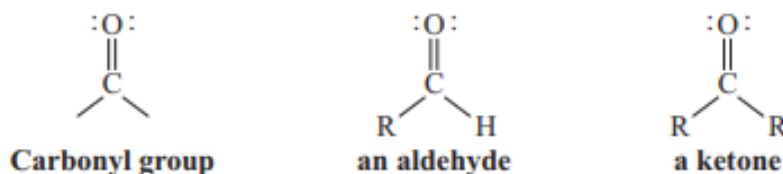
Undoubtedly! Vanillin and camphor are two well-known organic compounds with distinct functional groups. Vanillin contains an aldehyde functional group, while camphor features a keto functional group.


Vanilin
(used for vanila flavour)

Camphor
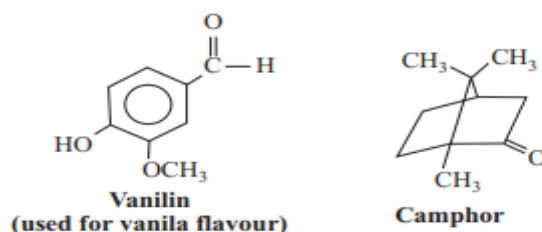
13.2. Nomenclature of C=O containing compounds *i.e.,* Aldehydes & Ketones

In the IUPAC system of nomenclature, aliphatic aldehydes are named as alkyl + al as suffix, derived from alkanals. The final "e" in the name of the corresponding alkane is replaced by "al".
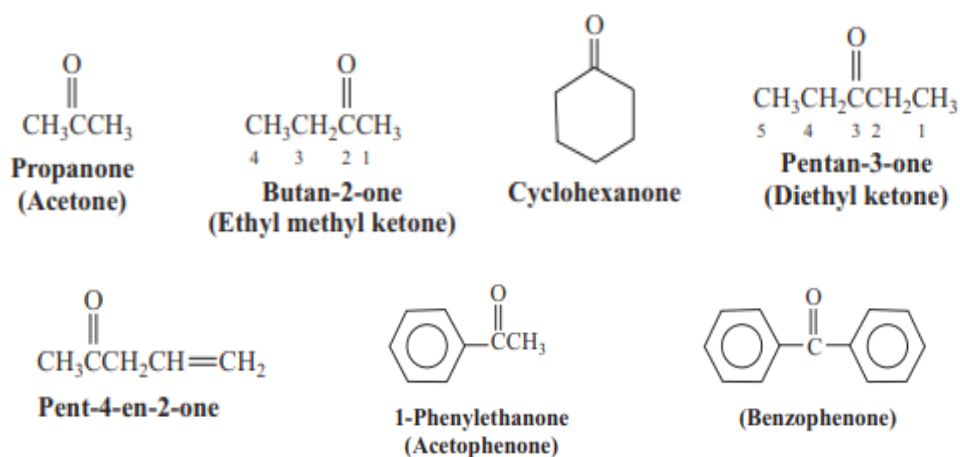
The following list includes several frequent aldehyde instances along with their names.

| Methanal (Formaldehyde) | Ethanal (Acetaldehyde) | Propanal (Propionaldehyde) | Benzenecarbaldehyde (Benzaldehyde) |

The chemical is called a carbaldehyde when the -CHO group is joined to a ring. The position of the carbonyl carbon in aldehydes is always at the last part of the carbon chain and is automatically assigned the number 1. Therefore, it is unnecessary to specify its position in the name of the aldehyde. The examples provided below demonstrate this characteristic.
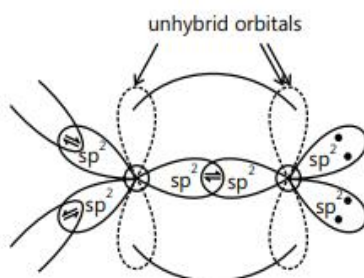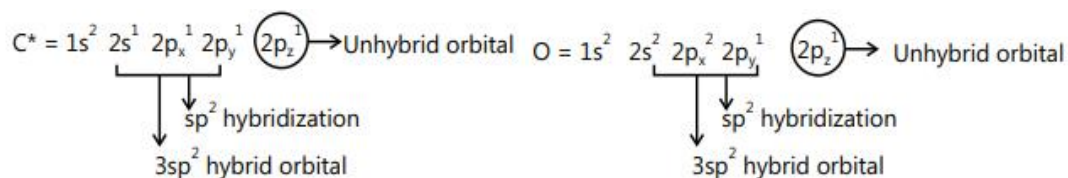

2-Bromopropanal   4-Chlorobutanal
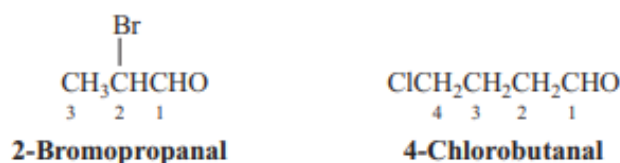
Ketones are designated as alkanones in the IUPAC nomenclature. Their names are derived by substituting the final "-e" in the name of the corresponding alkane with "-one". The carbon chain is numbered to ensure that the carbonyl group receives the lowest possible number. Here are some examples of ketones illustrating this principle:


Propanone (Acetone)   Butan-2-one (Ethyl methyl ketone)   Cyclohexanone   Pentan-3-one (Diethyl ketone)

Pent-4-en-2-one   1-Phenylethanone (Acetophenone)   (Benzophenone)

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13.3. About the structure of carbonyl compounds

Both the carbon atom and oxygen atom are in the sp^2 hybridized state in the carbonyl group. A C–O σ-bond is formed when one of the carbon atom's sp² hybrid orbitals overlaps with one of the oxygen atom's sp² hybrid orbitals. Two more σ-bonds are formed when the carbon atom's remaining two sp² hybrid orbitals overlap with either the sp³ orbital of carbon atoms (like in ketones) or one with the s orbital of carbon and the other with the s orbital of hydrogen (like in aldehydes).Another side, each of the two sp³ hybrid orbitals of the oxygen atom contains a lone pair of electrons. Un-hybridized orbitals present at the carbon and oxygen atom form a π-bond by sideways over-lapping. This structure is as.

