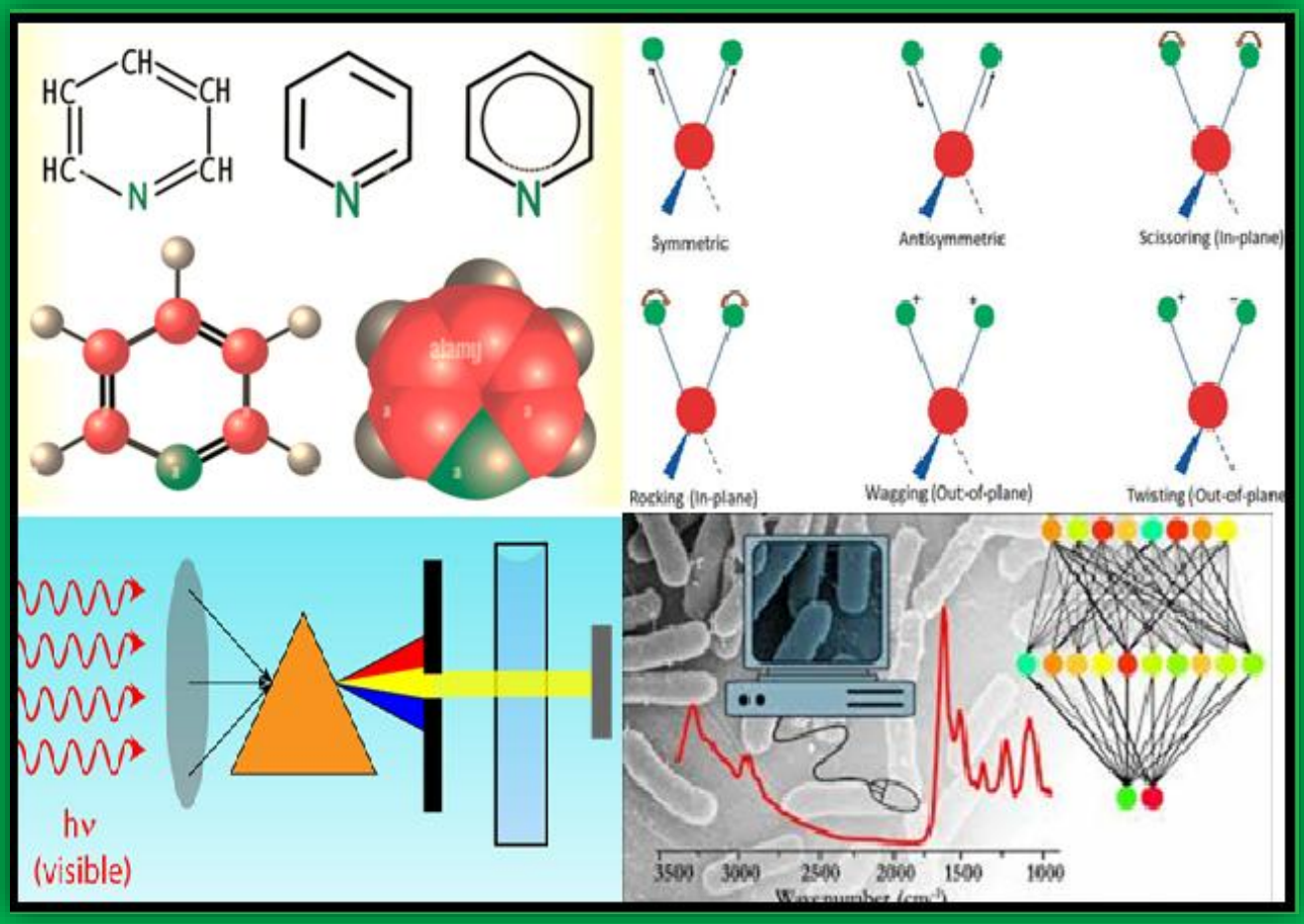
CHE (N)-302

B.Sc. VI TH Semester

ADVANCE CHEMISTRY-II& LABORATORY COURSE



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HALDWANI (NIANITAL), UTTARAKHAND-263139

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ADVANCE CHEMISTRY-II & LABORATOTY COURSE

BSc. Sixth Semester

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Title	**:**	**Advance Chemistry-II**
ISBN No.	**:**	
Copyright	**:**	**Uttarakhand Open University**
Edition	**:**	**2025**
Publishing By	**:**	**Uttarakhand Open University, Haldwani, Nainital-263139**

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UNIT-1: MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

Contant:

1.1 INTRODUCTION

Transition metal complexes possess a fascinating world of magnetism, a world shaped largely by the tiny but powerful unpaired electrons orbiting within their d-subshells. These electrons act like miniature magnets, and their behaviour determines whether a complex is gently repelled by a magnetic field or strongly drawn toward it. The more unpaired electrons a metal ion carries, the stronger its magnetic personality becomes, expressed as a larger magnetic moment. When all electrons are paired, however, the complex becomes calm and non-magnetic, showing the characteristic behaviour of diamagnetism.

At the heart of this magnetic behaviour lie a few key ideas:

- **Electron Spin:** Every electron spins like a tiny charged sphere, creating a magnetic dipole. Paired electrons spin in opposite directions, cancelling one another.
- **Unpaired Electrons:** When electrons remain unpaired in the $(n-1)d$The orbitals of transition metals dominate the magnetic behaviour of the entire complex.
- **Magnetic Moment (μ):** A quantitative expression of magnetic strength, closely linked to the number of unpaired electrons (n).
- **Spin-Only Formula:** For most transition metal complexes, the magnetic moment can be estimated using

$$\mu = \sqrt{n(n+2)}$$

These principles give rise to different types of magnetism:

- **Paramagnetism:** Attraction to a magnetic field due to unpaired electrons.
- **Diamagnetism:** Gentle repulsion, observed when all electrons are paired.
- **Ferromagnetism:** A powerful, coordinated magnetic behaviour where spins align in the same direction, creating permanent magnetism.

The magnetic moment provides clues about the **number of unpaired electrons**, helping chemists determine the **spin state** (high-spin or low-spin) and **geometrical structure** of a transition metal complex. Thus, magnetism becomes not just a physical property, but a guiding light in understanding the hidden architecture of coordination compounds.

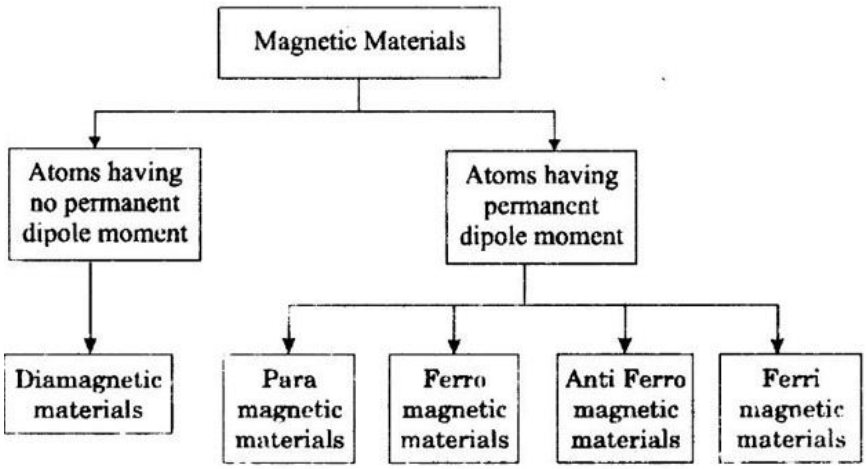
1.2 OBJECTIVES

After learning this unit, you will be able to:-

- To understand the basic concepts and origin of magnetism in transition metal complexes.
- To distinguish different types of magnetic behaviour.
- To study methods of measuring magnetic susceptibility, especially Gouy's and Quincke's methods.
- To use the spin-only formula for calculating magnetic moments.
- To recognise the effect of orbital contribution on magnetic moments of 3d-metal complexes.

1.3 TYPES OF MAGNETIC BEHAVIOUR

The main types of magnetic behaviour are diamagnetism, paramagnetism, and ferromagnetism, which describe how a material responds to an external magnetic field. Diamagnetic materials are weakly repelled, paramagnetic materials are weakly attracted, and ferromagnetic materials are strongly attracted and can retain magnetism. Antiferromagnetism and ferrimagnetism are related, subclass types.



1.3.1 Diamagnetism

Diamagnetism is a fundamental magnetic property in which a substance is weakly repelled or not repelled by an external magnetic field due to the absence of unpaired electrons.

In diamagnetic materials, all electrons are paired, and the small magnetic moments induced by their orbital motion oppose the applied magnetic field, resulting in a net negative magnetic susceptibility, and a diamagnetic substance has no magnetic moment.

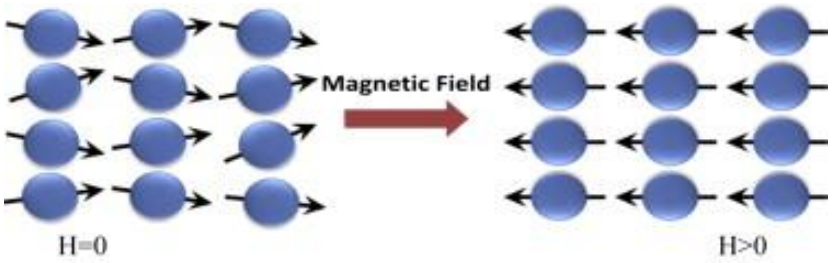
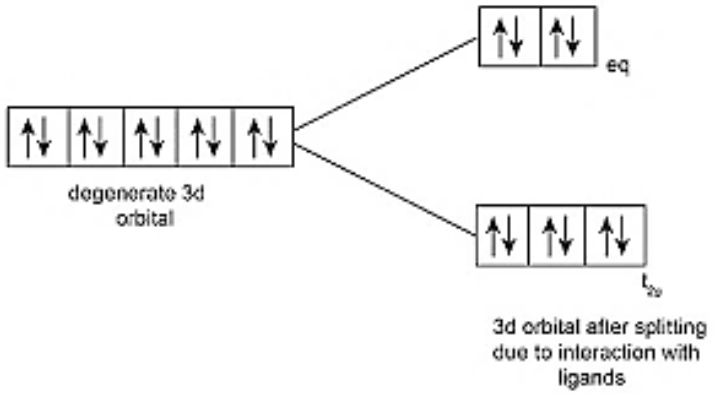


Fig.1.1 Diamagnetism

Example - Zn^{2+} ion (d^{10} configuration) and its complexes such as **$[Zn(H_2O)_6]^{2+}$** are diamagnetic because all d-electrons are paired.

Electronic configuration: of **Zn:** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$



Magnetic moment $(\mu) = \sqrt{n(n+2)}$, where n = number of the unpaired electrons

$\mu = \sqrt{0(0+2)}$

$\mu = 0$

1.3.2 Paramagnetism

Paramagnetism is a magnetic behaviour shown by substances that contain one or more unpaired electrons. These unpaired electrons act like tiny spinning magnets. When an external magnetic field is applied, these mini-magnets align in the direction of the field, causing the substance to be weakly attracted toward the magnet. However, once the magnetic field is removed, their alignment disappears, just like fireflies scattering after the light goes out. Paramagnetism arises due to positive magnetic susceptibility and the presence of unpaired electrons, which create a net magnetic moment. Example-Oxygen (O_2) gas is paramagnetic

because it has two unpaired electrons in its molecular orbitals. This is why liquid oxygen can be seen hanging between the poles of a strong magnet.

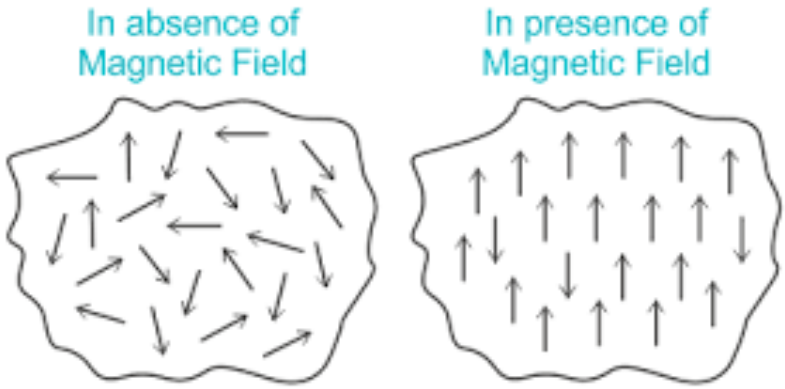
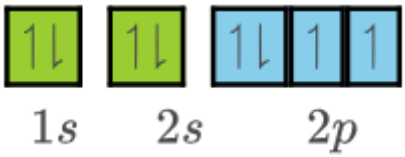


Fig.1.2 Paramagnetism

Electronic Configuration of Oxygen $1s^2\ 2s^2\ 2p^4$



Magnetic moment $(\mu) = \sqrt{n(n+2)}$, where n = number of the unpaired electrons

$\mu = \sqrt{2(2+2)}$

$\mu = 2.9\ MB$

1.3.3 Ferromagnetism

Ferromagnetism is a property of certain materials—such as iron—that exhibit high magnetic permeability and often significant magnetic coercivity, enabling them to form permanent magnets. Ferromagnetic materials are strongly attracted to a magnet because of their high magnetic permeability. Magnetic permeability refers to the ability of a material to become magnetised when exposed to an external magnetic field. For instance, the temporary magnetisation induced in a steel plate explains why the plate is attracted to a magnet. Whether the steel plate later becomes permanently magnetised depends on the strength of the applied magnetic field and the coercivity of that specific piece of steel, which can vary based on its chemical composition and any heat treatment it has undergone.

In these materials, atoms group into tiny regions called magnetic domains, and within each domain, all spins are parallel. When an external magnetic field is applied, these domains grow

and align to create a permanent, powerful magnet, even after the field is removed. Ferromagnetism arises due to exchange coupling between neighbouring atoms, causing parallel spin alignment and resulting in very high magnetic susceptibility.

Example- Iron (Fe) is the classic ferromagnetic material. When exposed to a magnetic field, the domains inside iron align, and it becomes a strong permanent magnet.

Other examples: Cobalt (Co), Nickel (Ni), and some rare-earth metals (e.g., Gd).

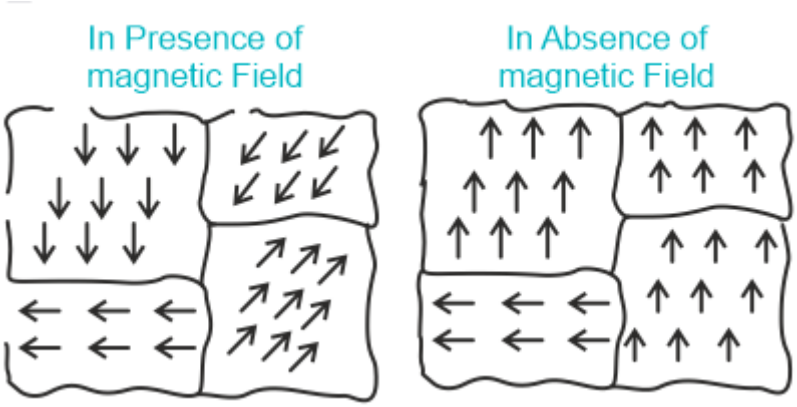


Fig. 1.3 Ferromagnetism

Ferromagnetism plays a crucial role in industry and modern technology. It is used in a wide range of electromagnetic and electromechanical devices, including electromagnets, electric motors, generators, transformers, magnetic storage systems (such as tape recorders and hard drives), and non-destructive testing of ferrous materials.

1.3.4 Antiferromagnetism

Antiferromagnetism is a fascinating magnetic behaviour in which the magnetic moments of neighbouring atoms align exactly opposite to each other. Instead of marching together like in ferromagnets, these atomic spins form a perfect "up–down, up–down" (↑↓) pattern. Because each magnetic moment is balanced by an equal and opposite one, the material shows zero net magnetisation its magnetic fields cancel out beautifully.

This highly ordered magnetic arrangement exists only at low temperatures. When the temperature rises above a characteristic limit called the Néel temperature, the orderly antiparallel spins break down. The material then transforms into a paramagnetic state, where magnetic moments are randomly oriented and respond weakly to external magnetic fields.

- **Antiparallel spin alignment:** Adjacent atoms have opposite spins (↑↓), unlike ferromagnets where all spins align in the same direction.

- **No net magnetization:** Because the opposing moments cancel each other, the overall magnetic moment becomes zero.
- **Néel temperature:** Below this critical temperature, the antiparallel spin order is stable; above it, the material loses its antiferromagnetic character.

Examples

- **Manganese oxide (MnO)** – A classic antiferromagnetic solid with perfectly balanced opposite spins.
- **Chromium (Cr)** - Exhibits antiferromagnetic ordering due to negative exchange interactions between its atoms.

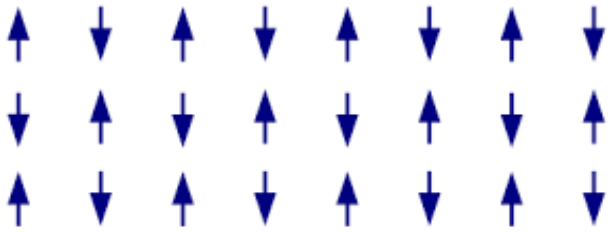


Fig. 1.4 Antiferromagnetism

1.3.5 Magnetic Induction, Magnetic permeability, and Intensity of Magnetization

Magnetic Induction (B)- Magnetic induction, also called magnetic flux density, is the measure of the magnetic field acting on a given area. It represents how strongly a magnetic field influences charged particles, magnetic materials, or current-carrying conductors placed within it.

In simple terms, it tells us how much magnetic "effect" is produced in a region.

$$\textit{Unit: Tesla (T),} \quad \textit{Formula: } B = \mu H$$

Magnetic Permeability (μ)- Magnetic permeability is the ability of a material to allow magnetic field lines to pass through it.A material with high permeability easily becomes magnetised, while one with low permeability resists magnetic field penetration.

In essence, it tells us "how well a material responds to an applied magnetic field."Unit: Henry per meter (H/m)

Types:

- Absolute permeability (μ)
- Relative permeability (μ_r)

Intensity of Magnetisation (M)- Intensity of magnetisation is the measure of the magnetic moment developed per unit volume of a material when it is placed in a magnetic field. It indicates how strongly the material becomes magnetised due to the alignment of its atomic magnetic moments.

Unit: A/m (Ampere per meter), Formula: $\boldsymbol{M = \frac{Magnetic\ moment}{Volume}}$

1.4 MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility is a measure of how strongly a material becomes magnetised when it is placed in an external magnetic field. The susceptibility constant, χ, relates the magnetisation (M) of a material its magnetic moment per unit volume to the applied magnetic field H.

For all materials except ferromagnets, this relationship is linear and can be expressed as:

$$M = \chi H$$

Where,

- **χ:** magnetic susceptibility
- **M:** magnetisation
- **H:** field intensity

Michael Faraday was the first scientist to study this magnetic response in materials that were considered "non-magnetic." He introduced the terms diamagnetic for substances with $\chi < 0$, and paramagnetic for those with $\chi > 0$.

1.4.1 Methods of Determining Magnetic Susceptibility

Magnetic susceptibility of a material can be measured using several experimental techniques based on how the substance responds to a magnetic field. These methods allow chemists and physicists to determine whether a material is diamagnetic, paramagnetic, or ferromagnetic, and to quantify the strength of its magnetic behaviour.

Two types of experimental methods are used to determine magnetic susceptibility,

1. **Gouy Method-** Used for *solid and powdered* samples. Very common in inorganic chemistry labs.
2. **Quincke's Method-** Used for *liquid paramagnetic* solutions using a U-tube arrangement.

1.4.1.1 Gouy Method

The Gouy Method is one of the most widely used experimental techniques for determining the magnetic susceptibility (χ_g) of solid and powder substances. The method is based on the fact that when a material is placed in a non-uniform magnetic field, it experiences a measurable force depending on its magnetic nature:

- Paramagnetic substances are attracted toward the region of a stronger magnetic field.
- Diamagnetic substances are repelled from the magnetic field.

Principle

Gouy's balance, named after the scientist who devised it, is generally used to measure paramagnetism. In this method, a finely powdered substance or solution is taken in a Pyrex cylindrical glass tube called a Gouy tube. The substance is weighed first without a magnetic field and then in the presence of a magnetic field (Figure 1.1). A paramagnetic substance will weigh more in the presence of a magnetic field than in its absence; the increase in weight gives a quantification of the paramagnetism of the substance. The greater the number of unpaired electrons in a substance, the greater will be the increase in its weight under a magnetic field. The magnetic susceptibility is measured from the difference in weight of the sample with and without magnetism.

When a substance is placed in an uneven (non-uniform) magnetic field, a magnetic force (F) acts on it. This force depends on:

- The magnetic susceptibility (χ) of the material,
- The volume of the sample present in the field, and
- The magnetic field strength (H).

This force produces an apparent change in weight, which can be measured using an analytical balance. From this change, the magnetic susceptibility can be calculated.

Experimental Arrangement

In the Gouy balance, the sample is filled in a long glass tube, which is suspended from one arm of an analytical balance.

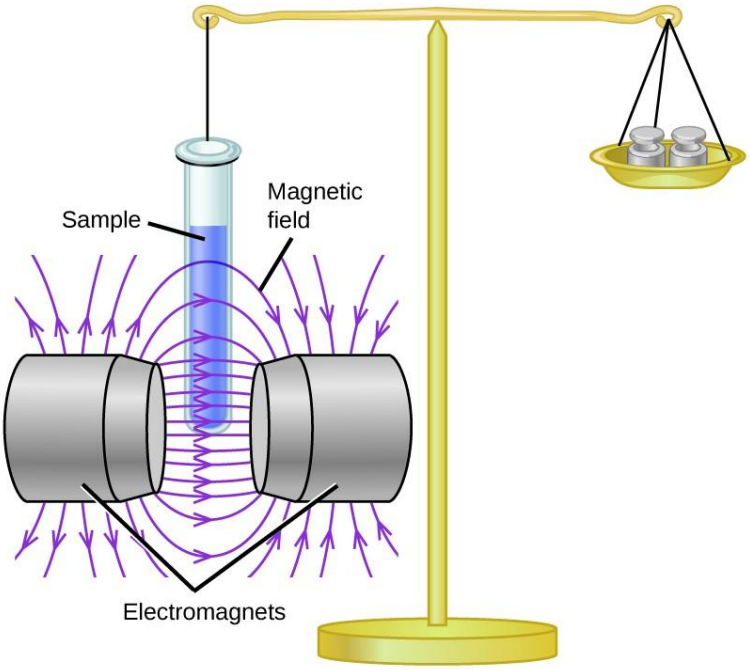


Fig.1.5 Gouy's Apparatus

The lower end of the tube is positioned between the poles of an electromagnet (where the field is strong), while the upper part remains outside the magnetic field. Depending on whether the substance is paramagnetic or diamagnetic, the sample exerts an upward or downward pull, producing a change in the balance reading.

Derivation

Magnetic Force on the Sample: Consider a sample with cross-sectional area A exposed to a magnetic field H. The magnetic force acting on the sample is given by:

$$F = \frac{1}{2}A(\mu_2 - \mu_1)H^2$$

where

$$\mu_2 = \mu_0(1 + \chi)(\text{permeability of the sample})$$
$$\mu_1 = \mu_0(\text{permeability of air})$$

Thus,

$$\mu_2 - \mu_1 = \mu_0\chi$$

Substituting into the force equation:

$$F = \frac{1}{2}A\mu_0\chi H^2$$

Relation with Apparent Weight Change

The force acting on the sample also equals the apparent weight change observed on the balance:

$$F = (m_2 - m_1)g$$

where

- $m_2 - m_1$= change in mass reading (in kg)
- g= acceleration due to gravity

Final Expression for Magnetic Susceptibility

Equating both expressions for force:

$$(m_2 - m_1)g = \frac{1}{2}A\mu_0\chi H^2$$

Solving for susceptibility:

$$\chi = \frac{2(m_2 - m_1)g}{A\mu_0 H^2}$$

This is the Gouy equation used to calculate magnetic susceptibility.

$$\boxed{\chi_g = \frac{2(m_2 - m_1)g}{A\mu_0 H^2}}$$

The forces are large because the amount of sample taken in the Gouy's tube is quite large and therefore, a chemical balance can also measure the changes in mass. The disadvantage of this method is that it requires perfect uniform packing of the substance in the Gouy's tube. Therefore, correct results cannot be obtained if the Gouy's tube has not been packed uniformly.

1.4.1.2 Quincke's Method

Magnetic susceptibility (χ) is a fundamental property that measures the extent to which a material becomes magnetised when placed in an external magnetic field. For liquids and solutions, one of the classical and accurate experimental techniques used to measure magnetic susceptibility is Quincke's Method, named after the German physicist G. Quincke.

This method is particularly used in physical chemistry to determine the magnetic behaviour of paramagnetic and diamagnetic substances in solution.

Principle

Quincke's method is based on the principle that when a liquid having magnetic susceptibility (χ) is placed in a non-uniform magnetic field, it experiences a magnetic force that causes the liquid to either rise (if paramagnetic) or fall (if diamagnetic) in a fine capillary tube. This change in height occurs because the magnetic pressure developed in the field tries to pull the paramagnetic liquid towards the stronger magnetic region or push the diamagnetic liquid away from it.

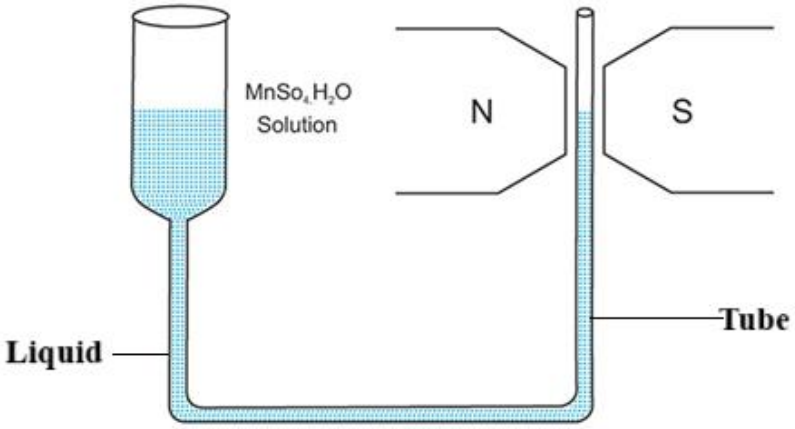


Fig. 1.6 Quincke's Apparatus

In equilibrium, this magnetic pressure is balanced by the hydrostatic pressure of the displaced liquid column, and the measured rise or fall directly gives the magnetic susceptibility. For experimenting, a Quincke's tube (a U-shaped tube with a narrow capillary limb) is used along with a strong electromagnet to produce the non-uniform magnetic field. A power supply controls the current through the electromagnet, while a Gauss meter or fluxmeter measures the magnetic field strength. A travelling microscope is used to observe the liquid meniscus accurately, and the setup also includes a thermometer to ensure constant temperature. This complete apparatus enables precise measurement of the liquid level change, which forms the basis for determining magnetic susceptibility by Quincke's method.

Derivation of the Formula

A liquid placed in a magnetic field develops an induced magnetisation $\mathbf{M = \chi H}$, where

- χ = magnetic susceptibility
- H = magnetic field strength.

In Quincke's method, the liquid in a U-tube is exposed to a strong **non-uniform magnetic field** produced by an electromagnet. The difference in magnetic field at the two surfaces creates a pressure difference that pushes the liquid column upward or downward.

This pressure difference is balanced by the hydrostatic pressure of the liquid column:

$$\text{Magnetic pressure} = \text{Hydrostatic pressure}$$

Magnetic Pressure

The magnetic pressure acting on a substance of susceptibility χ in magnetic field H is:

$$P_m = \frac{1}{2}\chi H^2$$

This pressure tends to move the liquid upward in the field.

Hydrostatic Pressure

If the liquid rises by height **h**, the hydrostatic pressure is:

$$P_h = \rho g h$$

where

- ρ = density of the liquid
- g = acceleration due to gravity
- h = rise (or fall) in liquid level.

Condition of Equilibrium

At equilibrium:

$$P_m = P_h$$

Therefore,

$$\frac{1}{2}\chi H^2 = \rho g h$$

Solving for χ:

$$\chi = \frac{2\rho g h}{H^2}$$

This is the fundamental working expression of Quincke's method.

Using Magnetic Induction B Instead of H

Since $\mathbf{B} = \mu_0 \mathbf{H}$, where μ_0 = permeability of free space,

$$H = \frac{B}{\mu_0}$$

Substitute into main equation:

$$\chi = \frac{2\rho g h \mu_0^2}{B^2}$$

This form is often used when magnetic induction (B) is directly measured.

1.5 SPIN-ONLY FORMULA

In coordination chemistry and magnetism, the magnetic moment (μ) of a transition-metal complex is often calculated assuming that the magnetic moment arises only from the spin of unpaired electrons. This is valid because in most transition-metal ions (especially 3d metals), orbital angular momentum is quenched due to the ligand field.

Spin-Only Formula

$$\boldsymbol{\mu_{\text{eff}} = \sqrt{n(n+2)}\ \text{BM}}$$

Where:

- μ_{eff}= effective magnetic moment (in Bohr Magnetons, BM)
- n= number of unpaired electrons in the metal ion

Spin-Only Formula use the spin-only formula because, in most 3d transition-metal ions, the strong ligand fields remove the orbital degeneracy of d-orbitals. This effect suppresses or "quenches" the orbital contribution to the magnetic moment, making the total magnetic moment arise mainly from the electron spin. As a result, the spin-only formula provides an accurate and reliable method for calculating magnetic moments in such complexes.