$C^* = 1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ \boxed{2p_z^1} \rightarrow$ Unhybrid orbital $O = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ \boxed{2p_z^1} \rightarrow$ Unhybrid orbital

$\downarrow sp^2$ hybridization $\downarrow sp^2$ hybridization

$3sp^2$ hybrid orbital $3sp^2$ hybrid orbital

Bonding pattern in carbonyl compounds

There is sp^2 hybridization with the carbonyl carbon atom. A π-bond is formed between its unhybridized p-orbital and an oxygen p-orbital. The carbons and oxygen form a double bond as a result. This double bond is more polarized, stronger, and shorter.
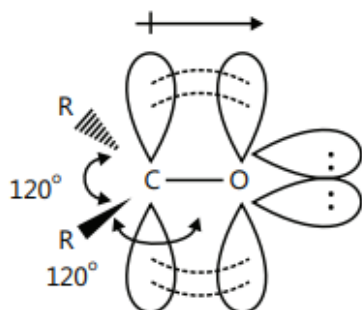

	Length Energy	
Ketone C =O bond	1.23 Å	178 kcal /mol (745 kJ/mol)
Alkene C = C bond	1.34 Å	146 kcal/mol (611 kJ / mol)

The large dipole moment of the carbonyl group's double bond arises from the significant electronegativity difference between oxygen and carbon. Since oxygen is more electronegative than carbon, it attracts the shared electrons in the bond more strongly, resulting in a partial negative charge on the oxygen atom and a partial positive charge on the carbon atom.
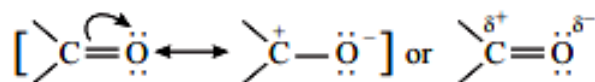

Due to this polarization, the oxygen atom acquires a partial negative charge (δ^-), while the carbon atom gains a partial positive charge (δ^+). Consequently, the carbonyl group exhibits polarity, rendering the oxygen atom nucleophilic and basic, and the carbon atom electrophilic. This polar nature dictates the physical properties and chemical reactions of aldehydes and ketones. Dipole-dipole interactions between the molecules of aldehydes and ketones explain their greater boiling temperatures when compared to hydrocarbons with identical molecular weights.Due to the hydrogen bonding between the carbonyl oxygen and hydrogen of alcohol, these compounds water soluble.
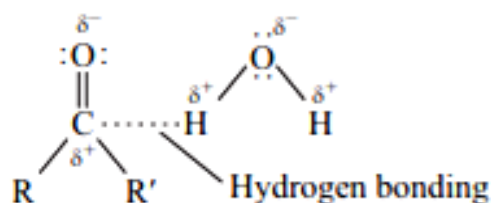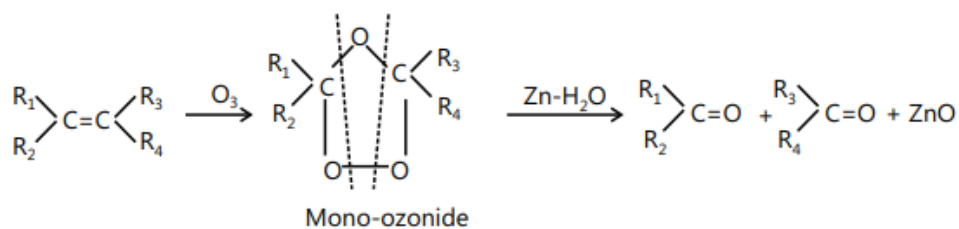

13.4. Synthetic procedures of Aldehydes and Ketones

13.4.1. Common methods for preparation of both

(i)   **Alkanoylation**, or Friedel-Crafts acylation, is the process used to create aromatic ketones. Here is an example of this procedure.
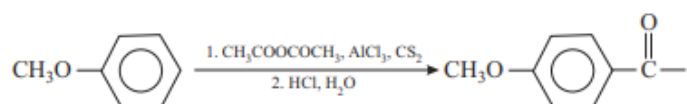

(ii)   The reaction of alkenes with ozone via ozonolysis gave these compounds.


Mono-ozonide

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(iii) **From Alkynes:** Alkynes undergo hydration to produce either aldehydes or ketones. Markovnikov's hydration typically results in the formation of ketones, while 'anti-Markovnikov's hydration' leads to aldehyde formation.
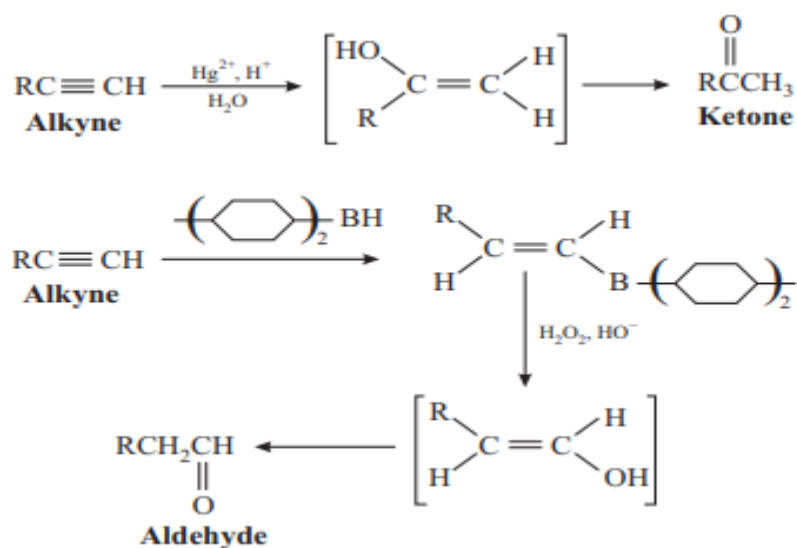
(iv) **By Oxidation of Alcohols**; As we discussed in previous chapter 10 the oxidations of 1° When alcohol is oxidized with PCC, an aldehyde is produced. When 2° alcohol is oxidized by $Na_2Cr_2O_7$ a ketone is produced.

(v) **Hydrogen cyanide (HCN);** when treated with Grignard reagent followed treatment with water gives an aldehyde *via* aldimine.
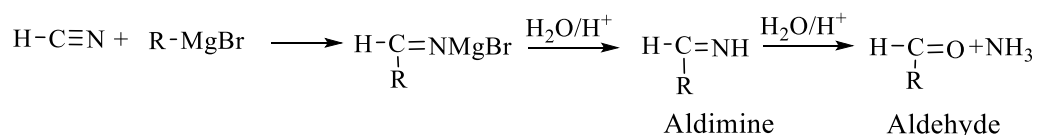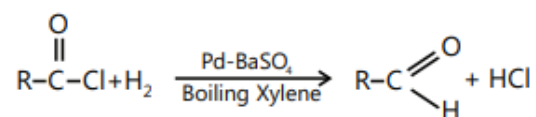

(vi) Alkylformates react with a Grignard reagent to make an aldehyde, which is the precursor of secondary alcohols. On the other hand, tertiary alcohols are produce by alkyl alkanoates undergoing a similar reaction, which results in the formation of a ketone.
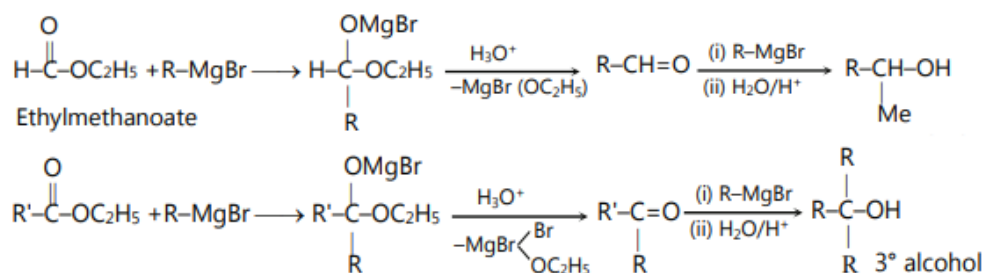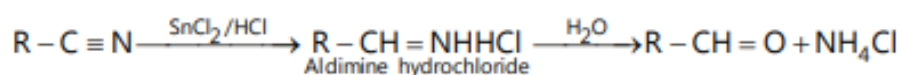
13.4.2. Methods that formed Aldehydes only

(i) **Rosenmund's Reaction**; In this process, acid chlorides are converted to aldehydes via reduction with hydrogen gas in boiling xylene, facilitated by palladium catalyst supported on barium sulfate.
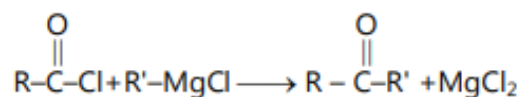
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+H_2 \xrightarrow[\text{Boiling Xylene}]{\text{Pd-BaSO}_4} R-C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagdown}} + HCl$$

(ii) **Stephen's Reduction**

$$R-C\equiv N \xrightarrow{\text{SnCl}_2/\text{HCl}} \underset{\text{Aldimine hydrochloride}}{R-CH=NHHCl} \xrightarrow{\text{H}_2\text{O}} R-CH=O+NH_4Cl$$

(iii) **Reimer-Teimann Reaction**; includes synthesis of 'phenolic aldehyde'

Phenol   Salicylic aldehyde
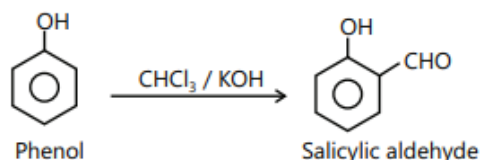
13.4.3. Methods that formed only Ketoness only

(i) **From** alkanoyl chloride and 'Grignard reagent'

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+R'-MgCl \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-R' +MgCl_2$$

(ii) **By 'acylation or benzoylation' of aromatic hydrocarbon (Friedel-Craft Reaction)**

$$C_6H_6 + CH_3COCl \xrightarrow[\text{AlCl}_3]{\text{Dry}} \underset{\text{(Acetophenone)}}{C_6H_5COCH_3} +HCl; \quad C_6H_6 + C_6H_5COCl \xrightarrow[\text{AlCl}_3]{\text{Dry}} \underset{\text{(Benzophenone)}}{C_6H_5COC_6H_5} +HCl$$
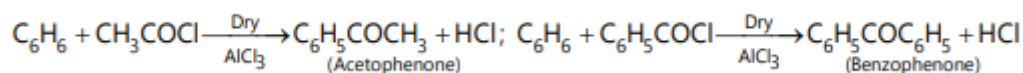
13.5. Chemical Reactions

Upon examining the structure of a carbonyl compound molecule, you'll notice three centers of reactivity within it, as depicted below.