Steps to Calculate the Magnetic Moment

1. Determine the oxidation state of the metal in the complex.
2. Write its electronic configuration.
3. Identify the number of unpaired electrons (n).
4. Apply the spin-only formula:

$$\mu = \sqrt{n(n+2)}$$

Example

Calculate the magnetic moment of $[Fe(H_2O)_6]^{2+}$

Step 1: Identify oxidation state

Fe in $[Fe(H_2O)_6]^{2+}$:

$$Fe + 6(H_2O) \rightarrow Fe^{2+}$$

So, oxidation state = **+2**.

Step 2: Write the electronic configuration

Atomic number of Fe = 26

$$Fe: [Ar]\ 3d^6\ 4s^2$$

$$Fe^{2+}: [Ar]\ 3d^6$$

Step 3: Find the number of unpaired electrons

In a weak ligand field (H_2O = weak ligand), Fe^{2+} is **high spin**. $3d^6$ high-spin configuration:

↑↓	↑	↑	↑	↑

Total unpaired electrons = 4

Step 4: Apply spin-only formula

$$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.90 \text{ BM}$$

1.6 ORBITAL CONTRIBUTION TO MAGNETIC MOMENTS

In transition metal complexes and coordination compounds, the observed magnetic moment arises from the combined contributions of electron spin and orbital angular momentum. While the spin angular momentum is always present for unpaired electrons, the orbital contribution depends strongly on the electronic configuration and the extent to which the orbital motion of electrons is "free" or "quenched." Understanding orbital contributions is essential for accurately interpreting magnetic properties, predicting geometries, and analysing electronic structures of complexes.

1.6.1 Origin of Orbital Magnetic Moment

Electrons possess both spin motion and orbital motion around the nucleus. Each type of motion generates a magnetic effect:

- **Spin Angular Momentum (S):** Associated with electron spin; always contributes when unpaired electrons are present.
- **Orbital Angular Momentum (L):** Arises due to the electron's motion in degenerate d-orbitals (like d_{xy}, d_{xz}, d_{yz}, etc.).

When orbital degeneracy exists, the electron can circulate between equivalent orbitals, producing an **orbital magnetic moment**. This orbital motion adds to the spin moment and results in higher experimental magnetic moment values than predicted by the spin-only formula.

Typical configurations where orbital contribution is significant include those with unquenched degeneracy, such as d^1, d^2, d^4(high spin), d^7(low spin), d^9, and various f-electron systems.

1.6.2 Orbital Quenching

In many coordination complexes, especially those of 3d transition metals, the ligand field splits the d-orbitals into groups of different energies (e.g., t_{2g} and e_g in octahedral fields). This splitting **removes the degeneracy** of the orbitals and restricts the electrons' ability to circulate freely between them.

As a result, the orbital angular momentum is **suppressed or "quenched."**

Why quenching occurs

- Distorted or asymmetric fields fix the spatial orientation of d-orbitals.
- Electrons become confined to specific orbitals rather than moving around a degenerate set.
- The contribution of *L* becomes very small, leaving the **spin-only magnetic moment** dominant.

Thus, for most 3d metal ions, the experimentally observed magnetic moments match closely with the spin-only values.

1.6.3 Cases with Significant Orbital Contribution

Although 3d complexes often show quenched orbital moments, some systems exhibit considerable orbital contributions, especially when:

(a) Degeneracy remains only partially removed

Examples:

- Tetrahedral complexes, where splitting is weaker.
- Distorted geometries that leave certain orbital combinations nearly degenerate.

(b) Heavier transition metals (4d and 5d series)

These have:

- Larger, more diffuse d-orbitals
- Stronger spin–orbit coupling
- Less effective quenching by ligand fields

Hence, orbital contributions can be large.

(c) Lanthanides and Actinides

Outer electrons shield the f-orbitals, and ligand fields cannot split them effectively. Thus, the orbital contribution remains dominant, giving very high magnetic moments.

1.6.4 Effective Magnetic Moment with Orbital Contribution

When orbital angular momentum is significant, the magnetic moment cannot be described by the spin-only formula:

$$\mu_{\text{spin}} = \sqrt{n(n+2)}$$

Instead, the total moment is given by the **Russell–Saunders coupling (L–S coupling)**:

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)}$$

In systems with strong spin–orbit coupling, the **Landé g-factor** must be considered:

$$\mu_{\text{eff}} = g_J\sqrt{J(J+1)}\mu_B$$

where:

- $J = L + S$for less than half-filled shells
- $J =\mid L - S \mid$for more than half-filled shells
- $g_J$is the Landé factor.

These equations apply especially to rare earth ions and some transition metals with unquenched orbital momentum.

1.6.5 Practical Importance of Orbital Contribution

Understanding orbital contributions is crucial because:

- It explains why some complexes show abnormally high magnetic moments.

- It helps predict geometry, ligand field strength, and electronic structure.
- It allows correct interpretation of spectroscopic and magnetic data.
- It is essential in the study of lanthanide magnetism, molecular magnets, and spintronic materials.

1.7 APPLICATION OF MAGNETIC MOMENT DATA OF 3D-METAL COMPLEXES

Magnetic moment measurements provide one of the most valuable experimental tools for understanding the electronic structure of coordination compounds, particularly those involving 3d-transition metals. Because the magnetic properties of these ions arise mainly from the number of unpaired electrons and the influence of ligand fields, magnetic moment data serve as a direct probe of the geometry, bonding, and electronic configuration of metal complexes. The following sections highlight the major applications of magnetic moment information in the study of 3d-metal complexes.

1.7.1 Determination of the Number of Unpaired Electrons

The primary application of magnetic moment data is the determination of the number of unpaired electrons in a complex. For most 3d-transition metals, the orbital contribution is largely quenched due to strong ligand fields, making the ***spin-only formula*** $(\mu = \sqrt{n(n+2)})$ sufficiently accurate. By comparing the experimentally measured magnetic moment with theoretical values, the number of unpaired electrons can be determined. This information directly leads to the identification of the electronic configuration and helps distinguish between different possible oxidation states of the metal ion.

1.7.2 Distinguishing High-Spin and Low-Spin Complexes

In octahedral complexes of 3d metals, especially those containing **d^4, d^5, d^6, and d^7** electronic systems, strong and weak ligand fields can give rise to either high-spin or low-spin arrangements.

Magnetic moment data help distinguish between these spin states:

- **High-spin complexes** show a larger number of unpaired electrons and therefore higher magnetic moments.
- **Low-spin complexes**, formed with strong-field ligands (e.g., CN^-, CO, phenanthroline), show fewer unpaired electrons and lower magnetic moments.

Thus, magnetic measurements serve as a practical method for identifying the ligand-field strength and the spin state of the complex.

1.7.3 Confirmation of Molecular Geometry

The geometry of a coordination complex strongly influences the electron distribution in the d-orbitals. Magnetic moment data therefore, assist in distinguishing between possible geometries such as **tetrahedral**, **square-planar**, or **octahedral**.

Examples include:

- **d^8 metal ions (Ni^{2+}, Pd^{2+}, Pt^{2+}):**
  - ❖ Square-planar complexes are usually **diamagnetic** (all electrons paired).
  - ❖ Tetrahedral complexes are typically **paramagnetic** with two unpaired electrons.
- **d^4 and d^5 systems:**
  - ❖ Octahedral high-spin complexes give higher magnetic moments.
  - ❖ Tetrahedral complexes often show characteristic moments.

Thus, magnetic measurements serve as an effective structural probe when other spectroscopic data are inconclusive.

1.7.4 Determination of Oxidation State

The oxidation state of a metal ion controls the d-electron count and subsequently the magnetic properties. Magnetic moments provide a simple experimental approach for oxidation state determination, especially when spectroscopic or analytical data are ambiguous.

For example:

- Fe^{2+} (d^6) high-spin complexes ($\mu \approx 5.0–5.5$ BM)
- Fe^{3+} (d^5) high-spin complexes ($\mu \approx 5.9$ BM)

Similarly, Cr^{2+}, Cr^{3+}, Mn^{2+}, and Mn^{3+} complexes exhibit characteristic magnetic moments that help in correct oxidation-state assignment.

1.7.5 Study of Jahn–Teller Distortion

The Jahn–Teller effect often leads to distortion in octahedral complexes of ions such as **Cu^{2+} (d^9)** and **Mn^{3+} (d^4)**. Such distortions alter the splitting pattern of d-orbitals, which in turn influences the magnetic moment. Magnetic measurements therefore support the presence of a Jahn–Teller distortion by showing slight deviations from ideal spin-only values.

1.8 SUMMARY

This chapter explores the magnetic properties of materials and how magnetic moment data help interpret 3d-transition metal complexes. It explains basic magnetic behaviours, including diamagnetism, paramagnetism, ferromagnetism, and antiferromagnetism, and how these arise from electron pairing and domain alignment.

Magnetic susceptibility is introduced along with its experimental determination using the Gouy Method for solids and the Quincke's Method for liquids. The spin-only formula, mainly applicable to 3d-metal complexes, is discussed along with the concept of orbital quenching and conditions where orbital contributions remain significant.

The chapter concludes with key applications of magnetic moment measurements, such as determining the number of unpaired electrons, distinguishing high-spin and low-spin complexes, identifying geometries, assigning oxidation states, and detecting Jahn–Teller distortions. Magnetic data thus serve as vital tools in understanding the structure and behaviour of metal complexes.

1.9 TERMINAL QUESTIONS

A. Short Answer Questions

1. What is magnetic susceptibility?
2. Why are Zn^{2+} complexes diamagnetic?
3. State the spin-only formula for magnetic moment.
4. What is the major difference between diamagnetism and paramagnetism?
5. Define orbital quenching.
6. What is the principle of the Gouy method?
7. Name one ferromagnetic and one antiferromagnetic material.
8. Write the relation between magnetic induction (B) and magnetic field strength (H).

B. **Long Answer Questions**

1. Explain in detail the different types of magnetic behaviour exhibited by chemical substances.

2. Describe the Gouy Method for determining magnetic susceptibility along with its derivation.
3. Discuss Quincke's Method and derive the expression for susceptibility in liquids.
4. What is the spin-only magnetic moment? Explain with suitable examples.
5. Describe the origin of orbital magnetic moments and the concept of orbital quenching.
6. How can magnetic moment data be used to distinguish between high-spin and low-spin complexes?
7. Explain how magnetic measurements help in determining the geometry and oxidation state of 3d metal complexes.
8. Discuss the role of magnetic data in identifying Jahn–Teller distortions.

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UNIT-2 ORGANOMETALLIC CHEMISTRY

CONTENTS:

2.1 INTRODUCTION

Organometallic chemistry is an important branch of modern inorganic chemistry that deals with compounds containing at least one direct bond between a metal atom and a carbon atom of an organic group. These compounds form a vital link between organic and inorganic chemistry and play a crucial role in understanding reaction mechanisms, bonding concepts, and catalytic processes. The field has expanded rapidly due to its extensive applications in industrial catalysis, polymer chemistry, pharmaceuticals, and materials science.

This unit focuses on the fundamental aspects of organometallic compounds, beginning with their definition, nomenclature, and classification. Special emphasis is laid on mononuclear metal carbonyls, which represent one of the most significant classes of organometallic compounds. The nature of metal–carbon monoxide bonding, including σ-donation and π-back bonding, is discussed to provide insight into their stability and reactivity. The unit also introduces general methods for the preparation of organometallic compounds and gives a brief account of metal–ethylenic (olefin) complexes, highlighting their bonding and importance. Finally, alkyl and aryl derivatives of alkali and alkaline earth metals are studied to understand their structure, reactivity, and role as reagents in synthetic chemistry.

2.2 OBJECTIVES

After completing this unit, students will be able to:

- Understand the scope and significance of organometallic chemistry and its relationship with organic and inorganic chemistry.
- Define organometallic compounds and explain their systematic nomenclature and classification.
- Describe the structure and properties of mononuclear metal carbonyls.
- Explain the nature of bonding in metal carbonyls with reference to σ-donation and π-back bonding.
- Discuss the general methods of preparation of organometallic compounds.

- Gain a basic understanding of metalethylenic (olefin) complexes and their bonding characteristics.
- Explain the preparation, properties, and reactivity of alkyl and aryl derivatives of alkali and alkaline earth metals.

2.3 MONONUCLEAR CARBONYLS

Mononuclear metal carbonyls are an important class of organometallic compounds in which a single metal atom is bonded to one or more carbon monoxide (CO) ligands. These compounds have the general formula M(CO)n, where *M* is a transition metal and *n* is the number of carbonyl ligands attached to the metal. Carbon monoxide acts as a neutral ligand and binds strongly to metals through synergic bonding, making metal carbonyls highly stable despite the toxicity of free CO gas.

Mononuclear carbonyls are usually formed by transition metals in low oxidation states, particularly from groups 6 to 10 of the periodic table. Typical examples include $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, and $Mn(CO)_5Br$. These compounds are generally volatile, low-melting, and diamagnetic, and many obey the 18-electron rule, which explains their stability.

2.4 NOMENCLATURE OF METAL CARBONYLS

The nomenclature of metal carbonyls depends on the number of metal atoms, the charge on the complex, the type and number of ligands, and their mode of coordination.

- Metal carbonyls may exist as neutral complexes, positively charged carbonyl cations, or negatively charged carbonylate anions.
- Carbon monoxide can coordinate to the metal either as a terminal ligand (bonded to one metal atom) or as a bridging ligand (bonded to two or more metal atoms).
- Metal carbonyls containing only CO ligands are called homoleptic carbonyls (e.g., $Ni(CO)_4$, $Fe(CO)_5$), whereas those containing CO along with other ligands are known as heteroleptic carbonyls.

- Complexes with a single metal atom are called mononuclear metal carbonyls, while those containing two or more metal atoms are termed polynuclear metal carbonyls (e.g., $Fe_2(CO)_9$, $Fe_3(CO)_{12}$).
- The number of CO ligands is indicated by Greek numerical prefixes followed by the word *carbonyl*.
- Carbon monoxide shows different bonding modes in metal carbonyls. Hapticity (η^n) indicates the number of ligand atoms bonded to the metal. CO usually acts as a monohapto (η^1) ligand. Bridging carbonyls are denoted by μ, for example μ^2-CO for CO bridging two metal atoms.

A. Name → Chemical Formula

1. Nickel tetracarbonyl → $Ni(CO)_4$
2. Iron pentacarbonyl → $Fe(CO)_5$
3. Chromium hexacarbonyl → $Cr(CO)_6$
4. Molybdenum hexacarbonyl → $Mo(CO)_6$
5. Tungsten hexacarbonyl → $W(CO)_6$
6. Cobalt tricarbonyl nitrosyl → $Co(CO)_3NO$
7. Manganese pentacarbonyl bromide → $Mn(CO)_5Br$
8. Rhenium pentacarbonyl chloride → $Re(CO)_5Cl$

B. Chemical Formula → Name

1. $Ni(CO)_4$ → Nickel tetracarbonyl
2. $Fe(CO)_5$ → Iron pentacarbonyl
3. $Cr(CO)_6$ → Chromium hexacarbonyl
4. $Mo(CO)_6$ → Molybdenum hexacarbonyl
5. $W(CO)_6$ → Tungsten hexacarbonyl
6. $Co_2(CO)_8$ → Dicobalt octacarbonyl
7. $Fe_2(CO)_9$ → Diiron nonacarbonyl
8. $Fe_3(CO)_{12}$ → Triiron dodecacarbonyl

2.5 CLASSIFICATION OF MONONUCLEAR CARBONYL

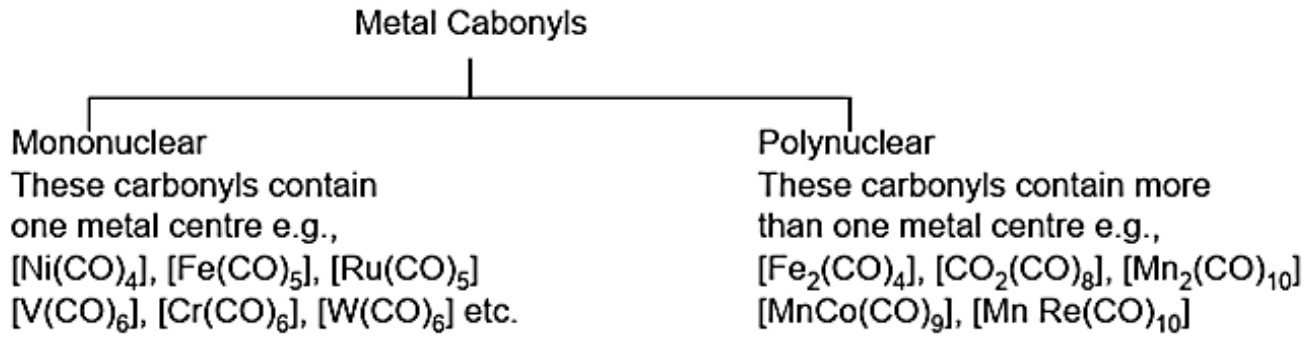
Mononuclear metal carbonyls contain only one metal atom bonded to carbon monoxide ligands and generally follow formulas such as $M(CO)_x$. Examples include tetrahedral $Ni(CO)_4$, trigonal-bipyramidal $Fe(CO)_5$, and octahedral $Cr(CO)_6$. These compounds mainly occur in two forms: neutral mononuclear complexes (like $Cr(CO)_6$) and ionic complexes (such as $[V(CO)_6]^-$or $[Mn(CO)_5]^+$). Most of them are stable because they satisfy the 18-electron rule and adopt characteristic geometries.

1. Classification Based on Structure and Geometry- They are grouped according to the number of ligands and the shape around the metal center:

- **Tetrahedral:** $Ni(CO)_4$, $Pd(CO)_4$
- **Trigonal bipyramidal:** $Fe(CO)_5$, $Ru(CO)_5$, $Os(CO)_5$
- **Octahedral:** $V(CO)_6$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$

2. Classification Based on Charge- Although they contain only one metal atom, mononuclear carbonyls may be neutral or charged:

- **Neutral complexes:** $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$
- **Anionic complexes:** $[V(CO)_6]^-$— vanadium (with an odd atomic number) forms an anion to gain stability
- **Cationic complexes:** for example, $[Mn(CO)_5]^+$



Key Features

- **Single metal atom:** The presence of only one metal center makes their structures relatively simple.
- **18-electron rule:** Most stable mononuclear carbonyls achieve an 18-electron configuration, similar to noble gases.

- **σ-donation and π-backbonding:** CO ligands donate electrons to the metal and also accept electrons back through π-backbonding, which strengthens the metal–carbon bond.
- **Magnetic behavior:** These compounds are generally diamagnetic (no unpaired electrons), except $V(CO)_6$, which is paramagnetic, as reported in NPTEL reference material.

2.6 GENERAL METHODS OF PREPARATION OF ORGANOMETALLIC COMPOUNDS

Some important methods used for the preparation of metal carbonyls are as follows:

1. Direct synthesis- Metal atoms in the reduced (free metal) state react directly with carbon monoxide under suitable temperature and pressure to form metal carbonyls.

At **25°C and 1 atm**

$$Ni + 4CO \rightarrow Ni(CO)_4$$

At **200°C and 10 atm**

$$Fe + 5CO \rightarrow Fe(CO)_5$$

2. Reduction method- Metal salts such as halides or oxides are reduced in the presence of carbon monoxide to form metal carbonyls.

$$CrCl_3 + Al + 6CO \rightarrow Cr(CO)_6 + AlCl_3$$

(Using **$AlCl_3$ / C_6H_6** as reaction medium)

$$WCl_6 + 3Zn + 6CO \rightarrow W(CO)_6 + 3ZnCl_2$$

(At **120°C**)

$$Os(CO)_8 \quad \rightarrow \quad Os(CO)_5 + 4CO_2$$

3. Photolysis / Thermolysis- Higher metal carbonyls such as $Fe_2(CO)_9$and $Os_3(CO)_{12}$are obtained by heating (thermolysis) or irradiating light (photolysis) on lower mononuclear carbonyls.

$$2Fe(CO)_5 \overset{hv}{\rightarrow} Fe_2(CO)_9 + CO$$
$$3Os(CO)_5 \overset{hv}{\rightarrow} Os_3(CO)_{12} + 3CO$$

4. Substitution reactions- Some metal carbonyls are formed when metal halides react with carbon monoxide in the presence of reducing agents.

$$VCl_3 + 6CO + Na \rightarrow V(CO)_6 + 3NaCl$$
$$CrCl_3 + 6CO + (C_2H_4)_3Al \rightarrow Cr(CO)_6 + 3AlCl_3$$
$$MoCl_6 + 6CO + Na \rightarrow Mo(CO)_6 + 6NaCl$$

5. Reaction of oxides with CO- Certain metal carbonyls are produced when metal oxides react with carbon monoxide.

$$OsO_4 + 9CO \rightarrow Os(CO)_5 + 4CO_2$$

2.7 PROPERTIES OF METAL CARBONYLS

2.7.1 Physical Properties

a. Physical state: Most metal carbonyls occur as liquids or as volatile (easily vaporised) solids.

b. Colour: Most mononuclear metal carbonyls are colourless to pale yellow. An exception is $V(CO)_6$, which is a bluish-black solid. Polynuclear carbonyls are usually darker in colour.

c. Solubility: These compounds dissolve well in organic solvents such as diethyl ether, benzene, acetone, carbon tetrachloride, and glacial acetic acid.

d. Magnetic properties: Except for $V(CO)_6$, all metal carbonyls are diamagnetic because their electrons are paired. Metals with even atomic numbers generally form mononuclear carbonyls. In dinuclear carbonyls, any unpaired electrons participate in forming metal–metal bonds.

e. Thermal stability: Most metal carbonyls melt or decompose at relatively low temperatures. Because of this and their volatility, they are **highly toxic**.

2.7.2 Chemical Properties

Metal carbonyls take part in several important types of reactions:

a. Ligand substitution reactions

Carbon monoxide ligands can be replaced (partially or completely) by other ligands, either thermally or photochemically. Monodentate ligands such as phosphines (PR_3), cyanides (CN^-), isocyanides (CNR), and ethers commonly substitute CO.

$$Fe(CO)_5 + 2CNR \rightarrow Fe(CO)_3(CNR)_2 + 2CO$$
$$Ni(CO)_4 + 2CNR \rightarrow Ni(CNR)_4 + 4CO$$
$$Fe(CO)_5 + 2PPh_3 \rightarrow Fe(CO)_3(PPh_3)_2 + 2CO$$

b. Reaction with sodium metal

Metal carbonyls can be reduced using sodium metal or sodium–mercury amalgam (Na–Hg).

$$Cr(CO)_6 + 2Na \rightarrow Na_2[Cr(CO)_5] + CO$$
$$Mn_2(CO)_{10} + 2Na \rightarrow 2Na[Mn(CO)_5] + CO$$

c. Reaction with sodium hydroxide

On reaction with NaOH, metal carbonyls form carboxylate-type complexes through nucleophilic attack by the hydroxide ion.

$$Fe(CO)_5 + NaOH \rightarrow Na[Fe(CO)_4COOH]$$
$$Na[Fe(CO)_4COOH] + NaOH \rightarrow Na[HFe(CO)_4] + NaHCO_3$$
$$Na[HFe(CO)_4] + H^+ \rightarrow H_2Fe(CO)_4 + Na^+$$

This sequence of reactions is known as the **Hieber base reaction**.

d. Reaction with hydrogen

Some metal carbonyls react with hydrogen to form **metal carbonyl hydrides**.

$$Co_2(CO)_8 + H_2 \overset{165^\circ C}{\rightarrow} 2[HCo(CO)_4]$$

2.8 PREPARATION, BONDING AND STRUCTURE OF MONONUCLEAR CARBONYLS

The methods of preparation, properties and structure of some mononuclear metal carbonyls are given below:

2.8.1 Nickel Tetracarbonyl ($Ni(CO)_4$)

Preparation

Nickel tetracarbonyl is obtained by passing carbon monoxide over metallic nickel at a temperature of **60–100°C**.

$$Ni + 4CO \overset{60^{\circ}C}{\rightarrow} Ni(CO)_4$$

It can also be prepared by passing CO through **alkaline suspensions** of nickel sulphide or nickel cyanide.

$$NiS + 4CO \rightarrow Ni(CO)_4 + S$$

$$Ni(CN)_2 + 4CO \rightarrow Ni(CO)_4 + C_2N_2$$

Properties

A. Physical Properties

- It is a colourless liquid.
- Melting point: −25°C
- Boiling point: 43°C
- It decomposes between 180–200°C.
- It is insoluble in water, but soluble in organic solvents.
- It is highly toxic and volatile.

B. Chemical Properties

1. Reaction with concentrated sulphuric acid

It forms nickel sulphate, hydrogen, and carbon monoxide.

$$Ni(CO)_4 + H_2SO_4 \rightarrow NiSO_4 + H_2 + 4CO$$

2. Reaction with moist nitric oxide

It produces a deep-blue nickel nitrosyl complex.

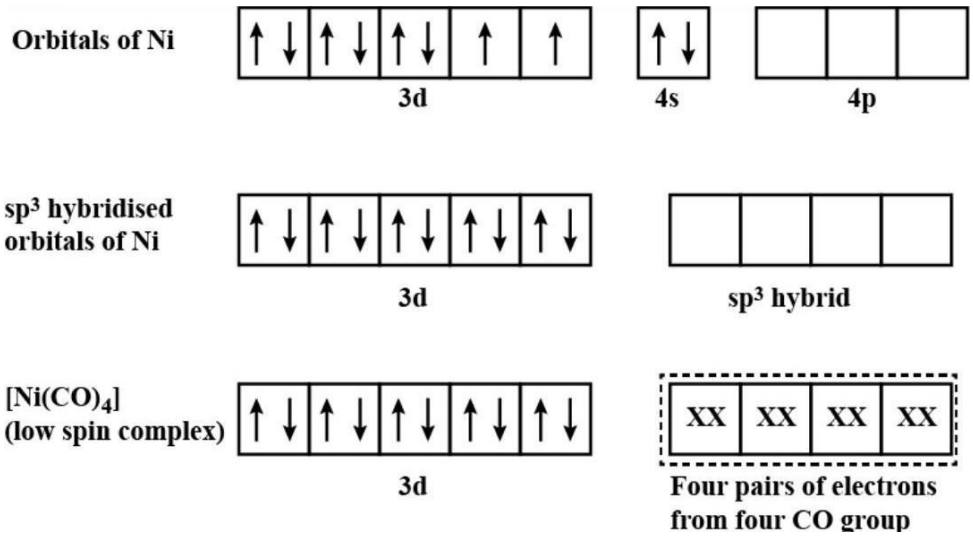
$$2Ni(CO)_4 + 2NO + 2H_2O \rightarrow 2Ni(NO)(OH) + 8OH^- + H_2$$

Uses

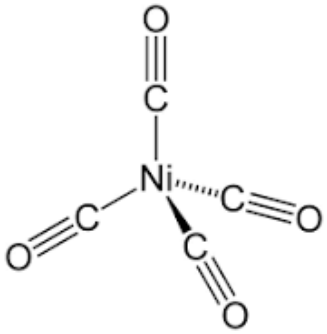
1. On heating, $Ni(CO)_4$decomposes to give pure nickel metal, so it is used in Mond's process for nickel purification.
2. It is used for nickel plating on other metals.
3. It acts as a catalyst in the manufacture of acrylic monomers in the plastics industry.

2.8.1.1 Structure of Nickel Tetracarbonyl ($Ni(CO)_4$)

Nickel tetracarbonyl is a mononuclear metal carbonyl compound in which a single nickel atom is bonded to four carbon monoxide ligands. In this complex, nickel exists in the **zero-oxidation state**, written as $Ni(0)$. The compound follows the **18-electron rule**, which accounts for its high stability.



In nickel tetracarbonyl, $Ni(CO)_4$, the nickel atom is present in the zero-oxidation state because carbon monoxide is a neutral ligand. The atomic number of nickel is 28, and in its free atomic state its electronic configuration is $[Ar]\ 3d^8\ 4s^2$. However, when nickel forms the complex with CO, the strong-field and π-acceptor nature of the CO ligands causes rearrangement and pairing of electrons.



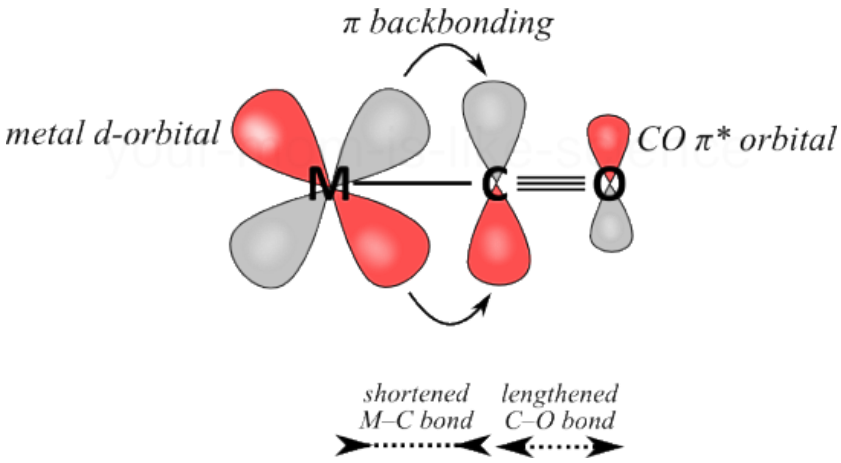
Tetrahedral structure

As a result, the two 4s electrons are shifted into the 3d subshell, giving nickel a filled $3d^{10}\ 4s^0$configuration in the complex. Thus, nickel contributes 10 valence electrons, and each of

the four CO ligands donates two electrons through σ-bonding, giving a total of $10 + 8 =$ 18electrons. This satisfies the **18-electron rule**, which explains the high stability and diamagnetic nature of the complex. Therefore, in $Ni(CO)_4$Nickel exists as $Ni^0$with a filled $3d^{10}$configuration, forming a tetrahedral and electronically stable metal carbonyl complex.