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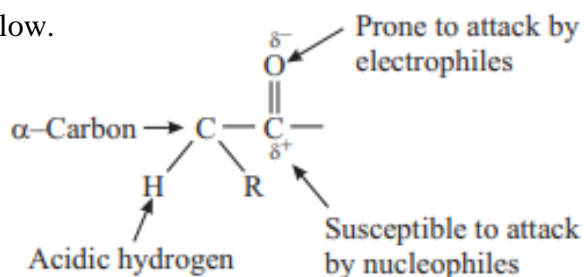
The oxygen atom is generally targeted by electrophiles due to its nucleophilic character, but the carbonyl carbon is more vulnerable to assault by nucleophiles due to its electrophilic nature. The hydrogen atom situated at the α-carbon is the third reactive site. It displays acidic characteristics and engages in distinct reactions discussed in this section.

The reactivity of ketones is less than comparison to aldehydesdue to some reasons

- Aldehydes possess only one alkyl group, whereas ketones have two. As alkyl groups are electron-donating, the carbonyl carbon in ketones, bonded to two alkyl groups, is comparatively less positively charged (electrophilic) than the carbonyl carbon in aldehydes. Consequently, it is less prone to nucleophilic attack.

- The presence of two alkyl groups in ketones leads to increased crowding around the carbonyl carbon compared to aldehydes. This crowding factor renders the carbonyl carbon of aldehydes more accessible to nucleophilic attack compared to the carbonyl carbon of ketones.

On the basis Aldehydes and Ketones undergo various reactions

13.5.1.'Nucleophilic Addition' Reaction

The general reaction depicting the addition of nucleophiles to the carbonyl group can be expressed as follows:
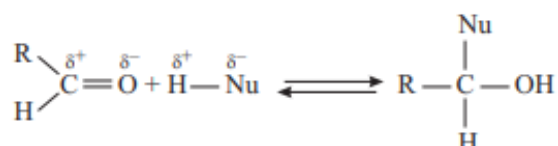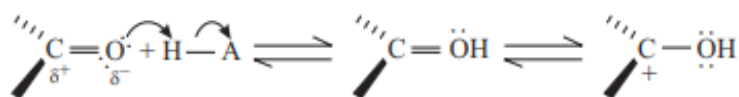

Concern mechanism involving following steps

Under basic conditions, the nucleophile attacks the carbonyl group, forming a tetrahedral intermediate. Following this, protonation from a solvent (such as water or alcohol) occurs
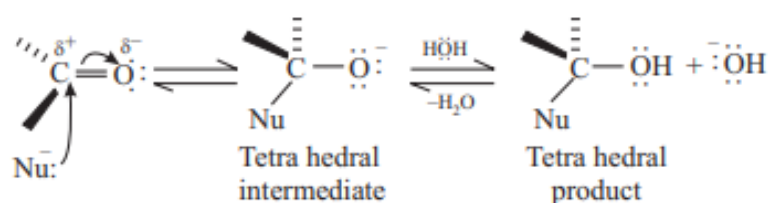
In acidic additions, the first step involves the protonation of the carbonyl oxygen

The next step involves the nucleophile attacking the carbonyl carbon, finalizing the addition process.
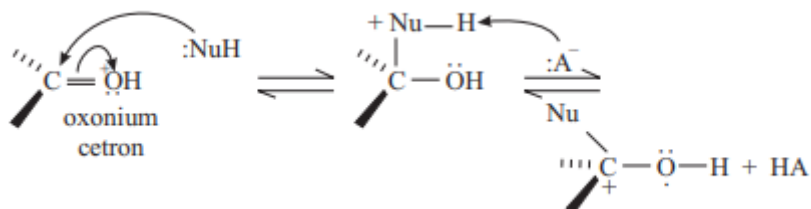
Some specific reactions of this category are as

(i) **Reaction with HCN; 'Cyanohydrins'** are produced when carbonyl compounds combine with hydrogen cyanide.
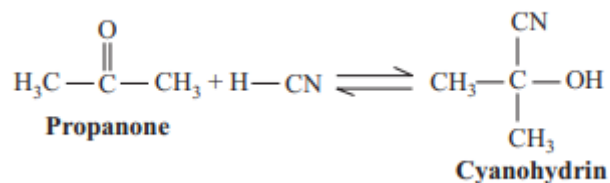
It is noteworthy that in comparison to the original carbonyl compound, the cyanohydrin has one more carbon atom.

(ii) **Reaction with R-OH;** When aldehydes and ketones react with alcohols, they form hemiacetals. The prefix "hemi" from Greek signifies "half", indicating that hemiacetals have both an -OH and an -OR group attached to the same carbon atom within their molecules.When an excess of alcohol is present, a second molecule of the alcohol reacts to produce an acetal.

Because acetals are stable in basic solutions, they are utilized as aldehyde and ketone protecting groups. Acetals are reversible in the aforementioned reaction; therefore treating them with diluted acids can convert them again to the carbonyl molecules.