In $Ni(CO)_4$, the nickel atom is surrounded symmetrically by four CO ligands, forming a tetrahedral geometry. Each CO ligand is bonded to the metal through the carbon atom (C-donor ligand). The bonding in this complex involves both σ-donation and π-backbonding:

- The carbon atom of CO donates a lone pair of electrons to nickel forming a **σ-bond**.
- Nickel, in turn, donates electron density back from its filled $3d$orbitals into the **empty π* orbitals of CO**, forming **π-backbonding**.



This synergic interaction strengthens the Ni–C bond and slightly weakens the C–O bond compared to free CO. Because all electrons are paired, $Ni(CO)_4$is diamagnetic.

The complex belongs to the T_d point group and has four equivalent Ni–C bonds. The tetrahedral arrangement minimises repulsion between ligands and gives the molecule its characteristic three-dimensional shape

2.8.2 Iron Pentacarbonyl ($Fe(CO)_5$)

2.8.2.1 Preparation

1. Direct synthesis- Iron pentacarbonyl is obtained by passing carbon monoxide over finely divided iron at **high temperature and pressure**.

$$Fe + 5CO \underset{100\text{ atm}}{\overset{200^{\circ}C}{\rightarrow}} Fe(CO)_5$$

2. Carbonylation of iron salts- It may also be prepared by carbonylation of **ferrous sulphide or ferrous iodide** in the presence of copper metal, which acts as a reducing agent.

$$2FeS + 10CO + 2Cu \underset{200\text{ atm}}{\overset{200^{\circ}C}{\rightarrow}} 2Fe(CO)_5 + Cu_2S$$

2.8.2.2 Properties

A. Physical Properties

1. $Fe(CO)_5$is a pale-yellow liquid.
    - ❖ Melting point: −20°C
    - ❖ Boiling point: 103°C
    - ❖ It decomposes at about 250°C
2. It is insoluble in water, but dissolves in methanol, acetone, glacial acetic acid, diethyl ether, and benzene.
3. It undergoes hydrolysis in the presence of acids or moisture.

B. Chemical Properties

1. Photochemical dimerization

In glacial acetic acid, a cold solution of $Fe(CO)_5$dimerizes under **ultraviolet light** to form iron nonacarbonyl.

$$2Fe(CO)_5 \overset{h\nu}{\rightarrow} Fe_2(CO)_9 + CO$$

2. Reaction with sodium in liquid ammonia

$$Fe(CO)_5 + 2Na \underset{\text{liq. } NH_3}{\overset{200\ C}{\rightarrow}} Na_2[Fe(CO)_4] + CO$$

3. Reaction with halogens

In non-aqueous solvents, $Fe(CO)_5$reacts with halogens to form stable tetracarbonyl halides:

$$Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4X_2 + CO$$

2.8.2.3 Structure of Iron Pentacarbonyl, $Fe(CO)_5$

Iron pentacarbonyl is a neutral metal carbonyl complex in which an iron atom is coordinated with five carbon monoxide (CO) ligands. The complex has a trigonal bipyramidal geometry, consisting of three CO ligands in the equatorial plane and two CO ligands in the axial positions. The Fe–C bond lengths in the axial positions are slightly longer than those in the equatorial positions, indicating weaker bonding due to greater repulsion along the axial axis. The complex is mononuclear, meaning it contains a single iron atom surrounded by five ligands.

Hybridization and Electronic Structure

The central iron atom undergoes dsp^3**hybridization**.

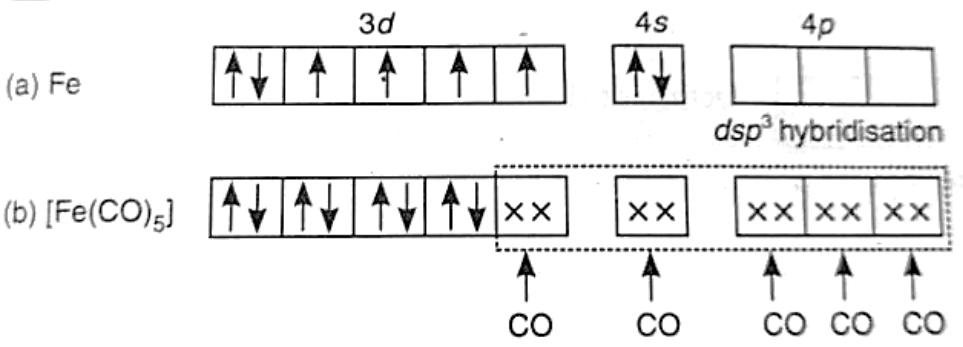
Free iron has the configuration:

$$Fe = [Ar]\, 3d^6\, 4s^2$$

Because CO is a **strong-field ligand**, the electrons pair up in the $3d$orbitals, giving:

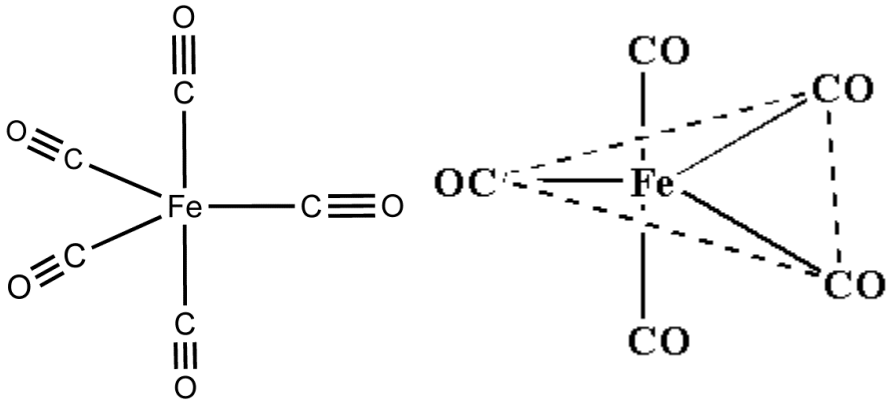
$$Fe \text{ in } Fe(CO)_5 = 3d^8\, 4s^0$$

Five dsp^3hybrid orbitals overlap with the **lone-pair orbitals of CO** to form five **σ-bonds**, while **π-backbonding** further stabilises the complex.



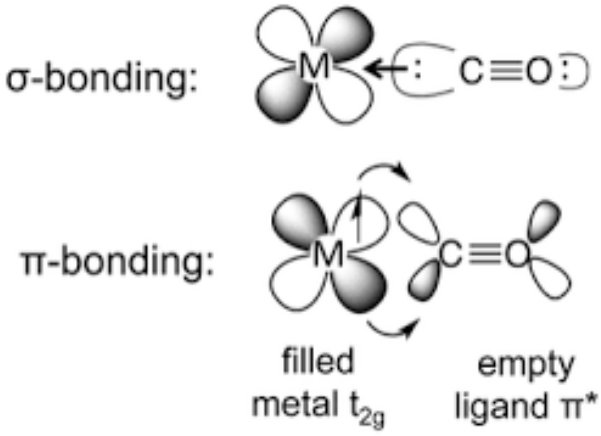
Formation of the $Fe(CO)_5$, dsp^3 hybridisation

In $Fe(CO)_5$, the iron atom is in the zero-oxidation state (Fe^0) and possesses the electronic configuration $3d^6\ 4s^2$. Upon complex formation, iron utilizes the 3d, 4s, and 4p orbitals to form sp^3d hybrid orbitals, which accommodate bonding with five CO ligands



Trigonal bipyramidal Structure

Each CO ligand donates a pair of electrons to the metal through **σ-bonding from the carbon atom**, while **π-backbonding** occurs when filled d-orbitals of iron donate electron density into the empty π* antibonding orbitals of CO. This synergic bonding strengthens the Fe–C linkage and weakens the C–O bond, which is reflected in the lowering of the CO stretching frequency in IR spectra.



The molecule is **electronically stable** because it satisfies the **18-electron rule**: iron contributes eight valence electrons (Fe^0: $3d^6\ 4s^2$), and the five CO ligands contribute ten electrons ($2e^-$ each), giving a total of 18 valence electrons. This stability accounts for the molecular nature, volatility, and relatively high reactivity of iron pentacarbonyl, making it an important precursor in organometallic chemistry and industrial metal-carbonyl processes.

2.9 EAN RULE

Effective Atomic Number (EAN) refers to the total number of electrons surrounding a metal atom or ion in a coordination complex. The concept was proposed by Sidgwick and is also known as the *inert gas rule*. According to this rule, the EAN of a metal atom or ion in a stable complex becomes equal to the atomic number of the noble gas located in the same period of the periodic table. Many organometallic compounds — particularly metal carbonyls and nitrosyl complexes — generally follow the EAN rule.

Calculation of EAN

The Effective Atomic Number of the central metal atom or ion in a metal carbonyl complex can be calculated using the following general formula:

$$EAN = Z - O + n \text{ (electrons donated by ligands)}$$

Where:

- **Z** = Atomic number of the metal
- **O** = Oxidation state of the metal
- **n (electrons donated by ligands)** = Total electrons donated by all coordinating ligands

Calculation of EAN of $Fe(CO)_5$

Metal: Iron (Fe)

Atomic number of Fe (Z): 26

Oxidation state of Fe in $Fe(CO)_5$: 0

Ligand: CO (each CO donates 2 electrons)

Number of CO ligands: 5

$$\text{Total electrons donated by ligands} = 5 \times 2 = 10$$

$$EAN = Z - O + \text{(electrons donated by ligands)}$$

$$EAN = 26 - 0 + 10 = 36$$

Result

EAN of $Fe(CO)_5$ = 36

Calculation of EAN for $Cr(CO)_6$

Metal: Chromium (Cr)

Atomic number of Cr (Z): 24

Oxidation state of Cr in $Cr(CO)_6$: 0

Ligand: CO (each CO donates 2 electrons)

Number of CO ligands: 6

Total electrons donated by ligands $= 6 \times 2 = 12$

EAN $= Z - O +$ (electrons donated by ligands)

EAN $= 24 - 0 + 12 = 36$

ResultEAN of $Cr(CO)_6 = 36$

Calculation of effective atomic number (EAN) in some metal carbonyls

Metal Carbonyls	**Atomic number of iron atom**	**Carbonyl groups**	**EAN**
$Ni(CO)_4$	28	4 x 2 = 8	36 [Kr]
$Fe(CO)_5$	26	5 x 2 = 10	36 [Kr]
$Ru(CO)_5$	44	5 x 2 = 10	54 [Xe]
$Os(CO)_5$	76	5 x 2 = 10	86 [Rn]
$Cr(CO)_6$	24	6 x 2 = 12	36[Kr]
$Mo(CO)_6$	42	6 x 2 = 12	54 [Xe]
$W(CO)_6$	74	6 x 2 = 12	86 [Rn]

2.10 18-ELECTRON RULE

The 18-electron rule states that a transition-metal complex is most stable when the total number of valence electrons around the metal atom equals 18. This corresponds to the filled valence shell configuration:

$$(ns)^2(np)^6(nd)^{10}$$

which is analogous to the **noble-gas configuration**.

The total electron count comes from:

- d-electrons of the metal (based on oxidation state)
- electrons donated by ligands
- metal–metal bonds (if present)

General Formula

Total Electron + Metal valence electrons + Electrons donated by ligand

A complex is said to **obey the 18-electron rule** when:

Total = 18 electrons

Examples

A. $Fe(CO)_5$

- Fe (Z = 26) → d^8 (oxidation state = 0 → 8 valence electrons)
- Each CO donates = 2e
- 5 CO ligands → $5 \times 2 = 10$e

$$8 + 10 = \boxed{18 \text{ electrons}}$$

$Fe(CO)_5$ follows the 18-electron rule.

B. $Cr(CO)_6$

- Cr (Z = 24) → d^6 (oxidation state = 0 → 6 valence electrons)
- 6 CO ligands → $6 \times 2 = 12$e

$$6 + 12 = \boxed{18 \text{ electrons}}$$

$Cr(CO)_6$ follows the rule.

C. $Ni(CO)_4$

- Ni (Z = 28) → d^{10} (oxidation state = 0 → 10 e)
- 4 CO ligands → $4 \times 2 = 8$e

$$10 + 8 = \boxed{18 \text{ electrons}}$$

$Ni(CO)_4$ also obeys the rule.

2.11 METAL-ETHYLENIC COMPLEXES

Ligands that contain C=C multiple bonds, such as ethyne, propene, butene, benzene, and cycloheptatriene, are collectively known as ethylenic ligands.

When ethylenic ligands coordinate with metal ions such as Ni^{2+}, Pt^{2+}, Pd^{2+}, and Rh^{2+}, the resulting compounds are called organo-ethylenic complexes. These complexes are widely studied in organometallic chemistry and have significant structural and catalytic applications.

Some of the most important examples of organo-ethylenic complexes are as follows:

1. Zeise's Salt - Potassium Trichloro(ethylene)platinate(II)

$$K[PtCl_3(C_2H_4)] \cdot H_2O$$

- First discovered olefin complex
- Ethylene is coordinated to Pt(II) through its C=C double bond
- Classical example supporting Dewar–Chatt–Duncanson bonding model

2. **Bis(ethylene)nickel(0)**

$$Ni(C_2H_4)_2$$

- Nickel(0) bonded to two ethylene ligands
- Follows the 18-electron rule
- Important intermediate in polymerisation catalysis

3. Bis(ethylene)platinum(0)

$$Pt(C_2H_4)_3$$

- Platinum coordinated with three ethylene ligands
- Exhibits strong π-back-bonding

4. Tris(ethylene)rhodium(I) Chloride

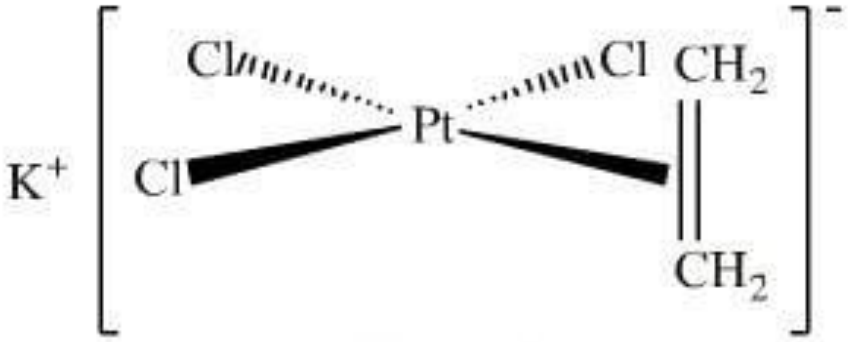
$$[RhCl(C_2H_4)_3]$$

- Rhodium(I) complex with three olefin ligands
- Used as a precursor in hydrogenation catalysts

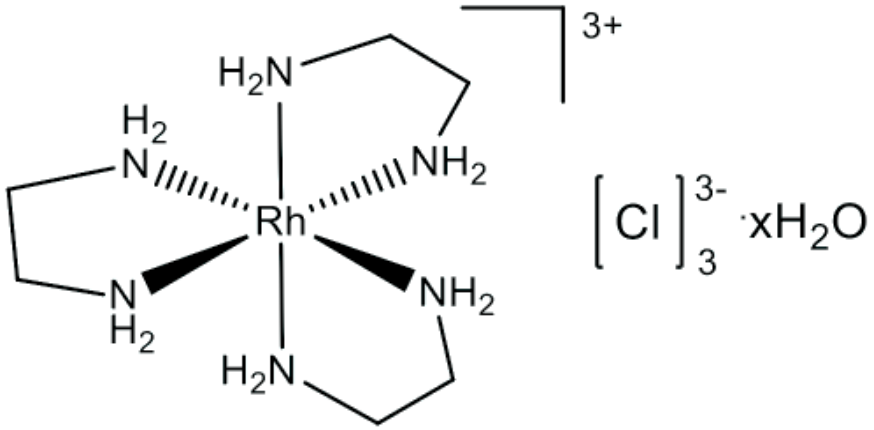
5. Dichloro(ethylene)palladium(II)

$$PdCl_2(C_2H_4)$$

- Square-planar Pd(II) complex
- Plays a role in olefin insertion and coupling reactions



Zeise's Salt
Potassium trichloro(ethylene)platinate(II)



Tris(ethylene)rhodium(I) Chloride

2.11.1 Bonding in Organo-Ethylenic (Olefin) Complexes

Organo-ethylenic complexes exhibit two types of bonding: σ-bonding and π-back bonding, which together explain the metal–olefin interaction.

2.11.1.1 σ-Bonding in Organo-Ethylenic Complexes

The bonding in an organo-ethylenic complex can be illustrated using **Zeise's salt**,

$$K[PtCl_3(C_2H_4)]$$

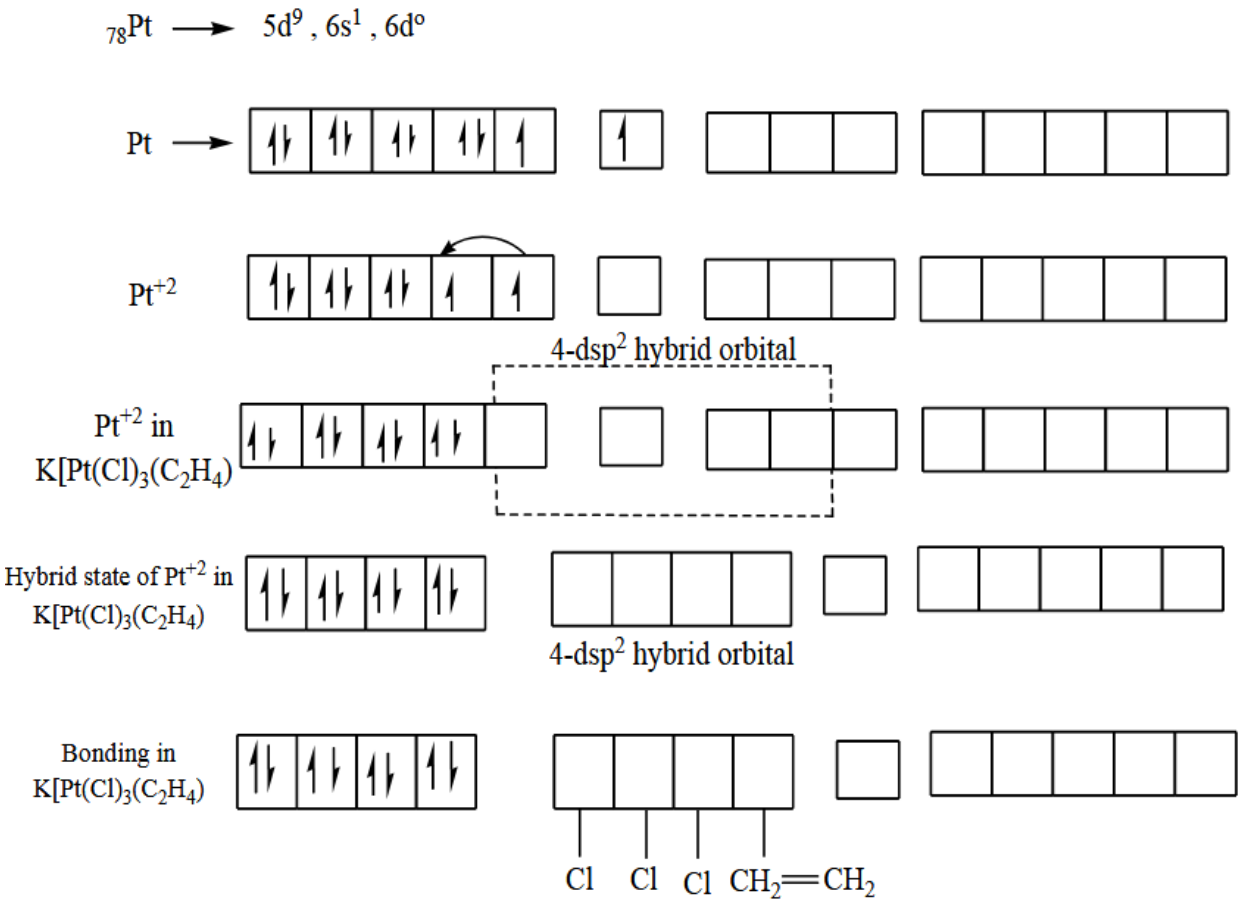
as an example.

In this complex, the central metal ion Pt^{2+} undergoes dsp^2 hybridization, producing four vacant dsp^2 hybrid orbitals. Out of these four orbitals:

- Three dsp^2 orbitals overlap head-on with the σ-orbitals of the three Cl^- ligands, forming three Pt–Cl σ-bonds.
- The fourth vacant dsp^2 orbital of Pt^{2+} overlaps with the filled π-bonding molecular orbital ($\pi_{C=C}$) of ethylene, forming a $C_2H_4 \rightarrow Pt$ σ-bond.

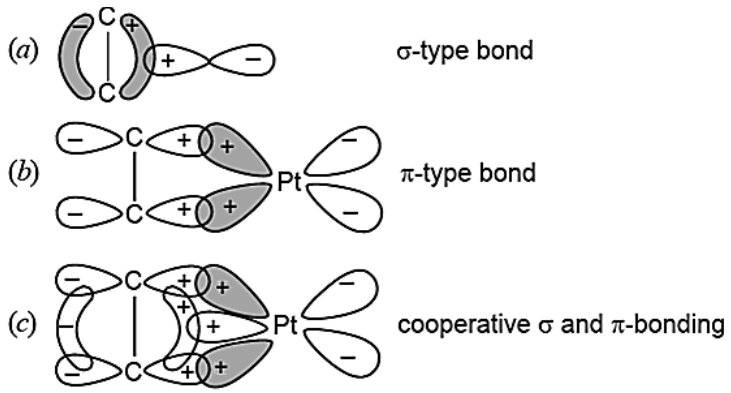
This σ-interaction between the ethylenic ligand and the metal is termed the organo-ethylenic (olefin–metal) σ-bond, and it can be represented as:

$$C_2H_4 \rightarrow Pt^{2+}$$



2.11.1.2 π-Bonding (Back-Bonding) in Organo-Ethylenic Complexes

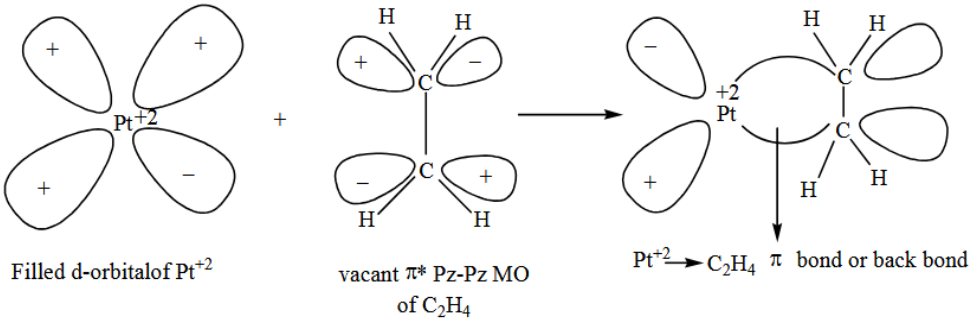
After the formation of the normal $C_2H_4 \rightarrow Pt^{2+}$ σ-bond, a second type of interaction takes place between the metal and the ethylenic ligand. In this step, a side-wise (lateral) overlap occurs between the filled d-orbitals of the metal ion (Pt^{2+}) and the vacant π* antibonding molecular orbital of the C=C bond in ethylene.



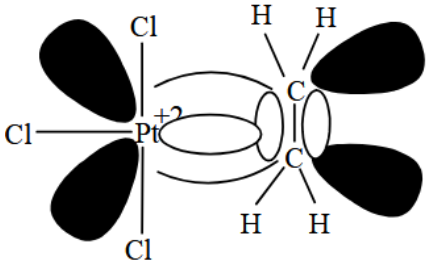
This results in the formation of a metal → ligand π-back bond, represented as:

$$Pt^{2+} \rightarrow C_2H_4$$

This π-back donation strengthens the metal–carbon interaction while simultaneously weakening and lengthening the C=C bond in the olefin. Thus, the metal–olefin bond is synergic in nature — the σ-donation from the ligand to the metal is complemented by π-back donation from the metal to the ligand.



Finally, the combined picture for both σ-bond and π-bond in the organ ethylenic complexes can be represented as-



2.12 METHODS FOR THE PREPARATION OF ORGANO-ETHYLENIC (OLEFIN) COMPLEXES

Several synthetic methods can prepare organo-ethylenic complexes. Some of the important methods are described below:

1. Reaction of Metal Carbonyls with Ethylenic (Olefin) Ligands

Metal carbonyls react with olefin ligands to form olefin-coordinated complexes. For example:

$$Mo(CO)_6 + \eta^6\text{-}C_7H_8 \rightarrow [Mo(CO)_3(\eta^6\text{-}C_7H_8)] + 3CO$$

$$Fe(CO)_5 + \eta^4\text{-}C_4H_6 \rightarrow [Fe(CO)_3(\eta^4\text{-}C_4H_6)]$$

In these reactions, one or more CO ligands are replaced by an olefin ligand, which coordinates through its **C=C bond**.

2. Reaction of Halo-Complexes with Olefin Ligands

Olefin complexes may also be obtained by ligand substitution in metal halo-complexes. For example:

$$K_2[Pt^{II}Cl_4] + C_2H_4 \rightarrow K[Pt^{II}Cl_3(C_2H_4)] + KCl$$

Here, ethylene replaces one chloride ligand and forms a Pt–olefin coordinated complex.

3. Reaction of Metal Halides with Olefin Ligands

Olefin ligands can also coordinate directly to metal halides:

$$2RhCl_3 + 4C_2H_4 \rightarrow Rh_2Cl_2(C_2H_4)_4 + 4Cl^-$$

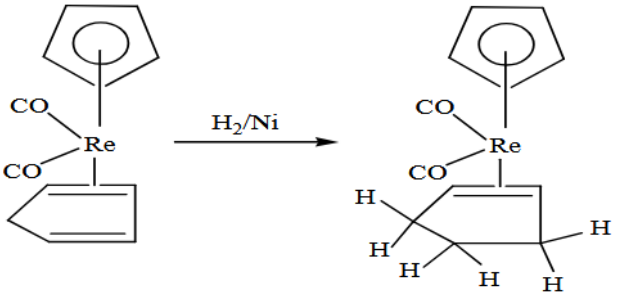
The resulting complex contains bridging and terminal olefin ligands.

2.12.1 Chemical Properties of Organo-Ethylenic Complexes

Organo-ethylenic complexes exhibit several important reactions due to the coordinated **C=C bond**.

1. Reduction (Hydrogenation Reaction)

When organo-ethylenic complexes are treated with hydrogen (H_2) in the presence of Ni catalyst, the coordinated olefin undergoes **hydrogenation**, converting the C=C bond into a saturated C–C bond.



This reaction is known as the reduction (hydrogenation) of organo-ethylenic complexes.

2. Substitution Reaction

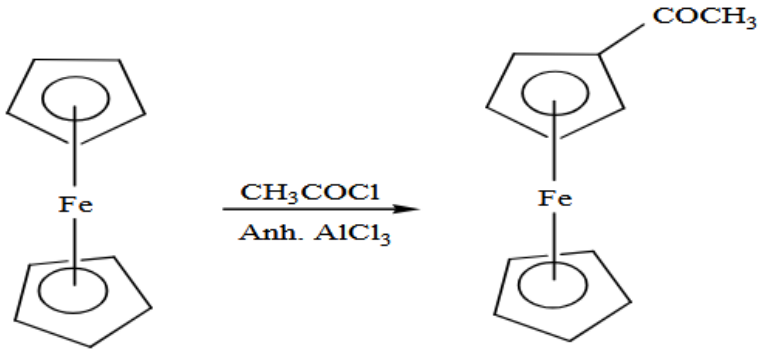
Organo-ethylenic complexes undergo ligand substitution when treated with phosphine ligands **(PR_3)**, where R = H, CH_3, C_2H_5, etc.

$$K[Pt(Cl)_3(C_2H_4)] + PR_3 \rightarrow K[Pt(Cl)_3(PR_3)] + C_2H_4$$

The olefin ligand is replaced by the **phosphine ligand**.

3. Acetylation Reaction

Acetylation takes place in the presence of acetyl chloride (CH_3COCl) and anhydrous aluminium chloride ($AlCl_3$), leading to the introduction of an acetyl group onto the metal-olefin complex.



The reaction proceeds via electrophilic substitution on the coordinated olefin.

2.13 ALKYL AND ARYL DERIVATIVES OF ALKALI AND ALKALINE-EARTH METAL ORGANOMETALLIC COMPOUNDS

The alkyl and aryl derivatives of alkali and alkaline-earth metals represent an important class of organometallic compounds in which a direct metal–carbon (M–C) bond is present. The metals involved belong mainly to Group-1 (Li, Na, K) and Group-2 (Be, Mg, Ca, etc.) of the periodic table. These compounds are highly reactive and play a significant role as reagents and intermediates in organic synthesis, polymerisation reactions, catalysis, and metallurgy. Typical examples include alkyl- and aryl-lithium compounds (RLi, ArLi), alkyl-sodium compounds (RNa) and organ magnesium derivatives such as R_2Mg and RMgX (Grignard reagents).

2.13.1 Methods of Preparation

1. Direct Metalation (Direct Combination Method)

An alkyl or aryl halide reacts directly with the metal.

(a) Alkali metals

$$2\ R–X + 2\ Na \rightarrow 2\ R–Na + X_2$$

(b) Organolithium (more common)

$$R–X + 2\ Li \rightarrow R–Li + LiX$$

This method is widely used for alkyl- and aryl-lithium compounds.

2. Metal–Hydrogen (or Proton) Exchange

Strongly basic organo-alkali compounds deprotonate hydrocarbons:

$$R–Li + R'–H \rightarrow R–H + R'–Li$$

Used especially for aryl-lithium and vinylic-lithium synthesis.

3. Transmetallation (Exchange with another Organometallic Compound)

$$R–Hg–R + 2\ Na \rightarrow 2\ R–Na + Hg$$

or

$$R–Li + MgX_2 \rightarrow R–MgX + LiX$$

This method prepares dialkyl magnesium and mixed magnesium halides.

4. Reaction of Metal with Unsaturated Hydrocarbons

Especially for **alkaline-earth metals**:

$$M + \text{Alkene/Alkyne} \rightarrow M–(\text{alkyl/alkynyl})$$

(e.g., Be–alkyls, Mg–alkyls under special conditions)

5. Grignard Reagent Formation (Alkaline-Earth: Mg)

$$R–X + Mg \rightarrow R–MgX$$

Prepared in **dry ether**, very important synthetic intermediates.

PROPERTIES

1. Nature of Bonding

- Alkali-metal alkyls/aryls: Highly ionic, strongly basic and nucleophilic
- Alkaline-earth derivatives: More polar-covalent (especially Mg, Be), less reactive than alkali analogues

2. Reactivity Toward Air and Moisture

All are air-sensitive and hydrolyze rapidly:

$$R–M + H_2O \rightarrow R–H + MOH$$

Therefore, they are handled under dry, inert atmosphere.

3. Solubility

- Alkali metal derivatives: soluble in hydrocarbon solvents or ethers
- Mg and Be derivatives: generally soluble in ether/THF (coordinating solvents)

4. Thermal and Chemical Stability

- Lithium alkyls are more stable than Na and K derivatives
- Higher reactivity follows:

$$R–K > R–Na > R–Li$$

2.14 SUMMARY

This unit introduces the fundamental concepts of organometallic chemistry, with special emphasis on mononuclear metal carbonyls. Organometallic compounds contain a direct bond between a metal and a carbon atom and act as a bridge between organic and inorganic chemistry. They play a crucial role in industrial catalysis, polymer formation, pharmaceuticals, and materials science.

The unit explains the structure, bonding, nomenclature, and classification of metal carbonyls.

The nature of metal–CO bonding is discussed in terms of σ-donation and π-backbonding, which accounts for their stability and adherence to the 18-electron rule. General methods for synthesising organometallic compounds, including direct synthesis, reduction, photolysis, and substitution reactions, are described.

The properties and reactivity of carbonyls are presented along with detailed case studies of $Ni(CO)_4$ and $Fe(CO)_5$, highlighting their preparation, geometry, and electronic structure. The Effective Atomic Number (EAN) rule and its application in calculating stability of metal carbonyls are also discussed.

2.15 TERMINAL QUESTIONS

1. Define organometallic compounds. How do they differ from coordination compounds?
2. Explain the role of σ-donation and π-backbonding in metal–carbonyl bonding.
3. Classify mononuclear metal carbonyls based on geometry and charge with suitable examples.
4. Describe the direct synthesis and reduction methods for the preparation of metal carbonyls.
5. Write the preparation and properties of Nickel tetracarbonyl, $Ni(CO)_4$.
6. Discuss the structure and bonding of Iron pentacarbonyl, $Fe(CO)_5$.
7. What is the EAN rule? Calculate the EAN for $Cr(CO)_6$ and $Fe(CO)_5$.
8. State the 18-electron rule. How does it explain the stability of metal carbonyls?
9. Explain why most mononuclear metal carbonyls are diamagnetic and volatile.

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UNIT 3 : SILICONES AND PHOSPHAZENES

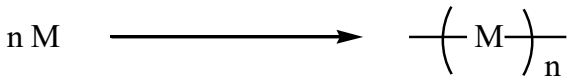
CONTENTS:

3.1. INTRODUCTION

All the covalent macromolecules, which do not have carbon in their compounds, are considered to be inorganic polymers. Covalently-bonded crystals (like oxides and halides), condensed phosphate etc., are the examples of inorganic polymers. These polymers possess distinctive physicchemical characteristics and unique physical, mechanical and electrical properties. These polymers are of extensive utility in everyday life, particularly in the area of engineering and technology.

The main point of similarity between inorganic and organic polymers is, that both can be prepared by the addition and condensation methods. The former method is used when polymers of higher molecular weight and greater mechanical strength are needed. Silicones and phosphazenes are examples of inorganic polymers. Inorganic elements can have different valences than carbon, and therefore, different numbers of side groups may be attached to a skeletal atom. This will affect the flexibility of polymers, their ability to react with chemical reagents and interactions with other polymers. Among inorganic polymers, silicones and phosphazenes are two important classes of polymers with high commercial potential.

All the macromolecules that are formed by the combination of a large number of small units are known as a polymer, and the process of their formation is called as polymerisation process.



Where n= Degree of polymerisation

$(M)_n$ = Polymer

M = Monomer

3.2. OBJECTIVES

After completing this unit, learners will be able to:

- **Understand the concept of inorganic polymers** and distinguish them from organic polymers.
- **Classify polymers and inorganic polymers** based on their structure, composition, and properties.

- **Explain the general properties of inorganic polymers** and relate them to their structure and bonding.
- **Describe the chemistry of phosphonitrilic halides (phosphazenes)** including their preparation, nomenclature, and structural features.
- **Discuss the methods of formation and properties of phosphonitrilic chlorides**, with emphasis on cyclic triphosphonitrilic chloride.
- **Interpret the structure and bonding in phosphazenes** using suitable theoretical models.
- **Explain silicones as important inorganic polymers** and classify different industrial types of silicone polymers.
- **Describe the preparation methods of silicones** and understand the chemistry involved in their synthesis.
- **Identify the properties and industrial applications of silicones** in various technological and commercial fields.
- **Develop an appreciation of the role of silicones and phosphazenes** in modern materials science and industry.

3.3 CLASSIFICATION OF POLYMERS

Depending on the catenating nature of elements, polymers can be divided into two different types, which are given below:

(a) Organic polymer: All the macromolecules that are formed by the catenation of carbon atoms are known as organic polymers.

Example:

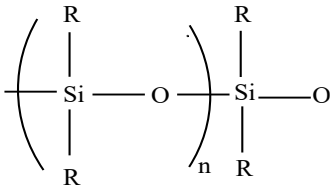
$$n\,CH_2{=}CH_2 \longrightarrow -\left(CH_2 - CH_2\right)_n-$$

Organic polymers are further divided into types, which can be given as:-

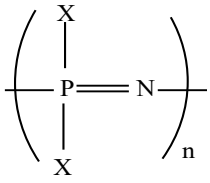
i. Synthetic polymer.
ii. Natural polymer.

(b) Inorganic polymers: All the macromolecules which are formed by the catenation of elements other then carbon are known as inorganic polymer.

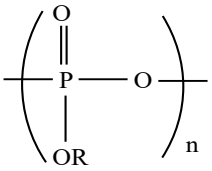
Example:

1. 

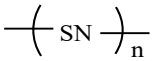
Silicon polymer

2. 

Phosphorzener

3. 

Polyphosphate

4. 

Poly sulphur nitride

3.3.1 Classification of inorganic polymers

There are different ways of classifying inorganic polymers.

Classification I: Depending on whether the polymer contains the atoms of only one element or of different elements in its backbone, the polymers are classified into the following two groups.

1. **Homo-atomic polymers:** These polymers contain the atoms of only one element in their backbones. Silicon, phosphorus, sulphur, germanium and tin form homo-atomic inorganic polymers. For example, sulphur tends to form chains or rings in its elemental form (S_8) and in several compounds, like persulphides (H-S-S-H, H-S-S-S-H, H-S-S-S-S-H etc.), polythionic acids, etc.
2. **Hetero-atomic polymers:** These contain the atoms of different elements in their backbones.

Classification II: Inorganic polymers can also be classified in another way, which is based on the type of reaction by which the polymes are formed. On this basis, inorganic polymers may be of the following ways:

1. **Condensation polymers:** Condensation polymers are those that are formed by the condensation process. In this process, two or more simple molecules of the same substance polymerise together and form the condensation polymer. One or more H_2O, NH_3, H_2, HCl etc. molecules are also eliminated.

   Examples

   (a) Cross-linked silicone is obtained by the polymerisation of many $RSi(OH)_3$ units.

   (b) When PCl_5 is partially hydrolysed by water, dichloro phosphoric acid, $PO(OH)Cl_2$ is obtained. When $PO(OH)Cl_2$ is heated, many molecules of this substance get polymerised and give rise to the formation of a condensation polymer. In this process, HCl is eliminated.

2. **Addition polymers:** These polymers are obtained when many simple molecules (monomers) combine.

   Examples:

   (a) Many molecules of sulphur trioxide may be polymerised by the addition of a small amount of water. This gives addition polymer.

   (b) When SO_2 reacts with propylene, CH_3-CH=CH_2 in the presence of benzoyl peroxide, an addition polymer is obtained.

3. **Coordination polymers**: These are formed by the addition of saturated molecules to each other or by combining a ligand with a metal atom. These polymers contain chelated metal atoms or ions.

Classification-III: According to this classification, the inorganic polymers can be classified into the following categories:

- **i.** Polymers containing two bridging bonds per unit, e.g, homo-atomic sulphur, selenium and teturium polymers.
- **ii.** The alternating silicone-oxygen polymers. Examples are silicones and related compounds.
- **iii.** The alternating phosphorus-nitrogen polymers. Examples are phosphonitrilic halides, $(NPX_2)N$.
- **iv.** The alternating phosphorus-oxygen polymers. Examples are metaphosphates, polyphosphates and cross-linked phosphates.

Classification-IV: The classification is based on the element which forms inorganic polymers. Thus, we have:

i. Polymers containing boron. Examples are: (a) Borazine, $(BH)_3$ $(NH)_3$ or $B_3N_3H_6$. (b) Substituted borzines like (i) B-trimethyl borzine, $[B(CH_3)_3$ $(NH)_3]$ (ii) Borozine $(BH)_3O_3$ (iii) N-timethyl borzine, $[B(CH_3)_3(NH)_3]$ (c) Boron nitride (BN)n.

ii. Polymers containing phosphours. Examples are: (a) Metaphosphates, (b) Polyphosphates, (c) Cros-linked phosphates, (d) Phosphonitricli halides, $[PNX_2]n$

iii. Polymers containing phosphorus. Examples are: (a) Metaphosphates, (b) Polyphosphates, (c) Cross-linked phosphates, (d) Phosphonitrilic hladies, $[PNX_2]n$.

iv. Polymers compounds of sulphur. Examples are nitrides of sulphur, thiazyl halides and imides of sulphur.

3.3.2 General properties of inorganic polymers

Some properties of inorganic polymers are given below:

(1) With a few exceptions, inorganic polymers do not burn. They soften or melt at high temperatures.

(2) Most of the inorganic polymers are built up of highly polar substances. Most of these polymers, however, react with the solvents. There are thus only a few inorganic polymers that actually dissolve in solvents properly.

(3) Inorganic polymers having cross-linked structures with a high density of covalent bonds are generally stiffer and harder than the organic polymers.

(4) The chain segments between cross-links in polymers having cross-linked structures are usually short. Consequently, these structures are not flexible enough to permit interaction of solvent molecules.

(5) Inorganic polymers are generally much less ductile than the organic polymers. Thus, while organic polymers such as polyethene can extend by about 20 percent or more before breaking, inorganic polymers break even when stretched by about 10 percent.

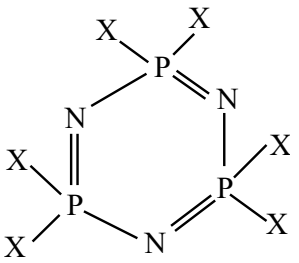
(6) Inorganic polymers, in general, are stronger, harder and more brittle than the organic polymers.

(7) Inorganic polymers can usually be obtained in pure crystalline as well as in pure amorphous forms. Organic polymers, on the other hand, have partial crystalline and partial amorphous structure.

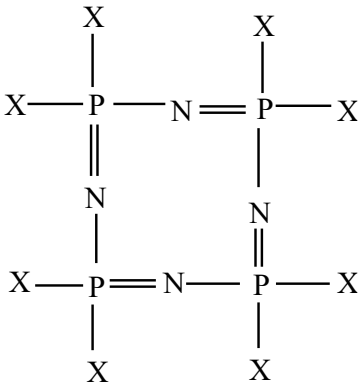
3.4 PHOSPHO NITRILIC HALIDE

Those macro molecules that have the general formula are called as $-(PNX_2)_n-$ phosphor nitrite halides, where X = F, Cl, Br and n = 3 to 7

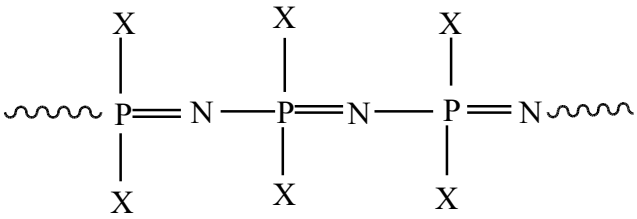
(1) Cyclic trimer



(2) Cyclic tetramer



(3) Linear polymer



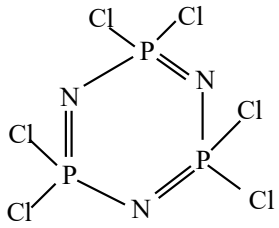
3.4.1 Phospho nitrilic chloride or phosphazenes

Phosphazenes were initially termed as phosphonitrilic polymers. Later on, the new term was used to represent phosphorus, nitrogen (azo), and P=N double bonds (ene), which are always present in these polymers. They are thus 'unsaturated PN compounds' containing phosphorus, mostly in +V state. As is usual with polymers, they may have a cyclic or chain

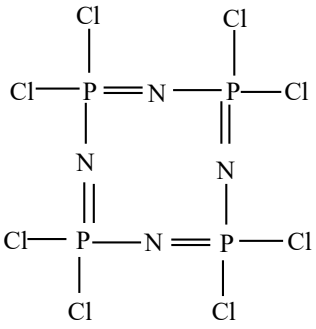
structure. The nitrogen in groups is in 2-coordination and phosphorus in 4-coordination. They contain the group which is isoelectronic with the groups of silicones. Their polymers differ in substitution on phosphorus and on the nature of those substituents, besides the way and the extent to which polymerisation has taken place. They are usually classified based on the number of phosphazene units that are incorporated in the structure:

All the compounds that having the general formula $(-PNCl_2-)_n$ are known as phosphor nitrialic chloride or those compounds which have the $(-PNCl_2-)_n$ repeating unit are known as phosphonitrilec chloride or phosphazene. In the phosphor nitrilic chloride n= 3 to7. Phosphonitrilic chloride can exist in three different forms, which are given below:

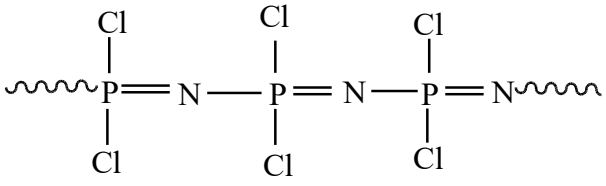
1. **Cyclic trimer**



2. **Cyclic tetramer**



3. **Linear polymer**



3.4.2 Nomenclature

Phosphor nitrilic chlorides are nomenclatured according to the number of repeating unites.

$(PNCl_2)_3$: Triphospho nitrilic chloride.

$(PNCl_2)_4$: Tetra phospho nitrilic chloride.

$(PNCl_2)_5$: Penta phospho nitrilic chloride.

$(PNCl_2)_6$: Hexo phospho nitrilic chloride.

$(PNCl_2)_7$: Hipta phospho nitrilic chloride.

3.4.3 Method of formation

Some of the methods by which phosphornitrilic chloride can be obtained are given below

1. **By the reaction of PCl_5 with ammonia:** Phosphorus penta chloride (PCl_5)when reacted with ammonia gives the corresponding phospho nitrilic chloride.

$$nPCl_5 + nNH_3 \longrightarrow (PNCl_2)_n + 3\,nHCl$$

Where n = 3 to 7

Example:

$$3PCl_5 + 3NH_3 \longrightarrow (PNCl_2)_3 + 9HCl$$

$$4PCl_5 + 4NH_3 \longrightarrow (PNCl_2)_4 + 12HCl$$

$$5PCl_5 + 5NH_3 \longrightarrow (PNCl_2)_5 + 15HCl$$

2. **By the reaction of PCl_5 with NH_4Cl:** Phosphorus pentachloride (PCl_5) when react with ammonium chloride gives corresponding phospho nitrilic chloride.

$$nPCl_5 + n\,NH_4Cl \longrightarrow (PNCl_2)_n + 4\,nHCl$$

Where n = 3 to 7

$$3PCl_5 + 3NH_4Cl \longrightarrow (PNCl_2)_3 + 9\,HCl$$

$$4PCl_5 + 4NH_4Cl \longrightarrow (PNCl2)_4 + 16HCl$$

$$5PCl_5 + 5NH_4Cl \longrightarrow (PNCl_2)_5 + 20HCl$$

3.4.4 Properties of the phosphor nitilic chloride

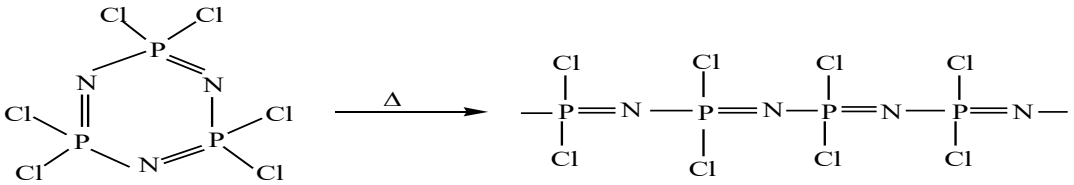
A. Physical properties

(1) $(NPCl_2)_3$ have melting point 114°C and boiling 256°C at 1 atm. pressure. It is readily soluble in ether, benzene and carbon tetrachloride.

(2) $(NPCl_2)_4$ have melting point 123ºC and boiling point 328.5ºC. It has lower solubility in ether, benzene and carbon tetrachloride than $(NPCl_2)$.

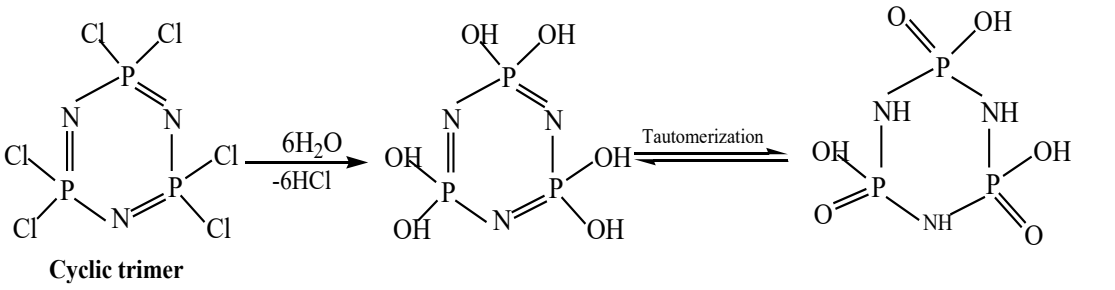
B. Chemical properties

(1) Effect of heat: When the cyclic trimeric phosphor nitrilic chloride are heated than they are converted into their corresponding liner trimer and tetramer respectively, but the liner phosphor nitrilic choride are not affected on heating.

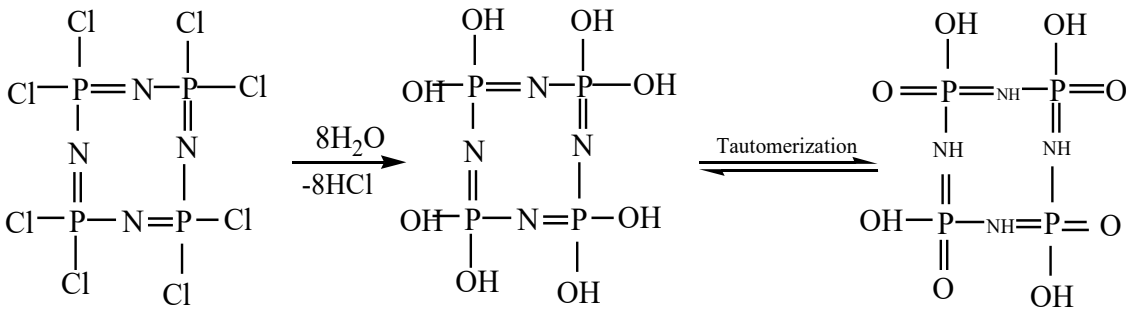


Cyclic trimer **Linear trimer**

(2) Hydrolysis: When the cyclic trimeric or tetrameric phosphonitric chlorides undergo hydrolysis than there can occur the formation of their hexa-hydroxy and octa-hydroxy derivative which can further undergo telomerisation.

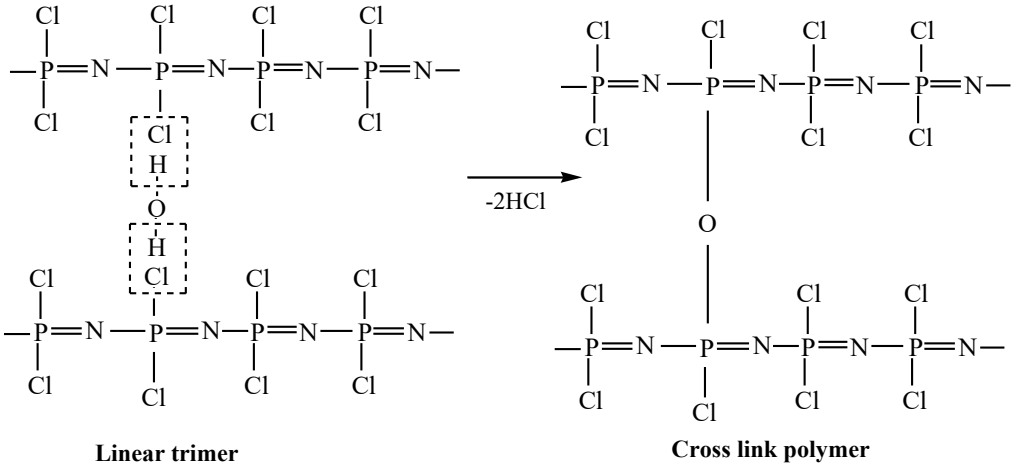


Cyclic trimer



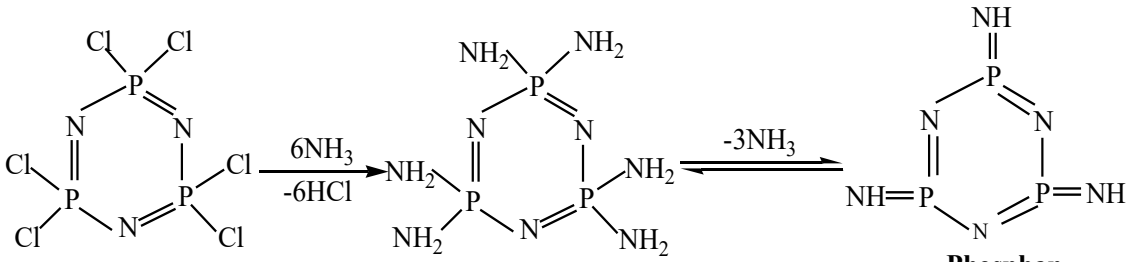
Cyclic tetramer

When the linear phosphor nitrilic chlorides react with H_2O, then there occur the formation of a cross-linked polymer occurs through the oxygen bridge.



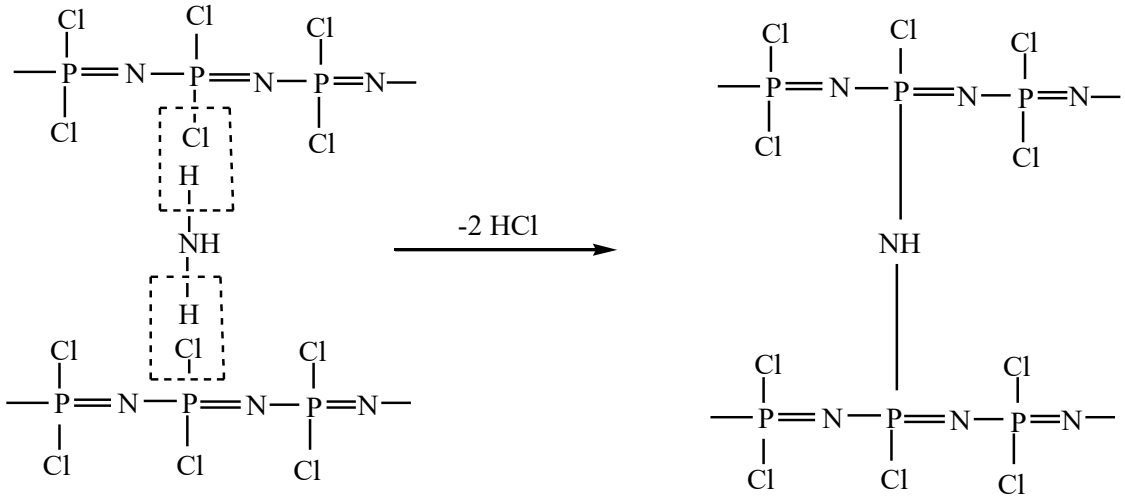
Linear trimer **Cross link polymer**

3. Reaction with the NH_3: When the cyclic trimeric or tetrameric phosphonitrilic chloride reacts with the NH_3 than there occur the formation of hexa- amino derivative and octa-amino derivative respectively, which can further eliminate the NH_3 to form the imino derivative.



Cyclic trimer **Phosphan**

While when the liner phosphor nitrilic chloride reacts with the NH_3 then there occurs the formation of cross liked polymer with the -NH-bridge.



1. **Nucleophilic substitution reaction:** When the phosphonitrilic chlorides react with nucleophilic reagents than there can occur then various nucleophilic substitution reactions can occur, some of which can be given as:

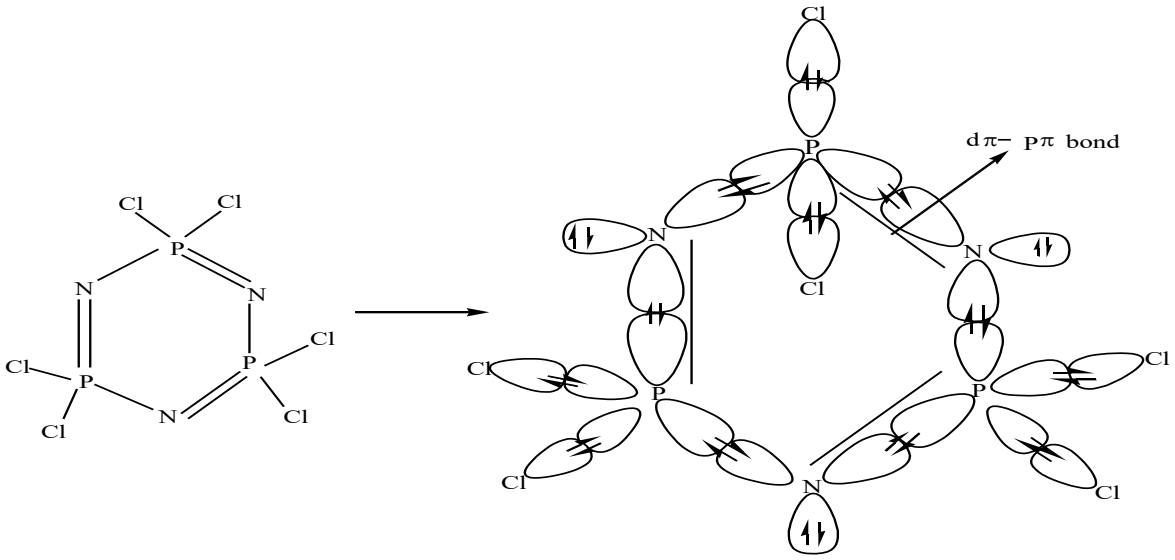
$$(PNCl_2)_3 + 6\,CH_3^-\,Li^+ \xrightarrow{-6LiCl} [PN(CH_3)_2]_3$$

$$(PNCl_2)_3 + 6\,L^+\,F^- \xrightarrow{-6LiCl} (PNF_2)_3$$

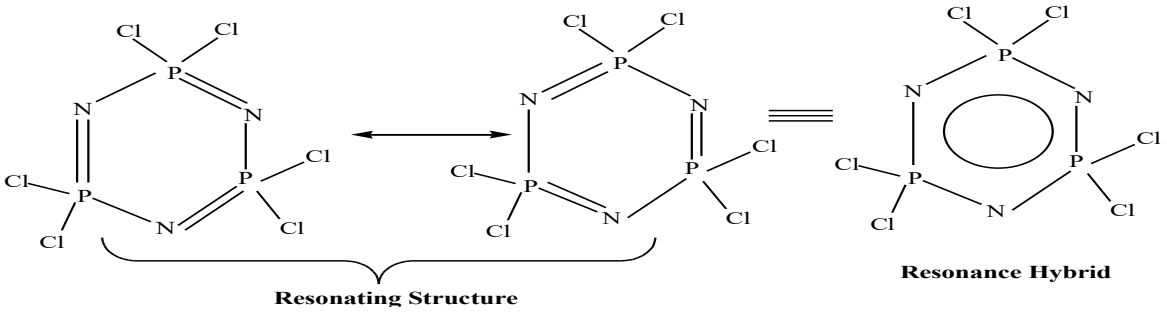
$$(PNCl_2)_3 + 6Na^+\,NH2^- \xrightarrow{-6NaCl} [(PN\,(NH_2))_2]_3$$

3.4.5 Structure of cyclic tri phospho nitrilic chloride

From X-ray diffraction method, it was observed that each P atom and N atom in the cyclic triphosphor nitrilic chloride have sp^3 and sp^2 hybridisation receptively. According to the Molecular orbital picture for this molecule can be represented as:



Due to the presence of an electron pair at one of the sp^2 hybrid orbital of each N atom, the cyclic tri phosphornitrilic chloride exhibit basic character. According to the above stricture cyclic tri-phosphonitrilic chloride should exhibit two types of the P-N bond length but experimentally it was observed that all the P-N bond length in the cyclic tri phosphor nitrilic chloride bring identical and intermediate to P=N and P-N, this indicate that this molecule will exist in the two different resonating structure as like to C_6H_6 and its actual structure will be somewhere intermediate to these two resonating structures known as resonance hybrid structure.