(iii)   Reaction with Sodium Bisulphite (NaHSO₃);

This addition is used to isolate carbonyl compounds from the mixture as we get a salt.

$$\text{>C = O} + NaHSO_3 \longrightarrow \text{>C–ONa} \longrightarrow \text{>C–OH}$$
$$\quad\quad\quad\quad\quad\quad\quad\quad SO_3H \quad\quad\quad\quad SO_3Na$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (salt)$$

The salt on acidification gives carbonyl compounds again

$$\text{>C–OH} \xrightarrow{H_2O} \text{>C–OH} \xrightarrow{-H_2O} \text{>C = O}$$
$$\quad SO_3Na \quad\quad\quad\quad\quad OH$$

13.5.2 'Addition-Elimination' or 'Condensation Reactions'

(i)   Reaction with NH₃ and its derivatives (NH₂-G).

Aldehydes and Ketones undergo a reaction with ammonia and primary amines, forming imines, which are compounds featuring a carbon-nitrogen double bond.

During the mentioned reaction, it seems that a molecule of water is eliminated from both the primary amine and the carbonyl compound. The reactions with other derivatives of ammonia are presented below

Phenylhydrazine   **a Phenylhydrazone**

$CH_3CH_2CHO + N_2NNH$—(2,4-dinitrophenyl)—NO_2 → $CH_3CH_2CH\ NNH$—(2,4-dinitrophenyl)—NO_2

**2, 4-Dinitrophenzylhydrazine**   **2, 4-Dinitrophenzylhydrazone**

13.5.3. 'De-oxygenation' Reactions

(i)   **'Wolff-Kishner' Reduction;** Upon heating an aldehyde or ketone in a basic solution of hydrazine in a high-boiling alcohol, the carbonyl group undergoes conversion into a methylene (CH₂) group.

$$C_6H_5-CCH_3 \xrightarrow[2.\ H_2O]{1.\ NH_2NH_2^-,\ OH/\Delta} C_6H_5-CH_2CH_3$$

Ethylbenzene
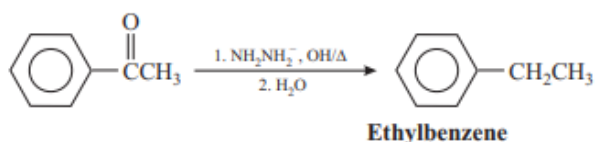
(ii)   **'Clemmensen' Reduction;** this refers to a chemical reaction where a carbonyl group, typically found in aldehydes or ketones, is reduced to a methylene group using zinc amalgam and hydrochloric acid under high-temperature conditions.

$$CH_3(CH_2)_5CHO \xrightarrow[HCl,\ H_2O]{Zn(Hg)} CH_3(CH_2)_5-CH_3$$

Heptanal   **Heptane**
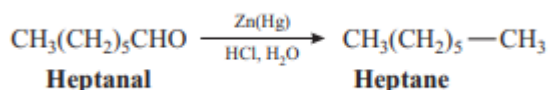
13.5.4. Reactions in which α-C atom involves

A strong base can readily absorb the very acidic α − hydrogen found in aldehydes and ketones.

keto form   α-Hydrogen   **enolate ion**
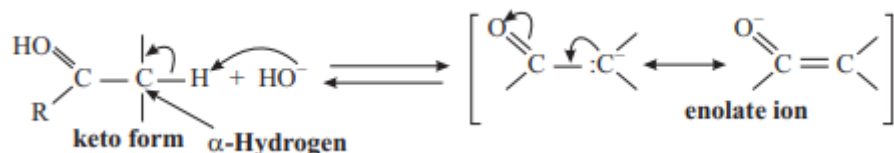
Resonance can stabilize the resultant anion, as previously demonstrated. An enolate ion is the term for it. It yields an enol when protonated.


enolate   **enol**

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(i) **Iodoform Test-Halogenation ;** Ketones containing an α-hydrogen atom undergo rapid reaction with halogens, yielding α-haloketones as the resulting product. This reaction is facilitated by both acidic and basic conditions.

$$(X_2 = Cl_2, Br_2 \text{ or } I_2)$$

Propanone   Bromopropanone
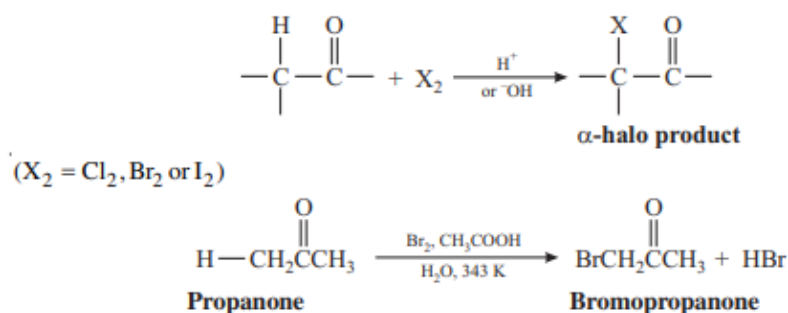
The tri-halo product is produced by repeated halogenation when the base is present.
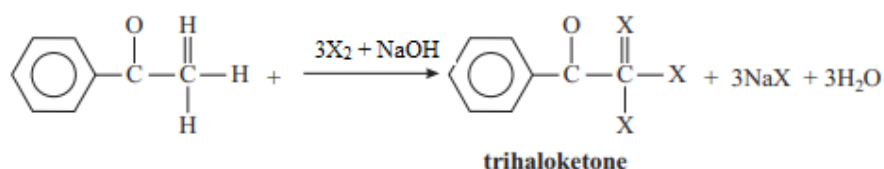

trihaloketone

The tri-halo ketone combines with OH– to produce a 'haloform' and a carboxylate ion in the end. The tri-halo group is an excellent leaving group.