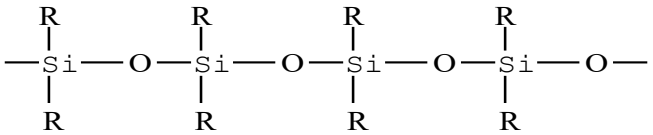


3.5 SILICON POLYMER

These compounds are polymeric organosilicone derivatives containing Si-O-Si linkages. These are also called polysiloxanes. We can represent them by the general formula $(R_2SiO)_n$. These may be linear, cyclic or cross-linked polymers and have very high thermal stability and are therefore also called high temperature polymers. Because of the high thermal stability of Si-O-Si chains, chemists have prepared a large variety of silicone polymers, which are very useful in high-temperature processes. Therefore, these find uses in high-temperature applications such as heat transfer agents and high-performance elastomers. Such qualities are not expected of organic polymers, which cannot withstand high temperatures.

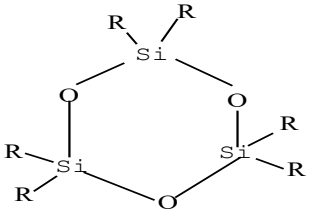
Types of silicone polymers

1. **Linear silicon polymer**

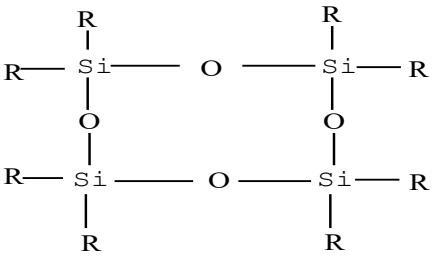


2. **Cyclic silicon polymer**

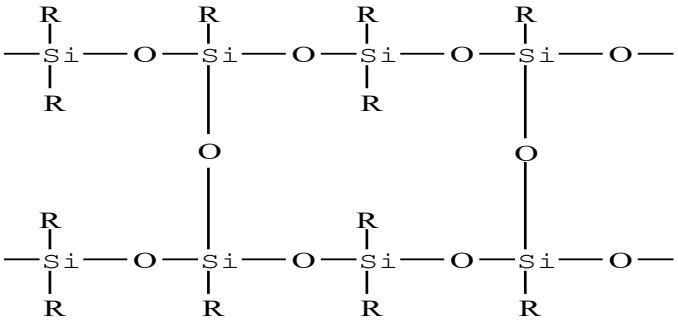
   a. **Cyclic trimer silicon polymer**



   b. **Cyclic tetra meric silicon polymer**



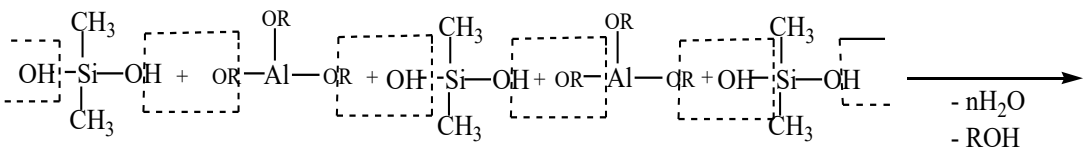
c. Cross linked silicon polymer

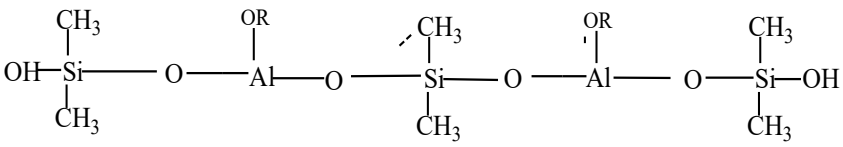


3.5.1 Types of silicon polymer on industrial bases

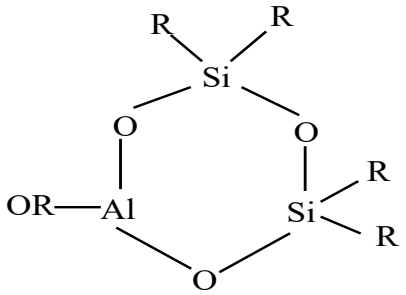
Based on industrial use, silicon polymer can be divided into four different types, which are given below:-

(i) High thermal silicon polymer: When hydrolysis of an organosilicon halide is carried out in the presence of the halides or alkoxides of Al, or Ti, a two-dimensional linear or cyclic silicone polymer is obtained. In this polymer, some Si atoms are replaced by Al or Ti atoms. High thermal silicones have exceptionally high thermal stability and remain unchanged, even in contact with a white-hot electrically-heated wire. The presence of Al and Ti atoms in the structure of the polymer increase the thermal stability.

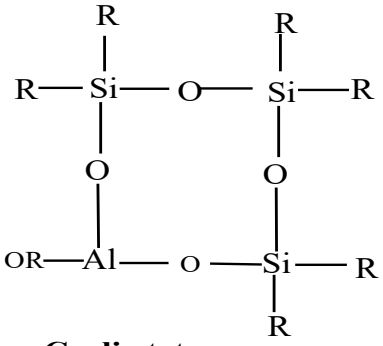




Linear polymer



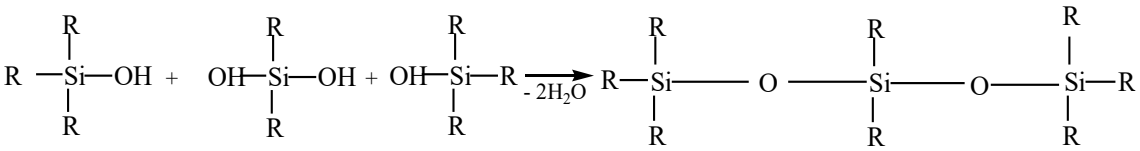
Cyclic trimer



Cyclic tetramer

Uses: Due to the high thermal resistance, this type of silicon polymer can be used in the formation of the external cover of the electrical wires.

(ii) Silicon fluid/oil: When the alkyl di-hydroxyl saline undergoes condensation with the trialkyl monohydroxy silane, then there occur the formation short-chain silicone polymer known as silicon fluid or oil.

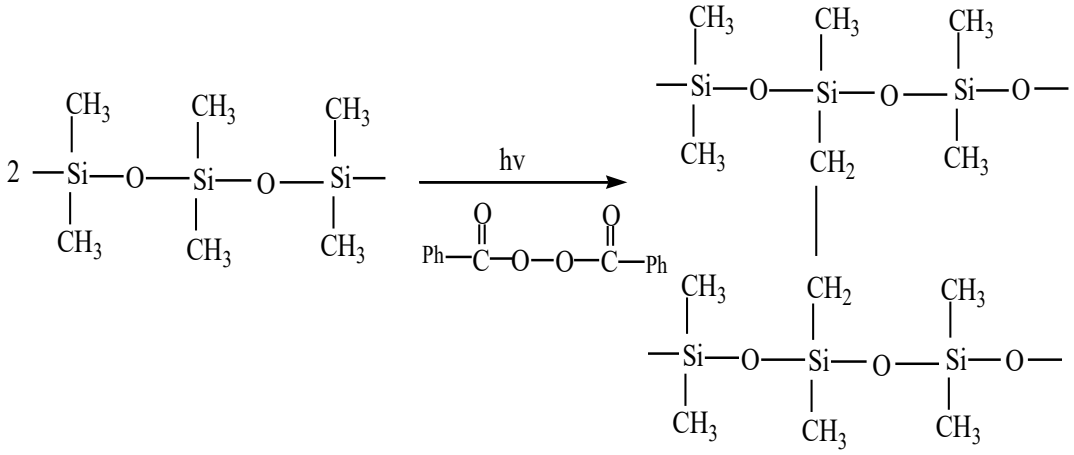


Silicon fluid/oil

Uses: Due to water repellent tendency of silicon fluid, it can be used as a water repellent material in the bather industry or paper industry.

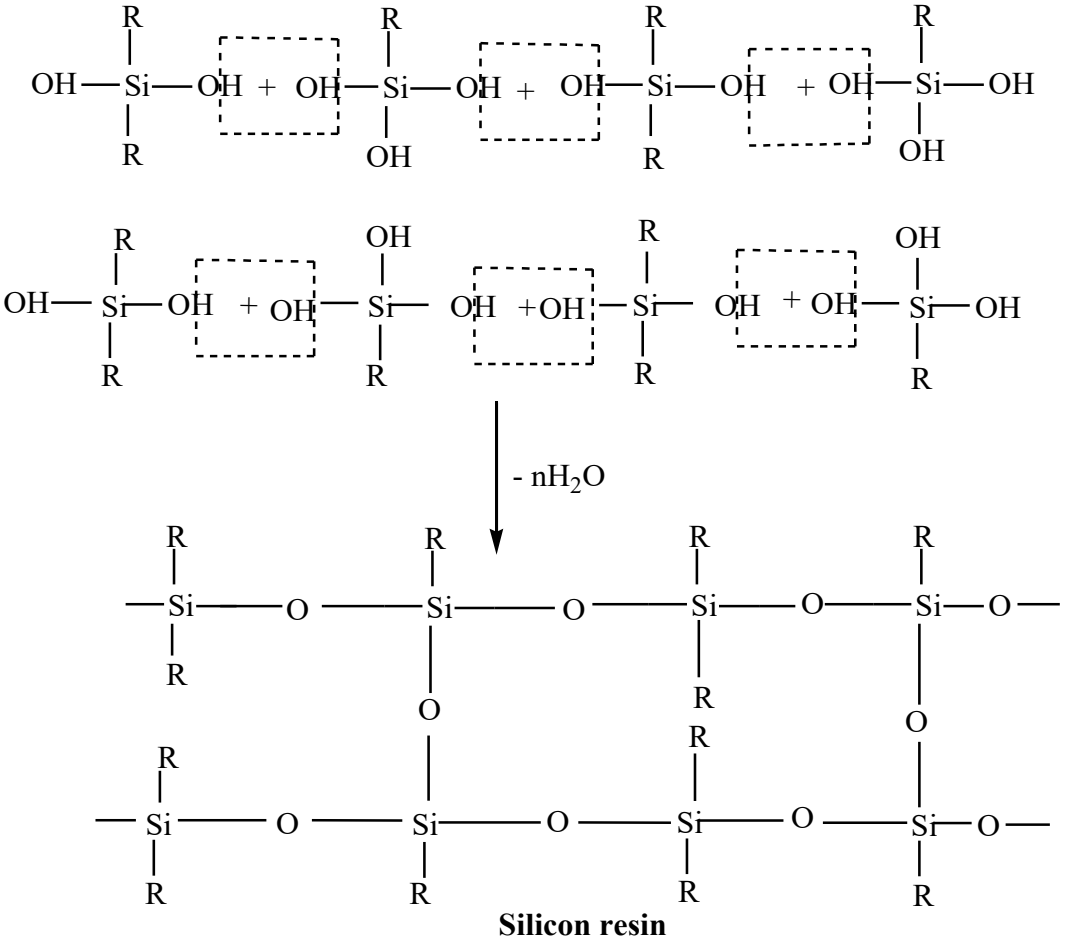
(iii) Silicon rubber: These are long-chain polymers with some cross-linking between the chains. They are made by the hydrolysis of $(CH_3)_2$ Si-O-Si$(CH_3)_3$ may be added to the reaction mixture to control the chain length of the polymer. Silicone rubbers consist of cross-linked type silicones with SiO_2 or ZnO as filler and vulcaniser, such as benzoyl peroxide. Silicone rubbers are especially valuable, since they retain their elasticity over a range of temperatures and are resistant to oils.

Silicone rubbers, which can withstand temperatures up to 400°C for 200 hours and up to 540°C for 90 hours, have also been prepared. Their resistance to 400°C for 200 hours and up to 5400ºC for 90 hours has also been prepared. Their heat resistance is much higher than that of many organic rubbers. It is due to their property to withstand high temperatures that they are used in sealing joints and steam of jet aircraft and insulating electrical parts like transistors, which cannot be heated.



Uses: Silicon rubber can be used in the formation of the parts of air craft.

(iv) Silicon resin: Silicone resin is obtained by blending silicone with organic resin, such as acrylic ester. If the hydrolysis of $(CH_3)_2SiCl_2$ is carried out in the presence of $(CH_3)SiCl_3$ and then polymerisation is allowed, a rigid silicone is obtained. This silicone is called silicone



Silicon resin

resins. These are of many types, like coating resins, laminating resins, release resins, water-repellent resins, moulding resins and electrical resins. These are stable to heat, water-repellent and have good electrical conductivity, chemical inertness and weather resistance. To

develop the best properties in them, baking or heat treatment is applied to them. These can withstand temperatures as high as 250ºC, and a coating made up treatment is given to them. These can withstand temperatures as high as 250°C, and the coating made up of silicone resin plus organic resins and Al can withstand temperatures up to 500°C.

Silicone rubber retains its shape and elasticity permanently, even after vulcanisation and has, therefore, been used in several ways. High molecular weight silicones, containing long chain or ring structure, are generally waxy or rubber-like solids.

3.5.2 Preparation of silicones

Silicones are prepared from pure silicon, which has been obtained by the reduction of silicon dioxide (silica) in the form of sand with carbon at high temperatures.

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

The production of silicones from silicon takes place in three stages:

a) Synthesis of chlorosilanes

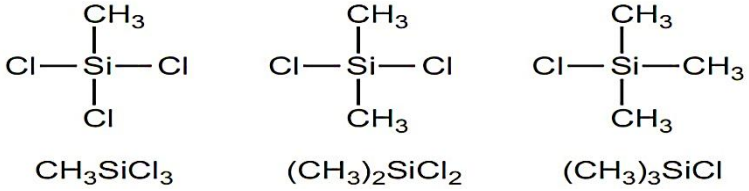
b) Hydrolysis of chlorosilanes

c) Condensation polymerisation

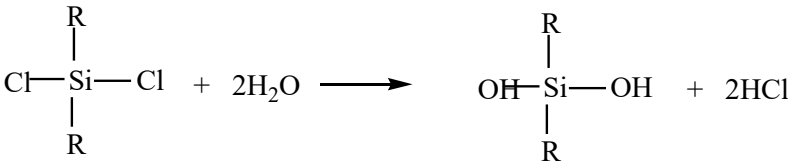
a. Synthesis of chlorosilanes: Silicon is first converted into chlorosilanes, e.g. $RSiCl_3$, R_2SiCl_2 and R_3SiCl, where R is an organic group. When chloromethane is passed through heated silicon at about 550 K under slight pressure and in the presence of a copper catalyst (often copper itself but other copper-containing materials can be used, for example, brass or copper (II) chloride), a volatile mixture of chlorosilanes distils over.

$$Si_{(s)} + 2CH_3Cl_{(g)} \longrightarrow (CH_3)_2SiCl_{2(g)}$$

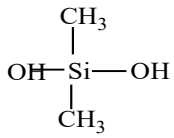
The mixture of liquids contains these three compounds:



b. Hydrolysis of chlorosilanes: A dichlorosilane is hydrolyzed to a molecule with two hydroxyl groups:

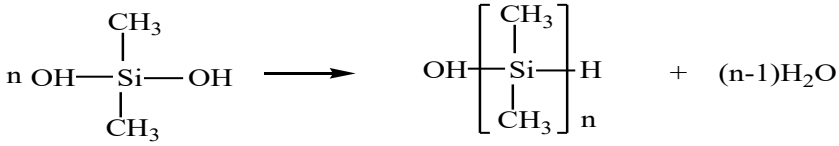


The product is a disilanol. The suffix -ol in a silanol is to show that the molecule contains at least one hydroxyl group attached to a silicon atom and the simplest example is dimethyldisilanol:



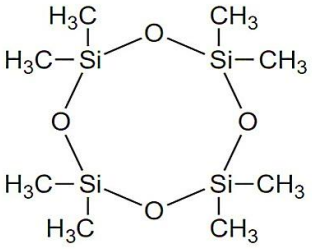
Diethyldisilanol

The hydroxyl groups of silanols react spontaneously to form a siloxane:

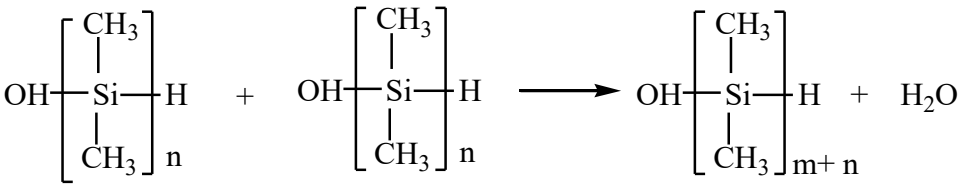


If R is a methyl group, the polymer is a poly(dimethylsiloxane).

Cyclic polymers, for example $\{(CH_3)_2SiO\}_4$, are also produced and then separated out.



c. Condensation polymerization: The oligomers condense rapidly in the presence of an acid catalyst to form long chain polymers:



Silicon fluid

The value of (m+n) is usually between 2000 and 4000.

3.5.3 Properties and uses of silicones

Physical properties: The following physical properties are common to all types of silicones:

(i) They have high thermal stability in the absence of air and withstand temperatures up to 250-300^{0}C.

(ii) They remain unaffected by most of the chemical reagents, such as weak acids, alkalies and salt solutions. Thus, silicones are chemically inert.

(iii) Many of the low molecular weight silicones dissolve in solvents like C_6H_6, ether and CCl_4.

(iv) They do not become too viscous on cooling and are, therefore, used for low-temperature lubrication.

(v) They are water repellent, i.e, they are not wetted by water and are, therefore, used in making waterproof cloth and paper by exposing cloth or paper to the silicone vapours.

(vi) All silicones have good insulating properties and can withstand high temperatures without charring. It is due to these properties that silicones are used as insulating materials for electric motors and other electric appliances.

(vii) They are non-toxic.

(viii) Properties and uses of high-thermal silicones, silicone resins, silicone oils, silicone rubbers and silicone greases have been given on the subsequent pages.

Uses:

a. Silicones have been used for making waterproof papers, wools, textiles, wood etc., after coating these articles with silicones.
b. The viscosities of silicones do not change with temperature changes; therefore, these are used as all-weather lubricants.
c. As an antifoaming agent in industrial processes.
d. As a mould releasing agent in the rubber industry and foundry. It avoids the sticking of the castings to the mould.
e. For making body implants in cosmetic surgery due to its inert nature.
f. Silicones are now incorporated in paints for resisting dampness and for waterproofing.
g. Due to their water repellent nature and high dielectric constant, silicones are used in electrical condensers.

3.6 SUMMARY

- Silicones and phosphazenes are inorganic polymers.
- Inorganic elements can show different valences than carbon, leading to variation in side groups and polymer properties.
- These differences affect polymer flexibility, reactivity, and interactions.
- Silicones are organo-silicon polymers with Si–O–Si linkages (polysiloxanes).
- General formula of silicones: $(R_2SiO)n$.
- Silicone polymers are highly thermally stable (up to 200–300°C) and have low glass transition temperature.
- Silicone fluids (oils) are linear polysiloxanes (50–200 units), low molecular weight, widely used (~60% of silicones).
- Prepared by hydrolysis of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$; chain length may vary.
- Silicone oils are used as water repellents for buildings and fabrics.
- Silicone resins are branched siloxanes with residual –OH groups, prepared from $PhSiCl_3$ and dichlorosilane by hydrolysis in toluene.

3.7 TERMINAL QUESTIONS

3.7.1 Short answer questions

1. What is meant by glass transition temperature?
2. Draw the general repeating unit in silicones.
3. What is the structure of cyclic $(NPF_2)_3$?
4. Which groups of elements in the periodic table have been explored for the formation of inorganic polymers?
5. Draw the general repeating unit in phosphazenes.
6. Draw resonance hybrid structures of cyclic $(NPCl_2)_3$.
7. Give one important use of silicone rubbers.
8. Give one important use of silicone oils.
9. What is meant by ring opening polymerisations?
10. Give the IUPAC names of $Cl_2siH_2HSi(OH)_3$ and $H_3Si\text{-}O\text{-}SiH_3$
11. General questions.How is cyclic $(NPCl_3)_2$ prepared? Give an account of it nucleophilic substitution reactions.

12. Name four main structural units of silicones and designate them.
13. Why do polyphosphazene chains prefer cis-trans conformations to a trans-trans conformation? Give thre important uses of polyphosphazenes.
14. Give equations to indicate the following reactions:
15. Draw polymeric backbones of silicones and phosphazenes.
16. Draw resonance hybrids of $(HPCl_2)_3$.
17. Explain important consequences of cross-linking in macromolecules.
18. Draw polymeric backbone of silicones.
19. What are silicones? How are cross linked silicones prepared?
20. Give islands model of bonding in cyclic $(NPCl_2)_3$.
21. Give a brief account of inorganic polymers with special reference to polyphosphazenes.
22. Silicones and phosphazenes are isoelectronic. What are its consequences?
23. Name three major classes of silicones elastomers.
24. What are silicones? Discus their polymerisation.
25. Draw polymeric backbones of silicones and phosphazenes.
26. Why does the π-system in cyclic $(NPCl_2)_3$ differ from p-system in C_6H_6?
27. What are silicones oils, silicones rubbers and silicones resins?
28. What is IUPAC name of [-Si $(CH_3)_2O$-]?
29. What are silicones? How will you prepare them?
30. What are phosphazenes? How will you prepare them? Discuss the structure of $(PNCl_2)$.
31. Write a short note on Silicones?
32. Discuss general properties of inorganic polymers.
33. What are different types of Silicones?
34. What are inorganic polymers? Classify them?
35. Discuss the preparation, properties and important reactions of phosphonitrilic halide.

3.7.2 Objective-type questions

1. Hydrolysis of borazine gives:

   (a) B_2O_3 (b) $B(OH)_3$

   (b) B_2H_6 (d) H_3N- BH_3

2. Which of the following bonds is present in silicones?

   (a) Si-Si-Si-Si (b) Si-C-Si-O-Si

(b) Si-C-Si-C-Si (d) –Si-O-Si-O-Si-

3. Hydrolysis of trialkyl chlorosilane gives:
   (a) R_3 Si-O-SiR_3 dimer
   (b) Cyclic (ring) silicone
   (c) Cross-linked silicone
   (d) None of these.
4. The strength and inertness of silicones are related to:
   (a) Stability of silica-like skeleton of -Si-O-Si-O-Si-
   (b) Very high bond energy of Si-O bond
   (c) High strength of Si-C bond
   (d) All of the above.
5. Hydrolysis of dialkyl dichlorosilane gives:
   (a) Linear silicone
   (b) SiO_2
   (c) Cross-linked silicone
   (d) None of these
6. The number of P-O-P bonds in cyclic metaphoshoric acid is:
   (a) Zero (b) 2
   (c) 3 (d) 4
7. Which of the following is a cyclic oxo acid?
   (a) $H_5P_3O_{10}$ (b) $H_6P_4O_{13}$
   (c) $H_5P_5O_{15}$ (d) $H_7P_5O_{16}$
8. Sodium hexametaphosphate is used:
   (a) As fertilizser
   (b) For softening water
   (c) In fruit ripening
   (d) None of the above.
9. Which of the following is obtained when P_4O_{10} is is heated with Na_2O at 1000°C.
   (a) Sodium tripolyphoshate ($Na_5P_3O_{10}$)
   (b) Sodium tripolyphosphate hexahydrate (NaH_2PO_4)
   (c) Sodium dihydrogen phosphate (NaH_2PO_4)
   (d) Sodium hydrogen phosphate (Na_2HPO_4)
10. Sodium hexametaphosphate is known as:
    (a Calgo (b) Permutit

(c) Nataliet (d) Nitrolim

11. Using Chlorobenzene (C_6H_5Cl) as solvent, the reagents needed for the synthesis fo borazine are:

(a) NH_4Cl, BCl_3

(b) NH_4Cl, BCl_3, $NaBH_4$

(c) NH_4Cl, $NaBH_4$

(d) NH_3, BCl_3

ANSWERS:

1.(b) 2.(d) 3.(a) 4.(d) 5.(a) 6.(c) 7.(c) 8.(b) 9.(a) 10.(a) 11.(b)

3.8 REFERENCES

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UNIT 4 : HARD AND SOFT ACID AND BASE (HSAB)

CONTENTS:

4.1 INTRODUCTION

Lewis acid and base theory (also known as e^- donor-acceptor theory) is a broad, widely applicable approach to the classification of chemical substances and the analysis of chemical reactions. According to this theory, a base is an electron pair donor, and an acid is an electron pair acceptor. Donation of an electron pair from base to acid results in the combination of the acid and base with a covalent bond. The bonded acid-base species is called an addict, a coordination compound, or a complex compound.

Since the strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Thus, from the above criteria, an acid-base reaction should be a rapid reaction. The HSAB concept is a shortening for "hard and soft (Lewis) acids and bases". Also known as the Pearson acid-base concept, HSAB is widely used in chemistry for explaining the stability of compounds, reaction mechanisms and pathways. Soft Lewis bases are those in which the donor atoms are easily polarised and have low electronegativity. While Hard Lewis bases are those in which the donor atoms have low polarisabilities and high electronegativities. A hard Lewis acid, like a hard base, is difficult to polarise, small in size, high positive charge, having small size and a noble gas electronic configuration. While soft acids, like soft bases, are readily polarised, they have a large size, a low positive or zero charge and do not have a noble gas configuration.

Hard Soft Acid Base Concept (HSAB Concept):

Experimentally, it was observed that certain ligands tend to form stable complexes with the lighter metal ions like Na^+, Li^+, Mg^{+2}, Sc^{+3}, $Ti^{+4,}$ etc., and certain other ligands have the tendency to form stable complexes with the heavier metal ions like Ag^+, Cu^{+2}, Hg^{+2}, Cu^{+2} etc.

Based on this preferential bonding nature of ligand (Lewis's base and Lewis's acid), Pearson had categorised both the acids and bases into three different categories each, which are given in the next section.

4.2 OBJECTIVES

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

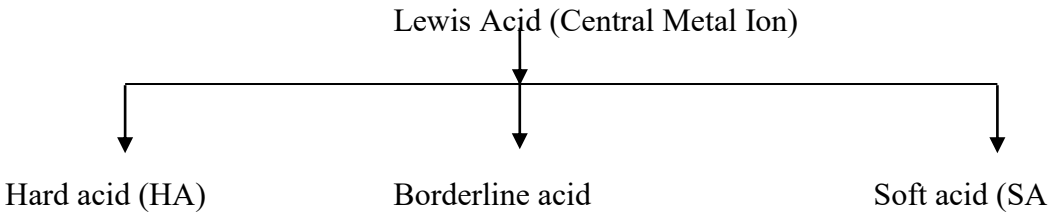
- To know the relationship between acid strength and the value of p*K*a.

- To understand the relationship between polarizability and the hardness or softness of an acid or base.
- To predict the stability of a chemical bond using the hard-soft acid base theory.
- To predict the relative acid or base strength of two organic compounds.
- To understand how the presence of a particular functional group affects the acid or base strength of another functional group.

4.3 CLASSIFICATION OF ACIDS AND BASES AS HARD AND SOFT

4.3.1 Classification of the Lewis's acid:

According to the Pearson, Lewis's acids can be of the three different types, which are given below:-



1. Hard acid: - All the Lewis acids having the following characteristic properties are known as hard acid:

(i) Should exhibit the smaller size.

(ii) Should have high + ve oxidation state.

(iii) Polaris ability should be very low (on the basis of this property they are known as hard).

(iv) Should have vacant d- orbital or approximate vacant d- orbital configuration (in the case of d – block elements)

2.Soft acid: All the Lewis acids having the following characteristic properties are known as soft acids:

(i) Should exhibit larger size.

(ii) Should have very low +ve oxidation state or zero oxidation state.

(iii) Polaris ability should be very high (on the basis by this property they are known as soft).

(iv) Should have filled d-orbital or approximate filed d-orbital configuration (in the case of d-black dements)

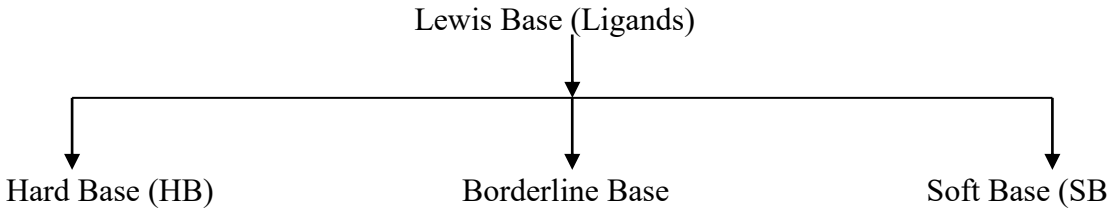
Borderline acids: - All the Lewis acids which exhibit the properties intermediate in between the hard & soft acids are known as borderline acids. Some of the samples of hard acid, soft acid & borderline acids are given in Table 1.1.

Hard acids	Soft acids	Borderline acids
Li^{+}	Cu^{+}	Fe^{+2}
Na^{+}	Ag^{+}	Co^{+2}
K^{+}	Au^{+}	Ni^{+2}
Mg^{+2}	Hg^{+}	Cu^{+2}
Ca^{+2}	Pt^{+2}	Zn^{+2}
Al^{+3}	Hg^{+2}	Pb^{+2}
Ba^{+2}	Pd^{+2}	Sn^{+2}
Ga^{+3}	Ed^{+2}	SO_2
La^{+3}	BH_3	Bi^{+3}
Cr^{+3}	I^{+}	Sb^{+3}
Cr^{+6}	Br^{+}	NO^{+}
Co^{+3}	Metal atoms at 0 O.S	GaH_3
Fe^{+3}		$B(CH_3)_3$
Si^{+4}		
Ti^{+4}		
Ce^{+3}		
Sn^{+4}		
SO_3		
BF_3, BCl_3, $B(OR)_3$, $Al(CH_3)_3$		
I^{+7}		
I^{+5}		
CO_2		

Table 1.1: *Examples of hard acid, soft acid & borderline acids*

4.3.2 Classification of the Lewis base

According to the Pearson concept, Lewis basis can be divided into 3 different types which are given below:-



1. **Hard base:** All the Lewis bases having the following characteristic properties are known as hard base:
   (i) Donor atom of the base should be highly electronegative like F, O, N & O.
   (ii) Polaris ability of the donor atom should be very high low.

2. Soft base: All the Lewis bases which have the following characteristic properties are known as soft bases:

(i) Donor atom of the base should be less electronegative.
(ii) Polaris ability of the donor atom should be very high.

3.Borderline base: All the Lewis bases which have the properties intermediate the soft & hard bases are known as borderline bases. Some of the examples of hard bases, soft bases and borderline bases can be given as:-

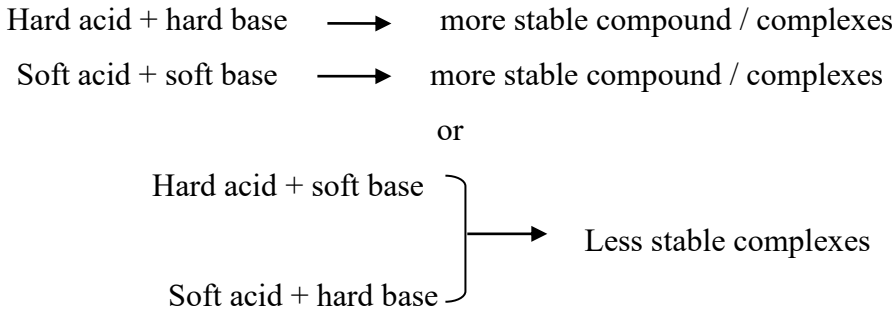
Hard base: H_2O, OH^-, CH_3COO^-, PO_4^{-3}, SO_4^{-2}, CO_3^{-2}, ClO_4^- NO_3^-, ROH, R-O^-, R_2O (Doner O), NH_3, R-NH_2, N_2H_4 (doner N), F^-, Cl^-

Soft base: R_2S, R-SH, R-S^-, I^-, SON^- , S_2O_3, R_3P, $(RO)_3P$, CN^-, RNC, CO, C_2H_4, C_6H_6 , H^-, R^-, S^{-2}

Borderline base: C_6H_5-NH_2, C_5H_5N, Br^-, SO_3^{-2}, NO_2^-

4.4 PEARSON'S HSAB CONCEPT: ACID BASE STRENGTH AND HARDNESS AND SOFTNESS

According to the Pearson HSAB concept, hard acid- hard base combination & soft acid-soft base combination give rise to the more stable compound or complexes in comparison to the hard acid–soft base & soft acid-hard base combination compound.



Explanation: Due to the very low polarise ability of hard acid and hard base their combination are ionic in nature while due to the very high polarize ability of soft acid and soft base their combinations are covalent in nature. Both these combinations of ionic and covalent nature have more stable combination due to which HSAB principle states the hard–hard and soft-soft combinations as a stable combination.

4.4.1 Applications of HSAB principle

4.4.1.1 Occurrence of metal ions on the earth

Lighter metal ions like Li^{+}, Na^{+}, Mg^{+2} , Ca^{+2} etc. exist in the form of there chlorides, carbonates, sulphates, phosphates (O^{-2}, CO_3^{-2} , SO_4^{-2}, PO_4^{-3}) on the earth crust but cannot exist in the form of their sulphides (S^{-2}) while on the other hand heavier metal ions like Ag^{+}, Hg^{+}, Cu^{+} etc. exist in the form of their sulphides on the earth crust and cannot exist in the form of CO_3^{-2}, O^{-2} , SO_4^{-2} etc.

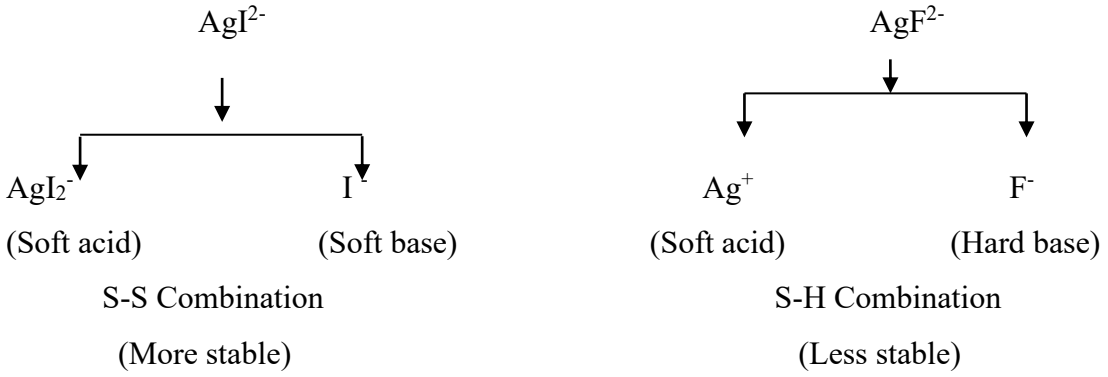
Explanation :- Lighter metal ions like Li^{+}, Na^{+}, K^{+}, Mg^{+2} , Al^{+3}, etc. form the stable hard – hard combination with the O^{-2} , CO_3^{-2}, SO_4^{-2}, PO_4^{-3} on the earth crust due to which they exist in the form of there oxides, carbonate, sulphates and phosphates while these lighter metal ion forms the less stable unstable hard soft combination with the sulphide ion due to which they connot exist in the form of there sulphides on the earth crust. Heavier metal ions like Ag^{+}, Hg^{+}, Cu^{+} etc. form the stable soft –soft combination with the S^{-2} ion due to which they can exist in the form of their sulphides on the earth crust while on the other hand, the heavier metal ions like Ag^{+}, Hg^{+}, Cu^{+} etc. form the unstable or less stable soft-hard combination with the O^{-2}, CO_3^{-2}, SO_4^{-2}, PO_4^{-3} etc. due to which they cannot exist in the form of there oxides, carbonates, sulphates and phosphates on the earth crust.

4.4.1.2 Stability of the compound/complexes

With the help of HSAB principle, we can compare the stability of various compounds or complexes.

(i) AgI_2^- is more stable than the AgF_2^-

Explanation: AgI_2^- containing soft- soft combination due to which accoding to the HSAB principle, AgI_2^- well be more stable while AgF_2^- containing soft –hard combination, will be less stable or sometime cannot exist.



(ii) $[Co(F)_6]^{-3}$ is being more stable then $[Co(I)_6]^{-3}$ ion.

Explanation: $[Co(F)_6]^{-3}$ ion containing hard-hard (H-H) combination is more stable while on the other hand, $[Co(I)_6]^{-3}$ ion having hard-soft (H-S) combination, will be less stable.

4.4.1.3 Stability of the complexes containing different ligand

According to the Pearson principle, a complex containing more than one type of the ligands (hard or soft), then the complex will be more stable.

$[Co(N)_5(F)]^{-3}$ ion is less stable than $[Co(CN)_5(I)]^{-3}$ ion

Explanation: $[Co(N)_5(F)]^{-3}$ ion containing soft CN^- & Hard F^- ligands will be less stable while on the other hand $[Co(N)_5(I)]^{-3}$ ion containing both the soft ligands (CN^- and I^-) will be more stable.

4.4.1.4 Occurrence of the chemical reaction

With the help of HSAB principle we can give the idea about the occurrence of the chemical reaction. According to HSAB principle, if the reactants present in the chemical reaction have less stable H-S & S-H combinations, then they will have the tendency to react with each other to generate the more stable H-H & S-S combinations i.e. in such condition chemical reaction will be possible. If the reactants have more stable H-H & S-S combinations, then they will not have the tendency to convert into the less stable H-S & S-H combinations by the reaction i.e. in such condition reaction will not be possible.

$$\underset{(H\text{-}S)}{Li} + \underset{(S\text{-}H)}{CsF} \longrightarrow \underset{(H\text{-}H)}{LiF} + \underset{(S\text{-}S)}{CsI}$$

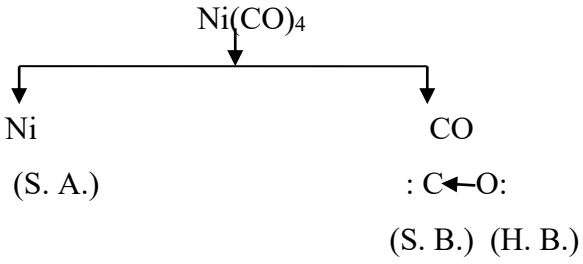
In the above reaction, both the reactants have less stable H-S & S-H combinations and the products have the more stable H-H & S-S combination so acc to HSAB principle the above Reaction will be possible.

$$\underset{(H\text{-}H)\ (S\text{-}S)}{BeF_2 + HgI_2} \longrightarrow \underset{(H\text{-}S)\ (S\text{-}H)}{BeI_2 + HgF_2}$$

In the above reaction, both the reactants have more stable (H-H, S-S) combinations and products haveless stable H-S and S-H combinations. Hence, according to HSAB principle, this reaction will not be possible.

4.4.1.5 Nature of the doner site in the ambident ligand

With the help of HSAB principle, we can also give an idea about the actual doner site of an ambident ligand.



When the C atom of the CO behave as a doner site, then there occur the formation of more stable S-S combination with the central metal atom (Ni) while when the O atom of CO behaves as a doner site, then there occurs the formation a less stable S-H combination with the central metal atom (Ni). Therefore, the actual doner site of CO will be carbon.

4.4.1.6 Solubility of the compounds

According to the HSAB concept, those compounds which have more stable H-H & S-S combinations, exhibit less solubility in the aqueous medium in compare to the compounds which have less stable H-S & S-H combinations.

Explanation: $Hg(OH)_2$ exhibits more solubility in the aqueous medium due to less stable H-S combination, while HgS exhibits less solubility in aqueous medium due to the more stable S-S- combination.

4.4.2 Limitation of HSAB principle

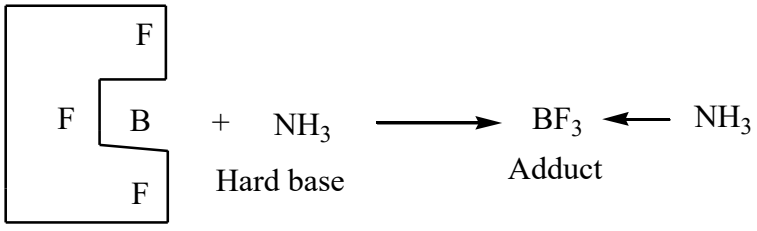
According to HSAB concept, chemical reactions have a tendency to occur in such direction which can generate the more stable H-H & S-S combination. But sometimes the chemical reactions can also occur in such direction which can generate the less stable S-H & H-S combination and this cannot be explained by HSAB concept of Pearson.

4.5 SYMBIOSIS

In sense of biology, symbiosis may be defined as the dependency on each other i.e. when the two spices come in the contact of each other than both are equally benefitted but in the sense of HSAB concept, symbiosis phenomena is different from the biological symbiosis.

According to HSAB concept, attraction of the soft base toward the centre which is attached with the soft bases or attraction of the hard base toward the centre which is attached with the hard bases is known as symbiosis.

Explanation: NH_3 exhibit the symbiosis phenomena with the BF_3 because the hard base NH_3 having the tendency to attach with B centre which is already attached with hard bases F^- ion.



4.6 THEORETICAL BASIS OF HARDNESS AND SOFTNESS

There are some theories that can explain the interactions in between the hard acids and hard bases and vice versa. No single theoy can explain this kind of interaction.

4.6.1 Electronegativity concept for the HSAB theory

According to the electronegativity theory, the interaction between HA and HB is ionic or electrostatic in nature. As hard acid and hard bases are small in size (HB is highly electronegative and HA is highly electropositive), the internuclear distance between them will be smaller. As a result, interaction between HA and HB will be highly stable.

4.6.2 Covalent concept for the HSAB theory (σ-bonding)

Soft acids have high polarising power and soft bases like I^- has high polarisability. Therefore, the interaction between SA and SB is covalent in nature.

4.6.3 Covalent concept for the HSAB theory (л-bonding)

Soft acids have fully filled d orbitals (low oxidation state) and soft bases are pi bonding ligands. Thus, SA has a good tendency to form π bonds with SB.

4.7 ELECTRONEGATIVITY AND HARDNESS AND SOFTNESS

Hardness and softness of acid and bases are related to electronegativity.Elements with high electronegativity are hard and elements with low electronegativity are soft.The relation between softness and hardness with electronegativity caqn be explain the fact that CF_3 is harder than CH_3 and BF_3 harder than BH_3.

For example: Lithium, sodium (Li^+ , Na^+),has low electronagativity, Li^+ Na^+ has relatively high tendency to attract electrons toward itself, and therefore, it has high electronegativity.This is because of extremely high second ionisation potential, and Li^+ become hard acid. Similarly in transition metal ions in low oxidation state such as

Cu+, Hg^{+}, Ag^{+}, Cd^{+2} etc have relatively high second ionisation energies and therefore have low value of electronegativity. Therefore, they are considered as soft acids. The same way we can consider hard and soft bases.

4.8 SUMMARY

The HSAB (Hard Soft Acid Base) theory categorizes chemical species as acids or bases and as "hard", "soft", or "borderline". It explains that soft acids or bases tend to be large and very polarizable, while hard acids or bases are small and non-polarizable. Since these categories are not absolute, there are species that are considered borderline, which lie in between hard and soft.

Hard acid – high positive charge, small size, not easily polarized

Soft acid – low positive charge, large size, easily oxidized, high polarizability

Hard base – low polarizability, high electronegativity, not easily oxidized

Soft base – high polarizability, diffuse donor orbital, low electronegativity, easily oxidized

HSAB provides a semi-quantitative method for understanding trends in acid-base reactivity: hard acids like hard bases and soft acids like soft bases.

4.9TERMINAL QUESTIONS

A. LONG AND SHORT QUESTIONS

1. Define soft base and give one example.
2. What is symbiosis?
3. How does HSAB principle govern the occurrence of minerals?
4. Define absolute hardness.
5. Give two examples of border line acids.
6. Which of the following is odd among the following:
   Li^{+}, Ga^{3+}, Cd^{2+}, K^{+}
7. Why is pyridine a border line base while ammonia is a hard base?
8. What are the limitations of HSAB principle?
9. What are hard and soft acids and bases? Explain the HSAB principle with suitable examples.
10. Discuss the effect of substituent on hardness and softness of an acid.

11. How does HSAB principle explain the validity of the following reactions?
12. Discuss the contribution of π-bonding in soft-soft interactions.
13. Discuss giving examples, the applications of HSAB principle.
14. What are the theoretical justifications of HSAB principle?
15. Describe the origin of concept of hard and soft acids and bases.
16. Predict which way the following reactions will proceed:
17. Explain the following.
    a. What are the characteristics of a soft acid and a soft base?
    b. Exaplin HSAB principle. Discuss its applications.
    c. Explain clearly why hard acids co-ordinate with hard bases and soft acids co-ordinate with soft bases.
    d. Hard-hard interaction is the major driving force for a reaction to proceed. Discuss
18. Explain the various limitations of HSAB principle.
19. What are hard acids and hard bases? Give their important characteristics.
20. What is HSAB principle? What are its uses?
21. How will you determine the relative strength of hard and soft acids and bases?
22. Why are hard-hard and soft-soft combinations preferred to hard-soft or soft-hard combination?
23. How does HSAB principle govern the occurrence of minerals?
24. What are hard acids and bases? Give their important characteristics.
25. How electronegativity can be used to explain hardness and softness of acids and bases?
26. Define HSAB principle. Discuss the applications of hard soft acid base principle.
27. State and explain HSAB principle.
28. Describe the contribution of π-bonding in soft-soft interactions.
29. What is symbiosis? Discuss theoretical basis of hardness and softness.

B. MULTIPLE CHOICE QUESTIONS :

1. Which of the following is not a hard base?

a)NH3 b)H_2O c) Cl^- d)CN^-

2.Which of the following is not a hard acid?

a) Na^+ b) Pd^{2+} c) Mg^{2+} d)Ti^{4+}

3.Hg^{2+} is classified as :

a) Soft acid b)Hard acid c) soft base d)Hard base

4.The term hard and soft acid and base was given by:

a) Bronsted b) Lewis c) Pearson d) franklin

5.Which of the following is not a border line acid:

a)Bi^{3+} b) BMe_3 c) CO_2 d) SO_2

6.In which the following pairs, both the species are not of the same type (hard- hard or soft – soft acid or base)?

a) NH_3 , CO b) H_2O, OH^- c) ROH, R_2O d) SO_3 , CO_2

7.Which of the following statement is false?

a) Soft acids are molecules or ions with larger number of valence electrons.

b)K^+ is a hard acid

c)Soft bases are easily oxidized

d)Hard bases have donor atoms with high polarizability.

8. According to SHAB concept, the Lewis bases were classified on the basis of which of the following?

a) Charge ion size b) Polarization consideration

c)Electron and coordinating ability d) All of a, b, and c

9. Which of the mentioned is not hard base according SHAB concept?

a) NH_3 b) N_2H_4 c) RNH_2 d)F

10.Incorrect statement for soft acids is:

a) Should exhibit larger size.

b) Should have very low +ve oxidation state or zero oxidation state.

c) Polaris ability should be very low.

d) Should have filled d-orbital

ANSWERS: B.

1. (d)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (c)
6. (a)	**7.** (d)	**8.** (d)	**9.** (d)	**10.** (c)

4.10REFERENCES/FURTHER READINGS

1. G. L. Miessler and D. A. Tarr. (2010). *Inorganic Chemistry*, 3rd ed. Pearson Education Int.

2. Wahid U Malik, G D Tuli, R D Madan. *Selected Topics in Inorganic Chemistry*, S. Chand Publishing.

UNIT 5: HETEROCYCLIC COMPOUNDS- I

CONTENTS

5.1 INTRODUCTION

Heterocyclic compound is a class of cyclic organic compounds that have at least one hetero atom (*i.e.* atom other than carbon) in the cyclic ring system. The most common heteroatoms are nitrogen (N), oxygen (O) and sulphur (S). Heterocyclic compounds are frequently abundant in plants and animal products, and they are one of the important constituents of almost half of the natural organic compounds known. Alkaloids, natural dyes, drugs, proteins, enzymes etc., are some important classes of natural heterocyclic compounds. Heterocyclic compounds can be easily classified based on their electronic structure. Heterocyclic compounds are primarily classified as saturated and unsaturated. The saturated heterocyclic compounds behave like the acyclic derivatives with modified steric properties. Piperidine and tetrahydrofuran are the conventional amines and ethers of this category. However, unsaturated heterocyclic compounds of 5- and 6- 6-member rings have been studied extensively because of their unstrained nature. The unstrained unsaturated heterocyclic compounds include Pyridine, Thiophene, Pyrrole, Furan and their benzo-fused derivatives. Quinoline, Isoquinoline, Indole, Benzothiophene, and Benzofuran are some important examples of benzo-fused heterocycles. Heterocyclic compounds have a wide application in pharmaceuticals, agrochemicals and veterinary products. Many heterocyclic compounds are very useful and essential for human life. Various compounds such as hormones, alkaloids, antibiotics, essential amino acids, haemoglobin, vitamins, dyestuffs and pigments have a heterocyclic structure.

In the present unit, students would be able to learn about the common five and six-membered heterocyclic compounds, such as Pyrrole, Furan, Thiophene, Pyridine and Piperidine etc.

5.2 OBJECTIVES

In this unit learner will be able to:

- Know about the most important simple heterocyclic ring systems containing heteroatom and their systems of nomenclature and numbering.
- Understand and discuss the reactivity and stability of hetero aromatic compounds.
- Study the important synthetic routes and reactivity for five- and six-member hetero aromatic compounds.
- Understand the important physical and chemical properties of five- and six-member

hetero aromatic compounds.

5.3 CLASSIFICATION OF HETEROCYCLIC COMPOUNDS

Based on the structural and electronic arrangement, the heterocyclic compounds may be classified
into two categories.

i. Aliphatic heterocyclic compounds

ii. Aromatic heterocyclic compounds

The aliphatic heterocyclic compounds are the cyclic amines, cyclic amides, cyclic ethers and cyclic thioethers. Aliphatic heterocycles that do not contain double bonds are called saturated heterocycles. The properties of aliphatic heterocycles are mainly affected by the ring strain. Examples of aliphatic heterocyclic compounds are shown in Figure 1.

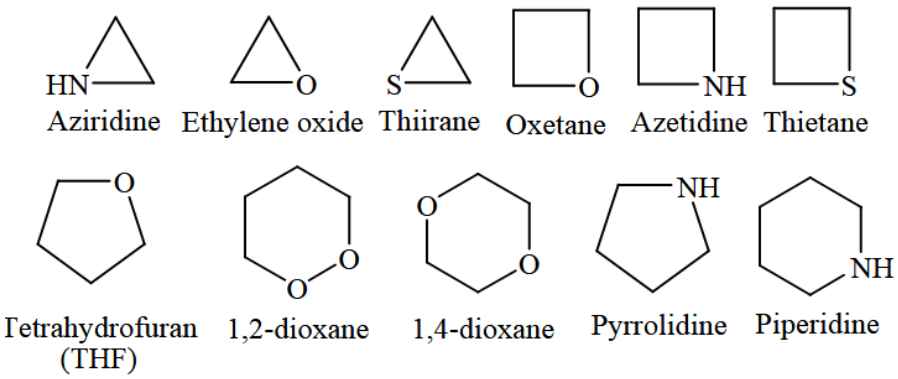


Figure 1. Examples of aliphatic heterocyclic compounds

However, aromatic heterocyclic compounds are analogous of benzene. The aromatic heterocyclic compounds also follow Huckel's rule. According to Huckel's rule an aromatic compound must be cyclic in nature with planar geometry due to conjugate double bonds and must have $(4n+2)\pi$ electrons. Examples of aromatic heterocyclic compounds are shown in figure 2.

A hetero cyclic ring may comprise of three or more than three atoms, which may be saturated or unsaturated. Also heterocyclic ring may contain more than one heteroatom, which may be either similar or different.

Based on the variety of structures, the heterocyclic compounds may also be divided into three categories.

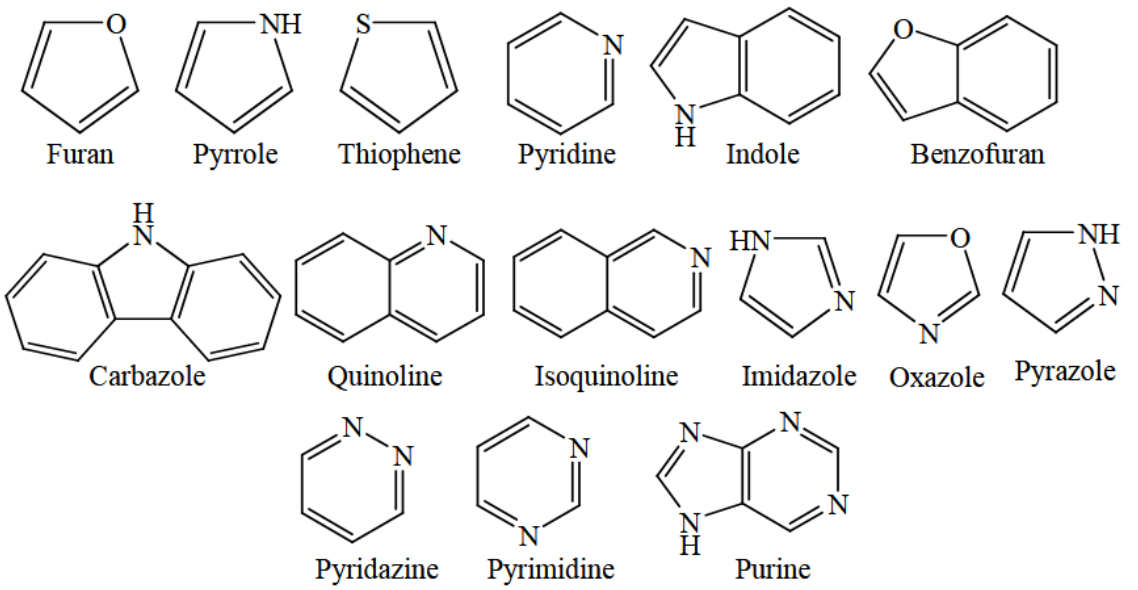


Figure 2. Examples of aromatic heterocyclic compounds

1. Five-membered heterocyclic compounds: These heterocyclic compounds may be considered to be derived from benzene by replacing one C=C bond with a hetero atom with a lone pair of electrons. Based on the number of hetero atom present in the cyclic ring, this class of heterocyclic compounds may be further subdivided into to following categories.

(A). Heterocyclic compounds with one hetero atom: Common examples of this class of compounds are furan, thiophene and pyrrole (Figure 3).

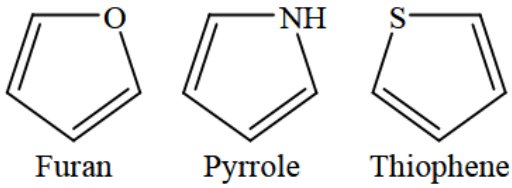


Figure 3. Five member heterocyclic compounds with one hetero atom

B. Heterocyclic compounds with more than one hetero atom: These hetero atoms may be the same or different. Common examples of this category of heterocyclic compounds are pyrazole, imidazole, thiazole, oxazole, triazole and tetrazole etc (Figure 4).

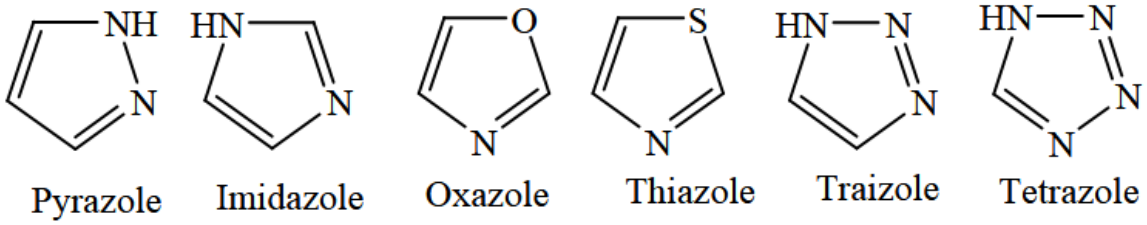


Figure 4. Five member heterocyclic compounds with two hetero atom

Six-membered heterocyclic compounds: This class of compounds may be considered to be derived from the replacement of a carbon atom of benzene by an iso-electronic atom. Similar to the five-membered heterocyclic compounds, the six-membered heterocyclic compounds may also be subdivided in to following categories.

a). Heterocyclic compounds with one hetero atom: Common examples of this class of compounds are pyridine, pyran, thiopyran, etc (Figure 5).