trihaloketone   Carboxylate ion   Haloform
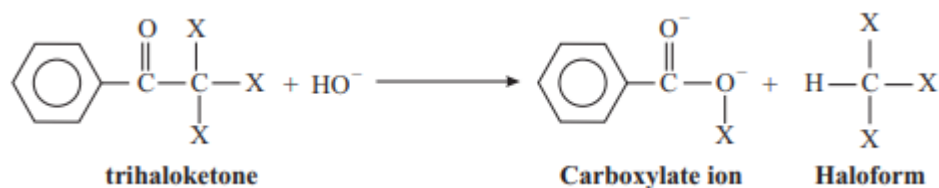
When iodine serves as the halogen, the product obtained is iodoform (CHI_3). Iodoform, a bright yellow solid with a distinctive melting point, forms the basis of the iodoform test. Consequently, methyl ketones yield a positive result in the iodoform test.

(ii) **Aldol Condensation**

Aldehydes containing α-hydrogen atoms, upon reaction with dilute sodium hydroxide (NaOH), undergo a process known as aldol condensation. This reaction can be demonstrated using ethanal as an example

Ethanal   Ethanal   3-Hydroxybutanal
                                                 (an Aldol)
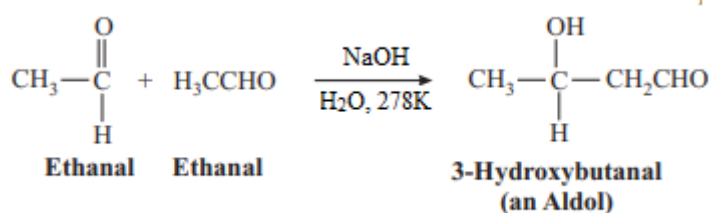
It's important to note that the resulting product contains both the aldehyde and the alcohol functional groups, hence it's termed as an aldol. Upon heating, the aldol addition product undergoes dehydration, forming an α, β–unsaturated aldehyde, which represents a condensation product.


Aldol → trans-But-2-enal + H_2O
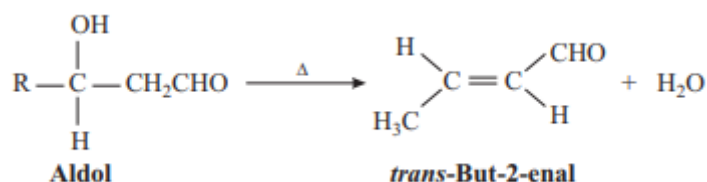
This whole sequence of reactions is named 'Aldol Condensation'

13.5.5. Other Reactions

(i) Cannizzaro Reaction

Aromatic or aliphatic aldehydes lacking α-hydrogens, when treated with concentrated KOH or NaOH, undergo a transformation yielding one molecule of alcohol and the sodium salt of the corresponding carboxylic acid. This reaction is referred to as the Cannizzaro reaction.

In this reaction, one molecule of the aldehyde undergoes oxidation to form the salt of a carboxylic acid (sodium or potassium salt), while another molecule of the aldehyde is simultaneously reduced to yield an alcohol molecule.
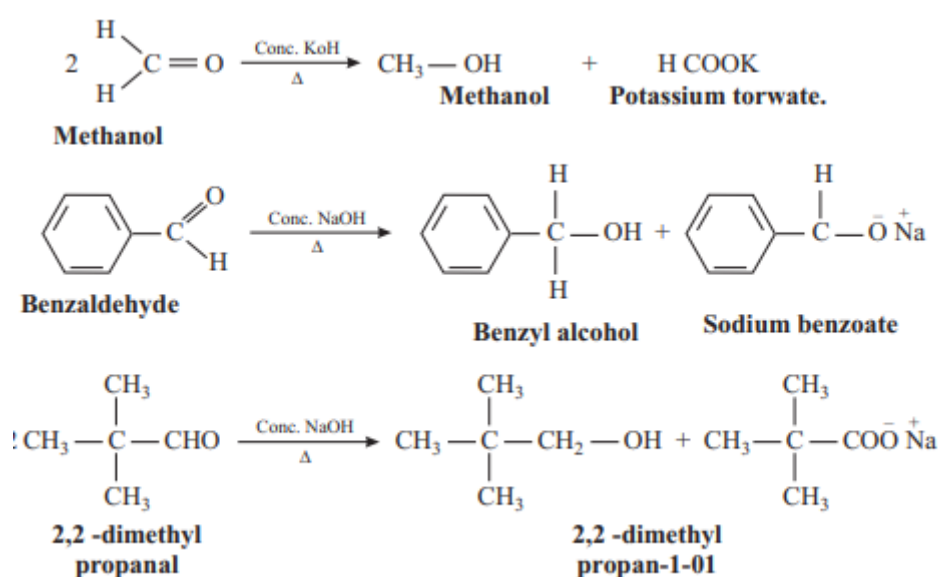
Therefore, we can say that disproportination has taken place, in which two molecules of the original aldehyde have undergone simultaneous oxidation and reduction to generate one molecule of a carboxylic acid and one molecule of an alcohol. This reaction is limited to aldehydes in which the carbon next to the CHO group does not contain hydrogen atoms.
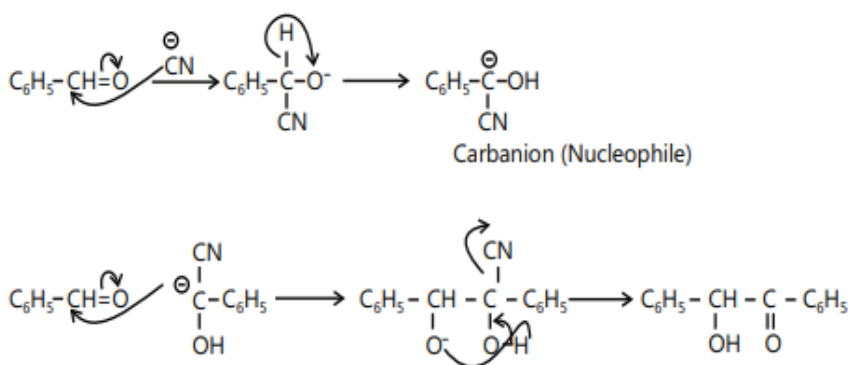
(ii)Wittig Reaction;The Wittig reaction is a widely used chemical reaction in organic chemistry for the synthesis of alkenes from aldehydes or ketones. It involves the reaction of a phosphonium ylide with a carbonyl compound (aldehyde or ketone) to form a new carbon-carbon double bond. The reaction proceeds via the formation of a betaine intermediate, which subsequently undergoes elimination to yield the desired alkene product. The Wittig reaction is an important tool for constructing carbon-carbon double bonds in organic synthesis.