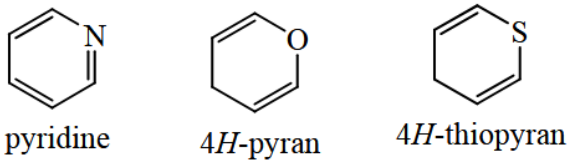


Figure 5. Six member heterocyclic compounds with one hetero atom

b). Heterocyclic compounds with more than one hetero atom: Common examples of this class of compounds are pyridazine, pyrimidine, pyrazine etc (Figure 6).

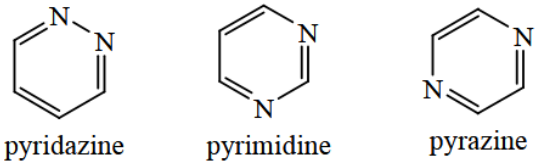


Figure 6. Six member heterocyclic compounds with more than one hetero atom

3. Fused or condensed heterocyclic compounds: This class of compounds may consist of two or more fused rings, which may be partly carbocyclic and partly heterocyclic. Common examples of this category of heterocyclic compounds are Indole, quinoline, Isoquinoline, Cabazole etc; or may be completely heterocyclic. Common examples of this category of heterocyclic compounds are purine, pteridine etc (Figure 7).

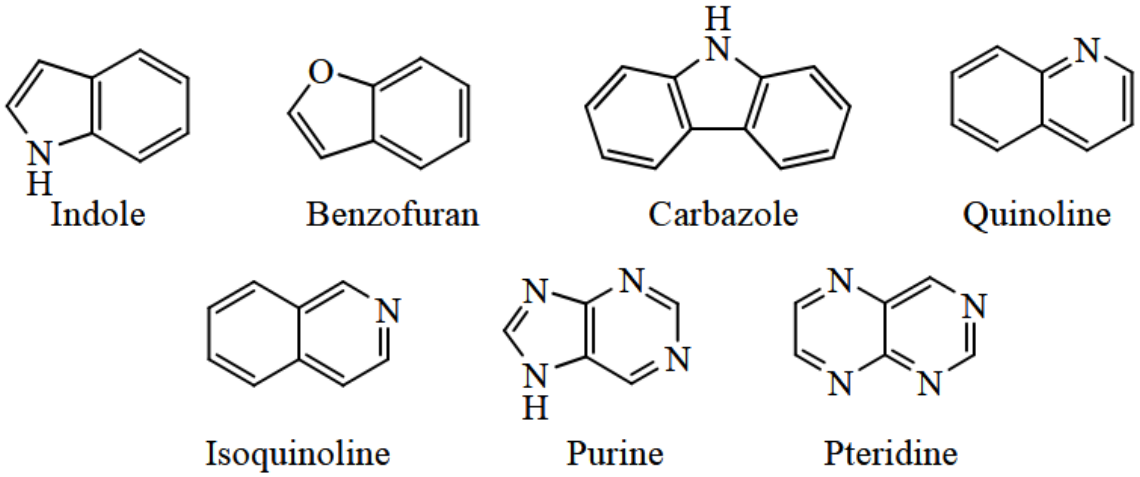


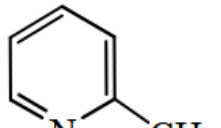
Figure 7. Fused or condensed heterocyclic compounds

5.4 NOMENCLATURE OF HETEROCYCLIC COMPOUNDS

The nomenclature of heterocyclic compounds is divided in to two categories, a) Trivial method of nomenclature and, b) Systematic method of nomenclature. However, most of the heterocyclic
compounds are known by their common trivial names.

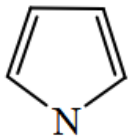
5.4.1 Trivial Method Of Nomenclatutre:

During the early days of organic chemistry, names of the heterocyclic organic compounds were given based on their occurrence, their first preparation and some characteristic properties. Heterocyclic compounds were named on the basis of their source from which the compound was obtained. Thus the name depended on the source of the compound. For example, picoline; picoline is derived from coaltar. This is based on Lattin word pictus means tarry.



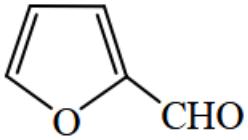
Picoline

Heterocyclic compounds were also named on the basis of their characteristic properties. For example, pyrrole; which is basic in nature; the name of pyrrole was originated from the Greek word for fiery red because of characteristic colour which the compound gives with pine splint dipped in hydrochloric acid.



Pyrrole

Similarly, the name Furfural is given based on it's source. Furfural means barn oil. Furfural was isolated from the distillation of barn.



Furfural

The trivial nomenclature was the first nomenclature method which has a significant role in the development of heterocyclic chemistry. However, this system has some disadvantages too. The trivial system does not give any structural information about the compound. At present just over 60 trivial names survive and recognized by IUPAC system of nomenclature. These recognized names are, however, significant because they are used as basis for constructing other compounds, more systematic names for polycyclic compounds and/or their derivatives. Examples of heterocyclic compounds with recognized trivial names are shown in figure 8.

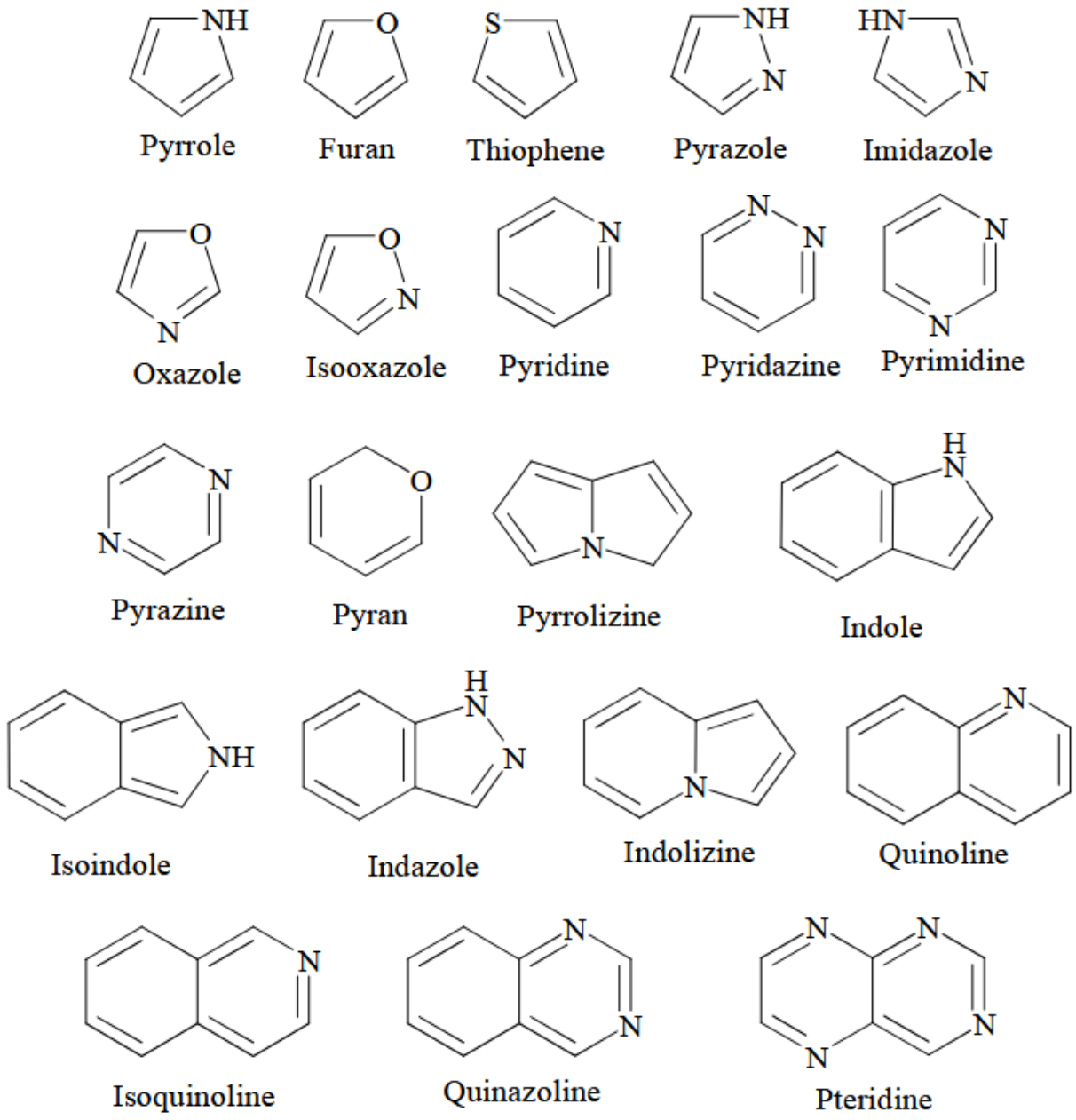


Figure 8. Some heterocyclic compounds with recognized trivial names

5.4.2 Systematic Method of Nomenclature:

This is most widely used nomenclature system for monocyclic heterocyclic compounds especially for three to ten membered ring systems. These members have various degree of unsaturation containing one or more heteroatoms. The systematic nomenclature gives important structural information. The most relevant system that is recommended by IUPAC for nomenclature of heterocyclic compounds is the Hantzch-Widmann system of nomenclature. This nomenclature system specifies the nature, position, ring size, number, and types of heteroatoms present in any heterocyclic compounds. This systematic method generally derived the nomenclature using the following syntax:

Name: Prefix + Stem + Suffix

Following are the important points to be remembered during the systematic nomenclature of heterocyclic compounds.

1. In this nomenclature the nomenclature of heterocyclic compounds are assigned by combining 'prefix' (that indicate the heteroatom present) with 'stem' (that indicate the ring size as well as the saturation and unsaturation in the ring) and 'suffixes. The common prefixes are shown in Table 1. It should be noted that final 'a' is dropped when prefix is followed by vowel.

2. Nomenclature of heterocyclic compound starts with the heteroatom appears first in the table 1.

Table 1: Common Prefix for Heteroatoms (arranged in the preferential order

S. No.	Heteroatom	Symbol	Prefix
1	Oxygen	O	Oxa
2	Sulphur	S	Thia
3	Selenium	Se	Selena
4	Nitrogen	N	Aza
5	Phosphorous	P	Phospha
6	Arsenic	As	Arsa
7	Antimony	Sb	Stiba
8	Bismuth	Bi	Bisma
9	Silicon	Si	Silia
10	Tin	Sn	Stanna
11	Lead	Pb	Plumba
12	Boron	B	Bora
13	Mercury	Hg	Mercura

3. If more than two different heteroatoms are present in any heterocyclic compound the prefixes

are listed in order in which they are appear in above table (Table 1).

4. If there are two or more than two hetero atoms of same types are present in a heterocyclic compound they are indicated by di-, tri- etc.

5. The position of saturated atom is numerically indicated with prefix 'H-' as a part of the name of the ring system. It should be noted that where, there is a choice of numbering, the indicated position is given the lowest possible number.

6. The size of a monocyclic ring (three to ten membered rings) is indicated by stem. The common 'stem' nomenclature is given in Table 2.

Table 2: Common Prefix for Heteroatoms (arranged in the preferential order)

S.No	Ring Size	Unsaturated Ring	Saturated Ring
1	3	iren	Irane
2	4	ete	Etane
3	5	ole	Olane
4	6	ine	Inane
5	7	epine	Epane
6	8	ocine	Ocane
7	9	onine	Onane
8	10	ecine	Ecane

Some examples of heterocyclic compounds with systematic nomenclature are shown in figure 9.

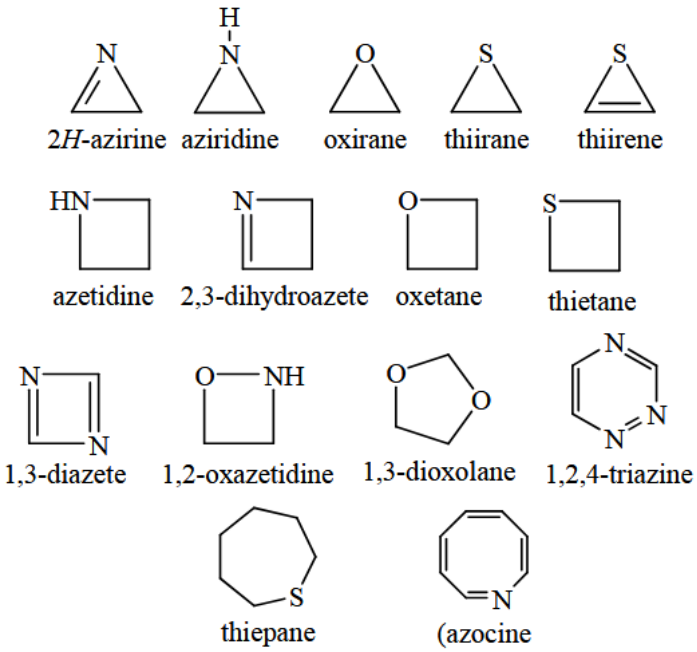


Figure 9. Examples of some heterocyclic compounds with systematic names

5.5 MOLECULAR ORBITAL PICTURE OF HETEROCYCLIC COMPOUNDS

Molecular orbital theory is widely used to interpret the structure of aromatic and hetero-aromatic compounds. According to Huckel approximation the electrons in the p-orbitals are treated separately from those electrons which are involved in the formation of the bonds in the plane of the ring. The six p-orbitals are combined to give six delocalized π molecular orbitals (3 π bonding molecular orbitals and 3 antibonding π molecular orbitals). Each of the six π -molecular orbitals can accommodate a maximum of two electrons. The 3 bonding π -molecular orbitals are of lower energies than the 3 antibonding π -molecular orbitals. Thus the electrons will be filled in lower 3 bonding π -molecular orbitals first. We will be discussing here the π -molecular orbitals of pyrrole and pyridine as model compounds of five and six membered heterocyclic compounds.

5.5.1 Molecular Orbital Picture of Pyrrole:

Five membered heterocyclic compounds with conjugated double bond can be considered as aromatic if the delocalization of π electrons is possible. Pyrrole, furan, thiophene etc are the most common examples of this class of compounds. These five membered heterocyclic compounds are structural homologue of cyclopentadienyl anion (Figure 10).

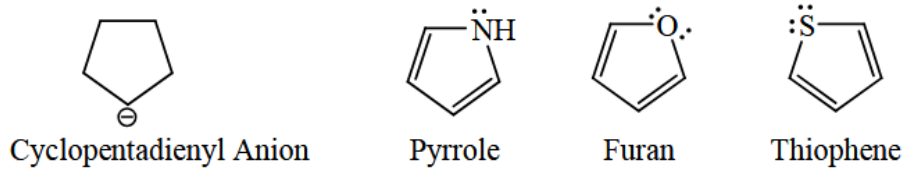
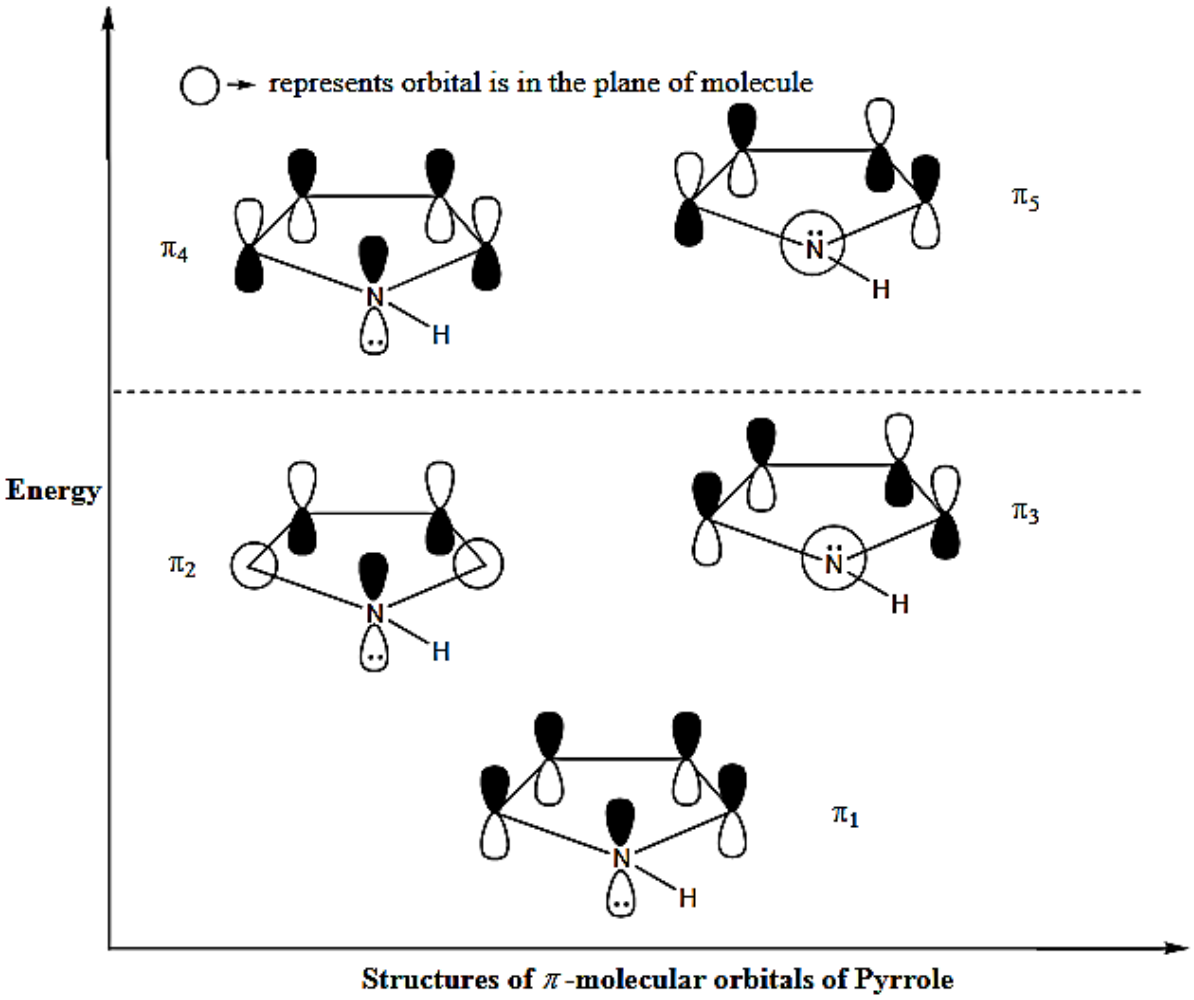


Figure 10. Examples of cyclopentadienyl anion structural homologue heterocyclic compounds

Pyrrole is the most fundamental member of this family. It is an aromatic compound with all 5 sp^2- hybridized atoms. The lone pair of heteroatom (*e.g.* N in the case of pyrrole) participates in the delocalization and constitutes an aromatic compound with 4n+2 π electrons (Huckel rule of aromaticity). The molecular orbital diagram of pyrrole is shown on figure 11.

If we recall the π -molecular orbital of benzene that we have studied in undergraduate chemistry course of semester one; where you could see that the π -molecular orbitals of benzene follow the rule of degeneracy (set of orbitals with same energy, same symmetry and similar orientation). However, the introduction of heteroatom by replacement of ring carbon leads the formation of non-degenerated set of π -molecular orbital. For example, we can see from the

figure 11, splitting of the π2 and π 3 levels; the orbital π 2 has a large orbital coefficient on nitrogen (due to more electro negativity of nitrogen than carbon) and thus lower in energy than π 3. The π 3 molecular orbital, in which the lone pair of the nitrogen atom lies on the perpendicular plane of the p-orbitals of ring carbon atoms helps to create two nodal points, hence, do not participate in the formation of ring current. Thus the nitrogen atom of π 3 has less orbital coefficient that π 2. In the five membered heterocyclic compounds six- π electron are distributed over five atoms therefore the carbon atoms of such heterocyclic compounds have more electron density than that of benzene.



Structures of π -molecular orbitals of Pyrrole

Figure 11. π -Molecular orbital of Pyrrole

Among the five constituting atoms of pyrrole, the nitrogen has maximum electron density than four carbon atoms this is because of the more electro-negativity of nitrogen. Similar description may also be made for the other five membered heterocyclic compounds like Furan and Thiophene

5.5.2 Molecular Orbital Picture of Pyridine:

Six membered heterocyclic compounds (with one heteroatom) are structural analogous to that of benzene but with a heteroatom replacing one of the carbon atom of the benzene ring. Pyridine is the most common example of this class of heterocyclic compounds. Pyridine is a planar molecule like benzene, since all the carbon atoms and nitrogen atom of the pyridine are of sp2- hybridized. The lone pair of electrons of nitrogen atom lies in the plane of the ring. Pyridine is also an aromatic compound with (4n+2) π -electrons (Huckel rule of aromaticity).

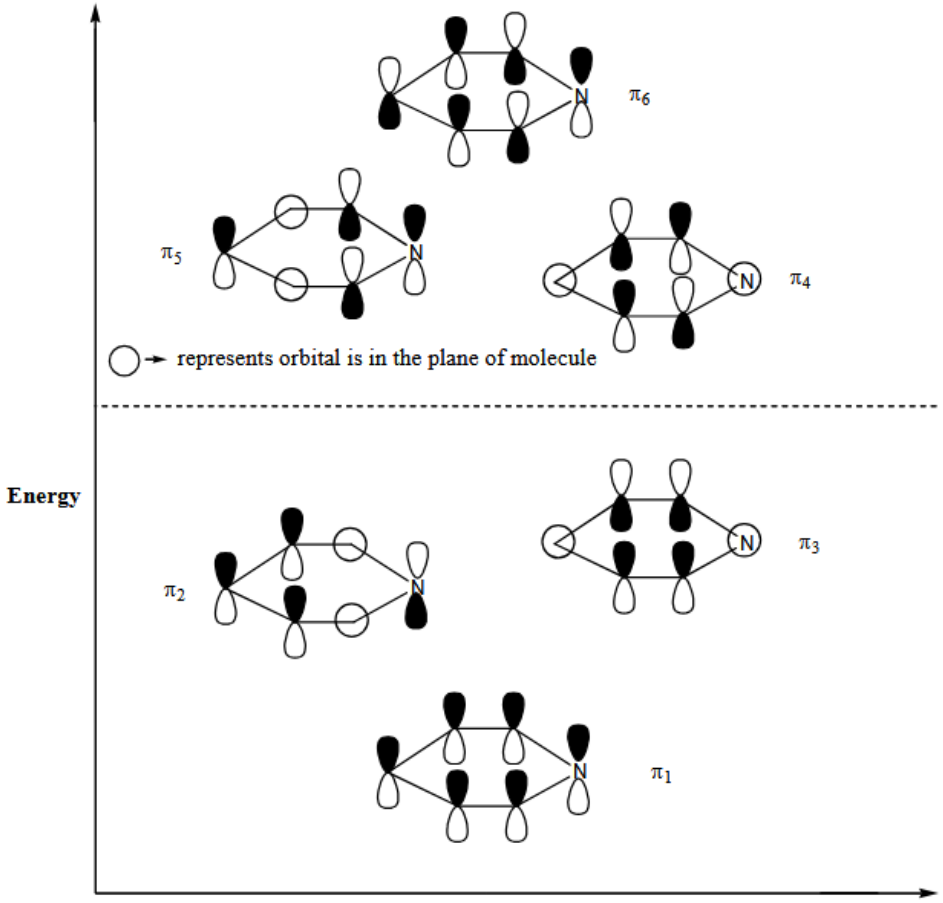


Figure 12. Π-molecular orbital representation of Pyridine

The six p-orbitals are combined to give six delocalized π-molecular orbitals. Each π-molecular orbital can contain two electrons. Out of six π -molecular orbitals, three are called bonding π -molecular orbital and three are called antibonding π -molecular orbitals. All six π-electrons are accommodated by three bonding π -molecular orbital. Similar to pyrrole, the π -molecular orbital of pyridine also have lower energy in comparison to benzene, this is because of the presence of nitrogen atom in place of a ring carbon. As already discussed in the previous section that the due to more electro-negativity of nitrogen than carbon the electron density at nitrogen atom is greater than the of carbon, thus nitrogen have a comparatively larger orbital coefficient

than carbon, therefore, the π -molecular orbital of pyridine are of lower energy than those of benzene. Similar to pyrrole, in pyridine also the introduction of a heteroatom by replacement of ring carbon leads the formation of a non-degenerated set of π -molecular orbital. For example, we can see from the figure 12, splitting of the π 2 and π 3 levels; the orbital π 2 has a large orbital coefficient on nitrogen (due to more electro electronegativity of nitrogen than carbon) and thus is lower in energy than π 3 (Figure 12).

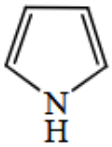
5.6 STRUCTURE AND AROMATICITY OF PYRROLE, FURAN, THIOPHENE AND PHRIDINE

5.6.1 Structure and Aromaticity of Pyrrole:

Structure and aromaticity of pyrrole can be discussed according to the following points.

1. The molecular weight determination method and related analytical studies revealed that the molecular formula of Pyrrole would be C_4H_5N.

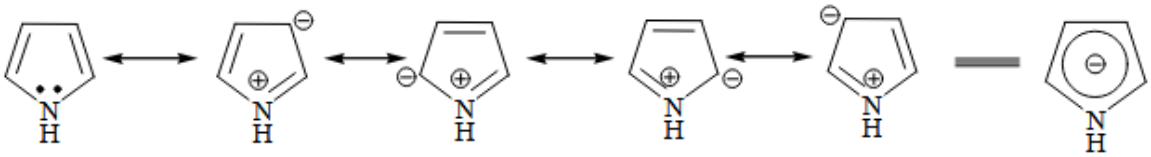
2. The possible structure of pyrrole can be given by considering the tetravalency of carbon and trivalency of nitrogen, and it is shown below:



Pyrrole

Pyrrole typically does not account for simple addition reactions, such as those of alkenes, under normal conditions. This is because of the delocalisation of the lone pair of the nitrogen atom through conjugation. This delocalisation provides extra stability to the double bonds of pyrrole.

Also, the proposed structure of pyrrole is considered as an aromatic compound since it follows Huckel's aromaticity rules (4n+2 electron rule). The aromatic nature and extra-stability of pyrrole can also be supported by the formation of its different resonating structures as shown in figure below. The structure of pyrrole is the resonance hybrid of all resonating structures.



The delocalization of lone pair of nitrogen in pyrrole through conjugation also suggests that the pyrrole molecule should have planar geometry. This is only possible when the orbitals of carbon and nitrogen in pyrrole are sp^2- hybridized. The three sp^2- hybridized orbitals of nitrogen contain one- one electron in each sp^2- hybridized orbital. The unhybridized *p*-orbital of nitrogen contains lone pair of electrons. Two sp^2- hybridized orbitals of nitrogen atom forms π-bond with two carbon atoms of the ring whereas the third sp^2- hybridized orbital of the nitrogen atom forms π-bond with hydrogen atom. Similarly, each sp^2- hybridized carbon forms two π-bonds with neighboring carbon atoms and one π-bond with a hydrogen atom. The unhybridized orbitals of each carbon contain one electron. These unhybridized orbitals of carbon and nitrogen form a delocalized electron cloud above and below the pentagonal ring of pyrrole. The delocalized electron cloud is shown in figure 13.

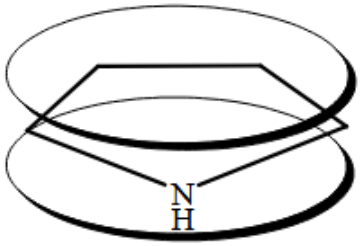


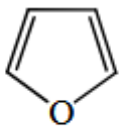
Figure 13. Delocalized electron cloud above and below the pyrrole ring

5.6.2 Structure and Aromaticity of Furan:

Structure and aromaticity of furan can be discussed according to the following points.

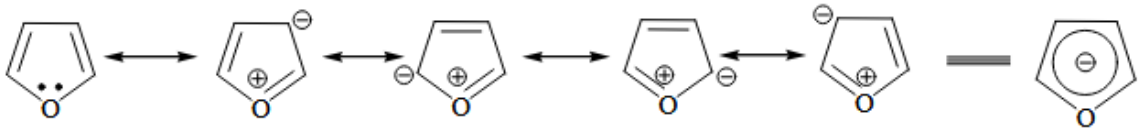
1. The molecular weight determination method and related analytical studies revealed that the molecular formula of Furan would be C_4H_4O.

2. The possible structure of Furan can be given by considering the tetravalency of carbon and bivalency of oxygen, and it is shown below.



Furan

3. Like Pyrrole, due to delocalisation of one of the lone pairs of electrons of oxygen in furan, it also does not explain the fundamental addition reactions like simple alkenes under normal conditions. The proposed structure of furan is also considered as an aromatic compound since it follows Huckel's aromaticity rules (4n+2 electron rule). The aromatic nature and extra-stability of furan are also supported by the formation of its different resonating structures as shown in the figure below. The structure of furan is the resonance hybrid of all resonating structures.



The delocalisation of lone pair of oxygen in furan through conjugation also suggests that the furan molecule should have planar geometry. This is only possible when the orbitals of carbon and oxygen in furan are sp^2- hybridized. The two sp^2- hybridized orbitals of oxygen contain one- one electron in each sp^2- hybridized orbital; however, third sp^2-hybridized orbital contains one lone pair of electron. The unhybridized p-orbital of oxygen contains two electrons. Two sp^2- hybridized orbitals of oxygen atom forms π -bond with two carbon atoms of the ring, whereas the third sp^2- hybridized orbital of oxygen atom accommodate lone pair of electron. Similarly each sp^2- hybridized carbon forms two π -bonds with neighboring atoms and one π -bond with hydrogen atom. The unhybridized orbitals of each carbon contain one electron. These unhybridized orbitals of carbon and oxygen form a delocalized electron cloud above and below the pentagonal ring of furan. The delocalized electron cloud is shown in figure 14.