**General Wittig Reaction: Synthesis of Alkenes**
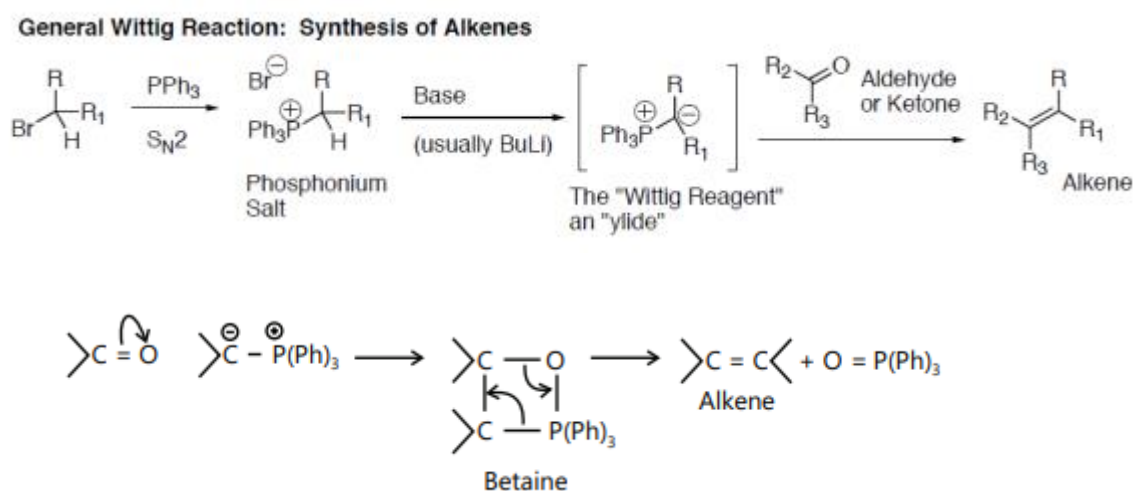
(iii)   Benzoin Condensation;

Benzoin is produced when benzaldehyde is heated with a strong alkali such as potassium cyanide or sodium cyanide in an ethanolic solution.

$$2C_6H_5-CH=O \xrightarrow{\overset{\ominus}{CN}} C_6H_5-CH-C-C_6H_5$$
$$\underset{OH\ O}{|\quad ||}$$
(Benzoin)
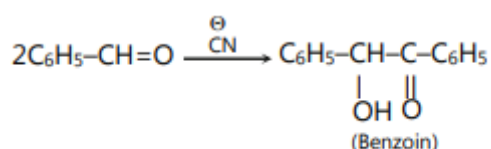
Reaction Mechanism:

Carbanion (Nucleophile)

(iv) **The Meerwein–Ponndorf–Verley** (MPV);

The reduction commonly referred to as MPV reduction stems from the simultaneous discoveries made by Meerwein, Schmidt, and Verley in 1925, along with Ponndorf's independent report in 1926. Hence, it's commonly termed the Meerwein-Ponndorf-Verley reduction, or simply the MPV reaction.
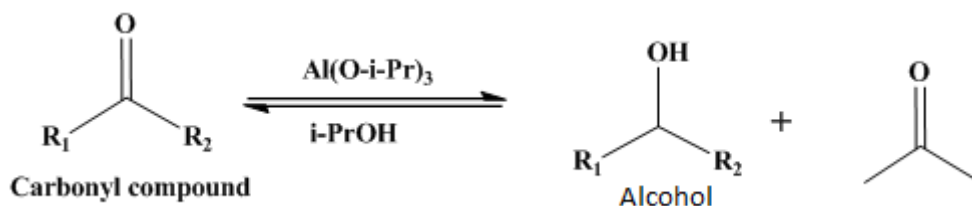
The MPV reaction boasts chemoselectivity while operating in mild reaction conditions, rendering it both operationally simple and cost-effective. Moreover, it exerts no influence on other double or triple bonds, nor does it impact enolizable carbonyl compounds like β-ketoesters or β-diketones.

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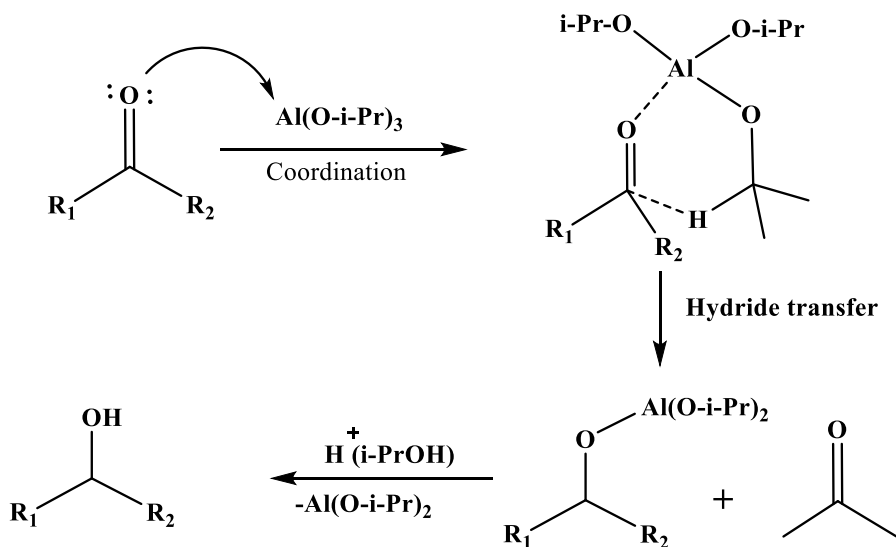
Treating an aldehyde or ketone with aluminum tri-isopropoxide in isopropanol solvents generates a six-membered cyclic transition state. This occurs as the carbonyl compounds coordinate with the catalyst's aluminum atom, enhancing the positive character of the carbonyl group. This coordination aids in the transfer of hydrides from the isopropyl group to the carbonyl carbon center.

The primary distinction between Oppenauer oxidation and MPV reduction lies in their respective functions. Oppenauer oxidation transforms alcohols into aldehydes or ketones, employing aluminum alkoxide as a catalyst. Conversely, MPV reduction converts aldehydes or ketones back into alcohols, also employing aluminum alkoxide as a catalyst. Consequently, the MPV reaction is considered the inverse process of Oppenauer oxidation. While ketone serves as the solvent in Oppenauer oxidation, alcohol serves as the solvent in the MPV reaction.

Summary

Aldehydes and **Ketones** are organic compounds characterized by the presence of the carbonyl group (C=O). Aldehydes have at least one hydrogen atom attached to the carbonyl carbon, while ketones have two alkyl or aryl groups attached. They exhibit lower boiling points compared to alcohols and carboxylic acids of comparable molecular weight and are generally soluble in water due to hydrogen bonding with water molecules, particularly for smaller molecules. Methods of preparation include oxidation of primary alcohols to aldehydes and secondary alcohols to ketones, ozonolysis of alkenes and nucleophilic addition to carbonyl compounds using organometallic reagents. In terms of reactions, aldehydes and ketones undergo nucleophilic addition at the carbonyl carbon, reduction to alcohols using reducing agents like sodium borohydride or lithium aluminum hydride, oxidation to carboxylic acids under harsh conditions, and can participate in the Cannizzaro reaction and aldol condensation. These compounds play essential roles in organic synthesis due to their versatile reactivity and structural diversity.

Keywords

- **Carbonyl compounds: Having** a functional group build from carbon atom double-bonded to an oxygen atom.
- **Reactivity**: The propensity of aldehydes and ketones to undergo chemical reactions due to the presence of the polar carbonyl group.
- **Nucleophilic-addition**: A reaction in which a nucleophile attacks the electrophilic carbon of the carbonyl group, forming a new bond.

- **Reduction**: A reaction where aldehydes and ketones are converted into alcohols by adding hydrogen or hydride donors.
- **Oxidation**: A reaction where aldehydes are converted into carboxylic acids or ketones into carboxylic acids or esters by adding oxygen or removing hydrogen.

MCQ.

1. Which functional group is present in both aldehydes and ketones?

(A) Carbonyl group   (B) Hydroxyl group

(C) Alkene group   (D) Ether group

Answer: (A)

2. What is a common property of aldehydes and ketones in terms of solubility?

(A) Insoluble in water

(B) Highly soluble in nonpolar solvents

(C) Highly soluble in water due to hydrogen bonding

(D) Insoluble in organic solvents.

Answer: C)

3. Which method is commonly used to prepare aldehydes from primary alcohols?

(A) Ozonolysis   (B) Friedel-Crafts acylation

(C) Oxidation with chromic acid   (D) Nucleophilic addition

Answer: C)

4. What type of reaction occurs when a nucleophile attacks the carbonyl carbon of an aldehyde or ketone?

(A) Substitution reaction   (B) Elimination reaction

(C) Nucleophilic addition reaction   (D) Redox reaction

Answer: (C)

5. What reaction converts aldehydes or ketones into alkanes using zinc amalgam and hydrochloric acid?

(A) Wolff-Kishner reduction   (B) Clemmensen reduction

(C) Grignard reaction   (D) Cannizzaro reaction

Answer: (B)

Short Answer Questions

1. Explain the structure and properties of carbonyl compounds.
2. What type of reaction occurs when a nucleophile attacks the carbonyl carbon of an aldehyde or ketone? Explain with example.
3. Describe the oxidation of aldehydes and ketones.
4. Write the two preparative methods of apdehydes.
5. Explain the witting reaction.

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