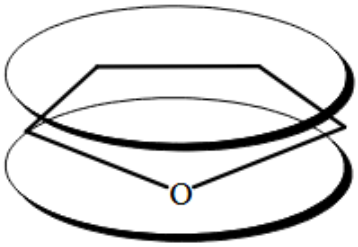


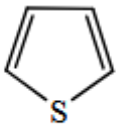
Figure 14. Delocalized electron cloud above and below the furan ring

5.6.3 Structure and Aromaticity of Thiophene:

Structure and aromaticity of Thiophene can be discussed according to the following points.

1. The molecular weight determination method and related analytical studies revealed that the molecular formula of Thiophene would be C_4H_4S.

2. The possible structure of Thiophene can be given by considering the tetravalency of carbon and bivalency of sulphur, and it is shown below.

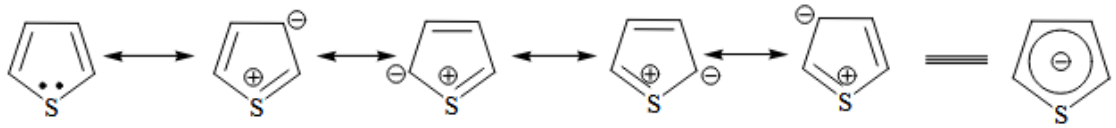


Thiophene

3. Like Pyrrole, due to delocalization of one of the lone pair of electron of oxygen in thiophene, it also does not explain the fundamental addition reactions like simple alkenes under normal condition. The proposed structure of thiophene is also considered as an aromatic compound

since it follows Huckel's aromaticity rules (4n+2 electron rule).

The aromatic nature and extra-stability of thiophene is also supported by the formation of its different resonating structures as shown in the figure below. The structure of thiophene is the resonance hybrid of all resonating structures.



The delocalization of lone pair of sulphur in furan through conjugation also suggests that the thiophene molecule should have planar geometry. This is only possible when the orbitals of carbon and sulphur in thiophene are sp^2- hybridized. The two sp^2- hybridized orbitals of sulphur contain one- one electron in each sp^2- hybridized orbital; however, third sp^2- hybridized orbital contains one lone pair of electrons. The unhybridized p-orbital of sulphur contains two electrons. Two sp^2- hybridized orbitals of sulphur atom forms π -bond with two carbon atoms of the ring, whereas the third sp2- hybridized orbital of sulphur atom accommodate lone pair of electron. Similarly each sp2- hybridized carbon forms two π -bonds with neighboring atoms and one π -bond with hydrogen atom. The unhybridized orbitals of each carbon contain one electron. These unhybridized orbitals of carbon and sulphur form a delocalized electron cloud above and below the pentagonal ring of thiophene. The delocalized electron cloud is shown in figure 15.

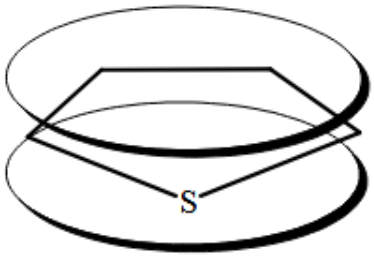


Figure 15. Delocalized electron cloud above and below the thiophene ring

4.6.4 Structure and Aromaticity of Pyridine:

Structure and aromaticity of Thiophene can be discussed according to the following points.

1. The molecular weight determination method and related analytical studies revealed that the molecular formula of Pyridine as C_5H_5N.

2. Pyridine was found to be basic in nature since it forms a salt with acids

$$C_5H_5N + HCl \longrightarrow C_5H_5N.HCl$$

Pyridine Pyridinium hydrochloride

3. Pyridine does not react with acetyl chloride and nitrous acid, it confirms that pyridine does not have a primary or secondary amino group. The above fact also confirms that the pyridine

is a mono-acidic tertiary base.

4. Pyridine also reacts with an equimolar amount of methyl iodide to form a quaternary ammonium salt.

$$C_5H_5N + CH_3I \longrightarrow [C_5H_5N^+(CH_3)]I^-$$

Pyridine N-methyl pyridinium iodide

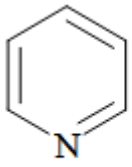
5. The molecular formula also indicates that it is a highly unsaturated compound; however, pyridine does not give the simple addition reactions like alkenes.

6. Pyridine is also found to be stable towards the oxidising agents.

7. Pyridine exhibits aromatic character like benzene and gives electrophilic substitution reactions such as halogenation, nitration and sulphonation.

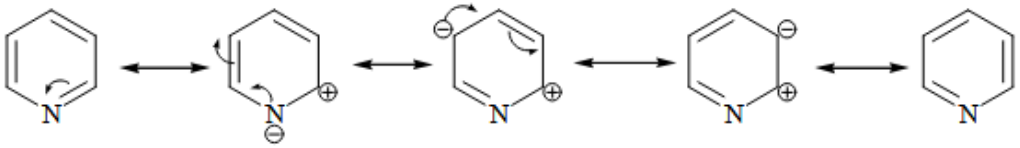
Last two reactions confirm the aromatic character of pyridine.

8. Based on above observations the possible structure of Pyridine can be given by considering the tetravalency of carbon and trivalency of nitrogen, and it is shown below.



pyridine

This structure is considered to be the resonance hybrid of the following structures.



Resonance in pyridine molecule is supported by the following points:

i. All the carbon, nitrogen and hydrogen atoms lie in the same plane all the carbon and nitrogen atoms of pyridine are sp2 hybridized.

ii. Each sp2- hybridized carbon forms two π -bonds with neighbouring atoms and one π-bond with hydrogen atom.

iii. The unhybridized p-orbital of each carbon atom is involved to form the π-bond with neighbouring atoms.

iv. The two of three sp2- hybridized orbitals of nitrogen contain one- one electron in each sp^2-hybridized orbital; however, the third sp^2- hybridized orbital of nitrogen contains lone pair of

electron. The unhybridized p orbital of nitrogen contains one electron which is involved to form π -bond with any of the neighboring carbon atoms.

v. All the carbon-carbon bonds in pyridine are of equal length (i.e. 1.39 Å).

vi. The carbon-nitrogen bonds are also of equal length (1.37 Å).

vii. These properties resists the pyridine from simple addition reaction of C=C double bond. Since in pyridine there is no true C=C double bond.

viii. The resonating structures represent that the more electron density at C-3, hence electrophilic substitution in pyridine takes place at C-3.

9. The delocalized electron cloud in pyridine is shown in figure 16.

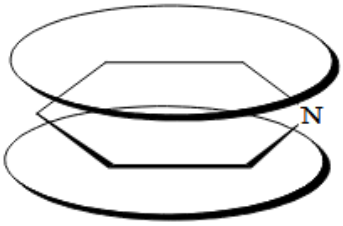


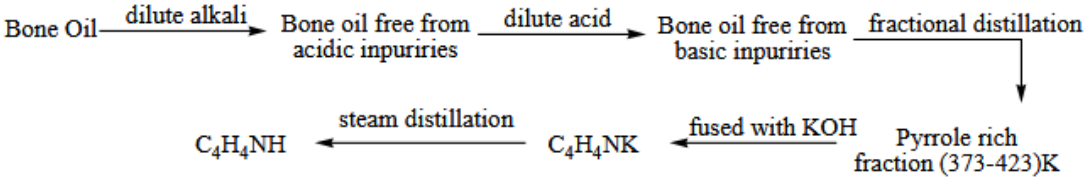
Figure 16. Delocalized electron cloud above and below the pyridine ring

5.7 METHODS OF PREPARATION AND CHEMICAL REACTION

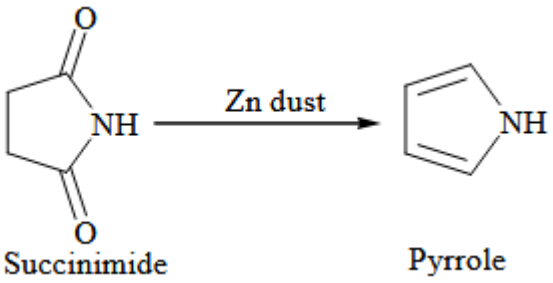
5.7.1 Methods of Preparation of Pyrrole:

Following are the general methods of preparation of pyrrole:

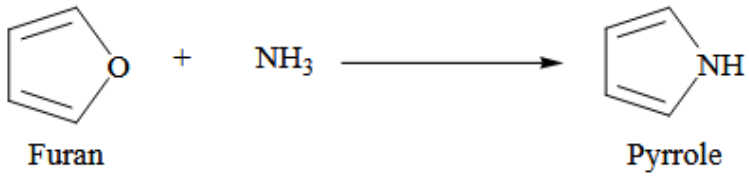
i. ***From bone oil***: Bone oil is rich of pyrrole. The basic and acidic impurities of Bone oil are removed by sequential treatment of it with dilute acidic and dilute basic solutions. The treated Bone oil is then subjected for fractional distillation, the fraction obtained between 373K and 423K is collected. The collected fraction is then purified with KOH to obtained potassiopyrrole. Steam distillation of potassiopyrrole gives pure pyrrole.



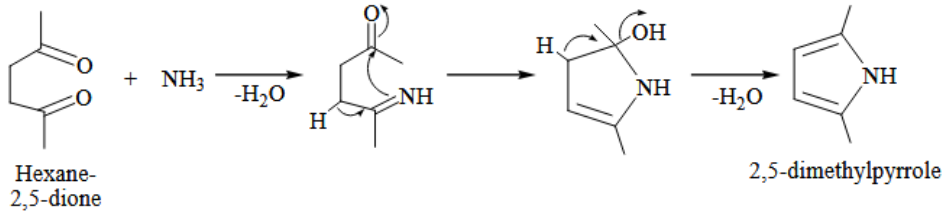
ii. ***From succinimide:*** Succinimide when is distilled with Zn dust it reduces the succinimide to pyrrole.



iii. ***From Furan***: Industrially pyrrole is prepared by passing a mixture of furan and ammonia over alumina over 400° C.



iv. Pall-Knorr synthesis: In this method, when a 1,4-diketone is heated with ammonia a primary amine it gives the corresponding pyrrole derivatives.



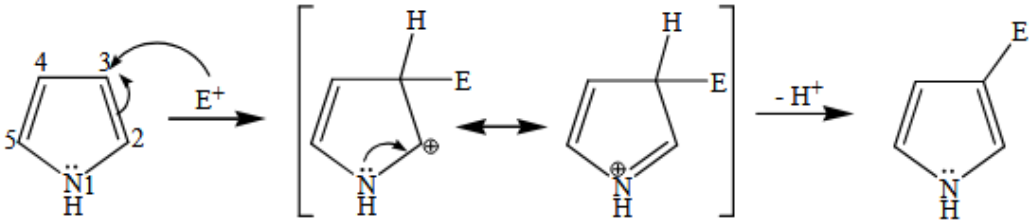
5.7.2 Properties of Pyrrole:

i. Physical Properties of pyrrole: Pyrrole is a colorless liquid with boiling point 131° C. It is highly sensitive to air, when pyrrole is exposed to air it turns brown and gradually resinifies. Pyrrole is slightly soluble in water but completely miscible in ether and ethanol.

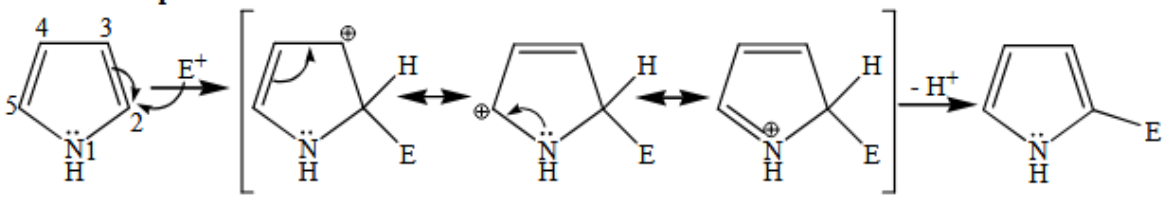
ii. Chemical Properties: Pyrrole is an aromatic compound and more reactive than benzene. Because of the aromatic nature pyrrole gives all characteristic reactions (electrophilic substitution reactions) of aromatic compounds such as halogenation, nitration, sulphonation, Friedel-Crafts reactions etc. Pyrrole undergoes electrophilic substitution at the position C-2. Approach of the electrophile at position C-2 leads the formation of three resonating structures; however, only two resonating structures are obtained when the electrophile approaches at position C-3. Thus the intermediate obtained by the approach of electrophile at position C-2 is more stable than the intermediate obtained by the approach of electrophile at position C-3. This is the reason that electrophilic attack occurs at position C-2. Following mechanism is suggested

for the electrophilic attack at position C-2.

Attack at position C-3:



Attack at position C-2:

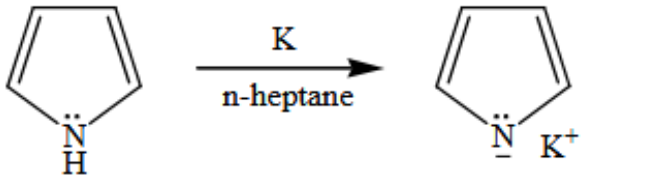


E= electrophile

All the electrophilic substitution reactions of pyrrole occur at position C-2 and follow the similarmmechanism as shown above.

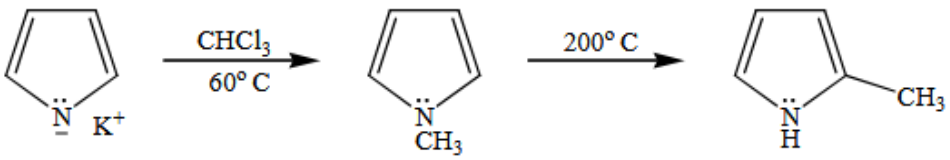
a) ***Acidic Character of Pyrrole***: The lone pair of nitrogen usually participates in resonance and thus makes the pyrrole aromatic. That is the reason, the lone pair of nitrogen could not be available free to react with a proton.

However, pyrrole can behave as a weak acid. When pyrrole is heated with potassium in n-heptane as solvent, stable potassium pyrrolide is formed.



Pyrrole Potassium pyrrolide

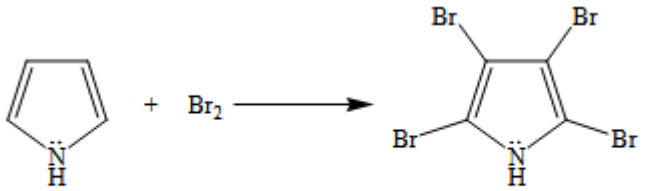
Potassium pyrrolide when reacts with alkyl halide at 60° C to give N-alkyl pyrrole. The N-alkyl pyrrole can easily rearrange to C-alkyl pyrrole.



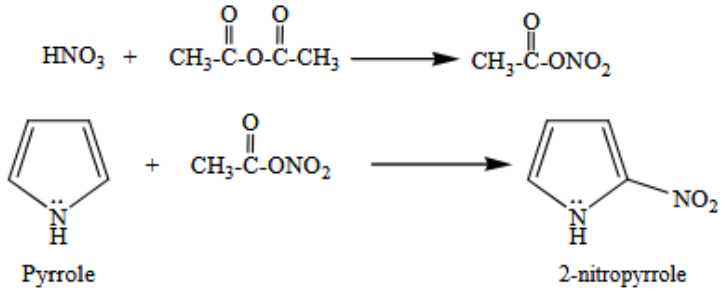
Potassium pyrrolide 1-Methylpyrrole 2-Methylpyrrole

b) ***Electrophilic Substitution Reactions of Pyrrole:*** Pyrrole undergoes electrophilic substitution reactions at position C-2.

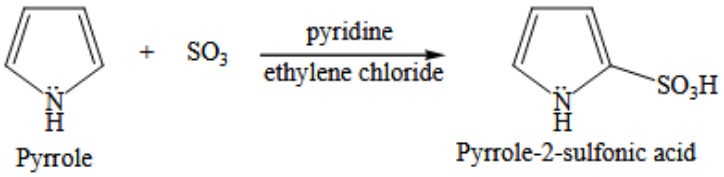
i. ***Halogenation:*** Pyrrole reacts with halogens [X_2 (X_2 = Cl_2, Br_2 and I_2)] to give tetrahalopyrrole. For example, Reaction of bromine with pyrrole gives tetrabromopyrrole.



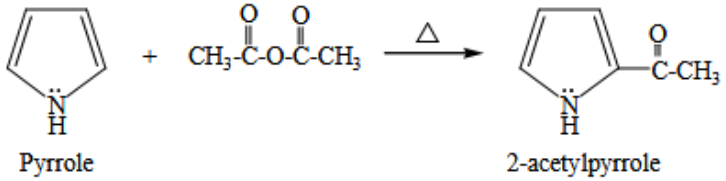
ii. ***Nitration:*** Nitration of pyrrole is achieved by reacting it with HNO_3 in acetic anhydride. The reaction of HNO_3 and acetic anhydride resulted acetyl nitrate in which $–NO_2$ acts as an electrophile.



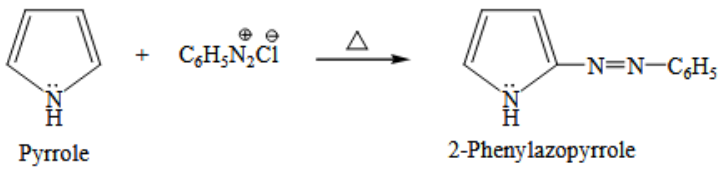
iii. ***Sulphonation:*** Sulphonation of pyrrole is achieved by reacting it with sulfur trioxide (SO_3) – pyridine mixture in ethylene chloride.



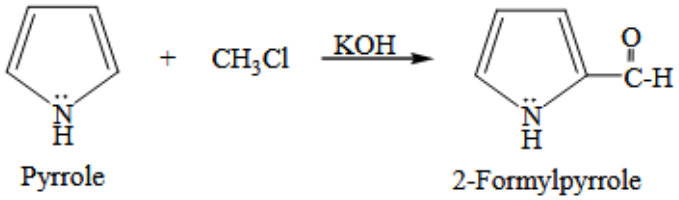
iv. Friedel-Crafts Acylation: Reaction of pyrrole with acetic anhydride under heating condition gives 2-acetylpyrrole.



v. ***Diazotization:*** Pyrrole reacts with benzenediazonium chloride in acidic medium to give 2-phenylazopyrrole.

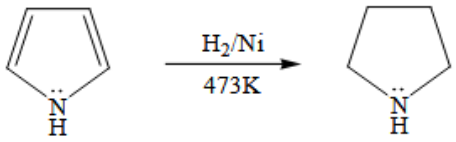


vi. ***Reimer-Tiemann Reaction:*** Pyrrole reacts with Chloroform in presence of KOH to give 2-Formylpyrrole. This reaction is known as Reimer-Tiemann reaction. It also takes place through electrophilic substitution reaction mechanism.



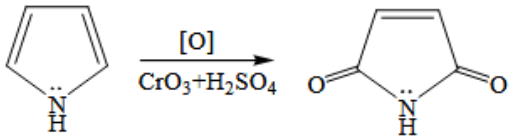
Pyrrole 2-Formylpyrrole

c) Reduction: Pyrrole can be reduced to pyrrolidine (tetrahydropyrrole) by H_2 gas in Raney Ni at very high temperature (473K).



Pyrrole Pyrrolidine

d) Oxidation: Pyrrole when oxidized with Chromium trioxide in H_2SO_4, it gives Malecimide.

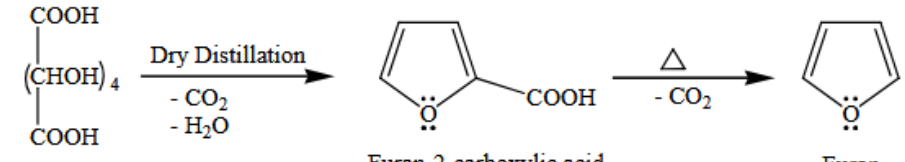


Pyrrole Pyrrole-2,5-dione (Malecimide)

5.7.3 Methods of Preparation of Furan:

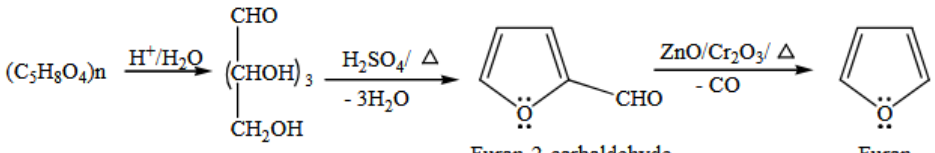
Following are the general methods of preparation of Furan:

i. ***From Mucic acid:*** Dry distillation of mucic acid first gives Furoic acid which on decarboxylation by heating gives Furan.



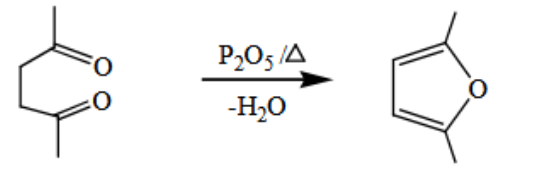
Mucic Acid Furan-2-carboxylic acid (Furoic acid) Furan

ii. **From Furfural:** Furan is synthesized from furfural which is obtained by acid-hydrolysis of pentose sugars.



Pentose sugar Aldopentose Furan-2-carbaldehyde (Furfural) Furan

iii. Paal-Knorr Synthesis: Dehydration of 1,4-diketone with P_2O_5 (phosphorous Pentaoxide) gives derivatives of Furan.



Hexane-2,5-dione 2,5-dimethylfuran

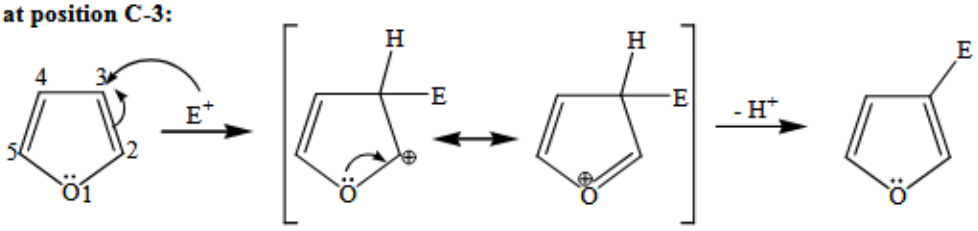
4.7.4 Properties of Furan:

i. Physical Properties of Furan: Furan is colorless liquid. Its boiling point is 31.4° C. It has an odor similar to Chloroform. It is insoluble in ether but soluble in most of the organic solvents.

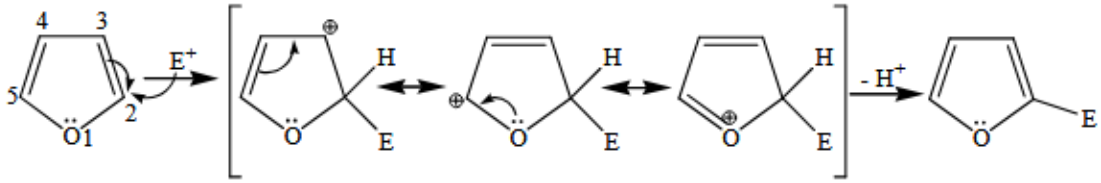
ii. Chemical Properties of Furan: furan is an aromatic compound and more reactive than benzene. Because of the aromatic nature, furan gives all characteristic reactions (electrophilic substitution reactions) of aromatic compounds such as halogenation, nitration, sulphonation, Friedel-Crafts reactions etc.

Similar to pyrrole, furan also undergoes electrophilic substitution at the position C-2. Approach of the electrophile at position C-2 leads the formation of three resonating structures; however, only two resonating structures are obtained when the electrophile approaches at position C-3. Thus the intermediate obtained by the approach of electrophile at position C-2 is more stable than the intermediate obtained by the approach of electrophile at position C-3. This is the reason that electrophilic attack occurs at position C-2. Following mechanism is suggested for the electrophilic attack at position C-2.

Attack at position C-3:



Attack at position C-2:

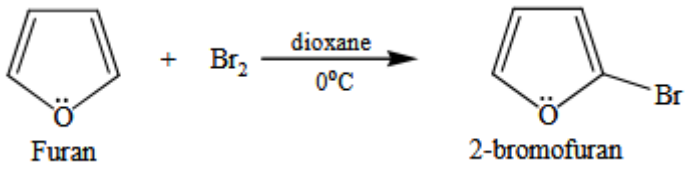


E= electrophile

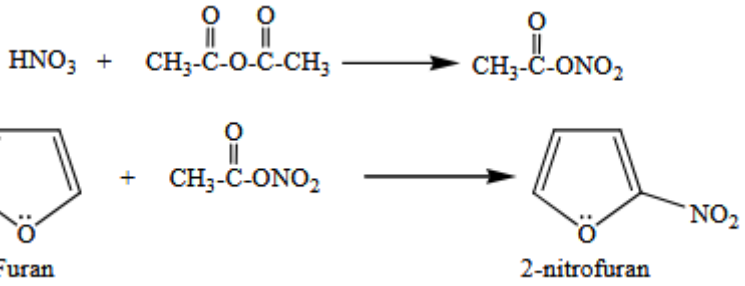
a) ***Electrophilic Substitution Reactions of Furan:*** Furan undergoes electrophilic substitution reactions at position C-2.

i. ***Halogenation:*** Furan reacts with halogens [X_2 (X_2 = Cl_2, Br_2 and I_2)] to give 2-

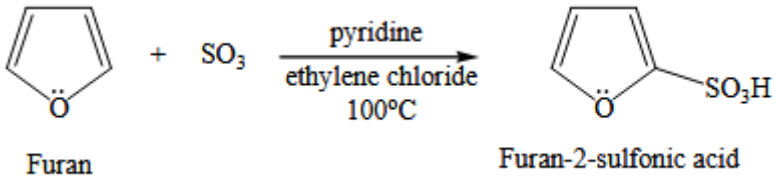
halofuran. For example, reaction of bromine with Furan gives 2-bromofuran.



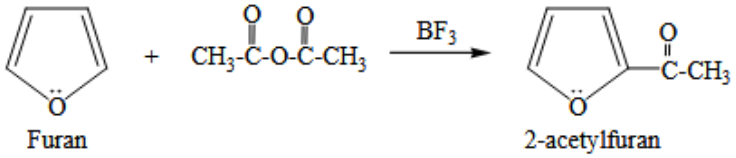
ii. ***Nitration:*** Nitration of furan is achieved by reacting it with HNO_3 in acetic anhydride. The reaction of HNO_3 and acetic anhydride resulted acetyl nitrate in which–NO_2 acts as an electrophile.



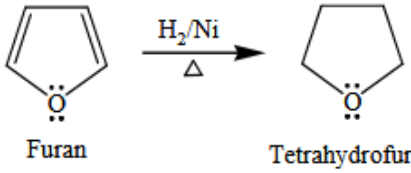
iii. ***Sulphonation:*** Sulphonation of Furan is achieved by reacting it with sulfur trioxide (SO3) – pyridine mixture in ethylene chloride at 100° C.



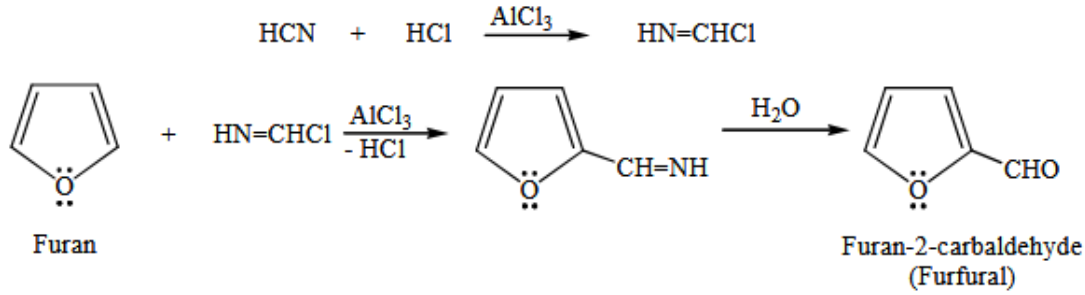
iv. Friedel-Crafts Acylation: Reaction of furan with acetic anhydride in presence of BF_3 gives 2-acetylfuran.



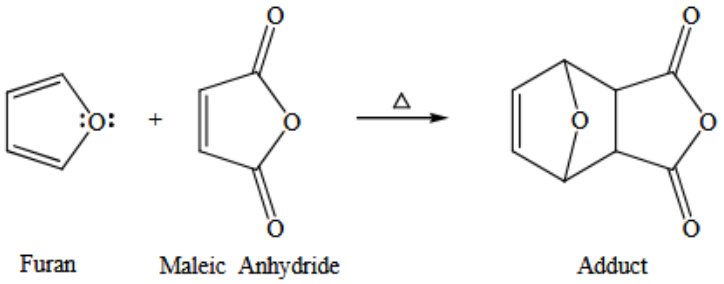
b) Reduction: On catalytic hydrogenation of furan, the tetrehydrofuran (THF) is obtained. THF is used as a solvent in place of ether in the Grignard reactions.



c) Gattermann Koch Synthesis: When furan is treated with a mixture of HCN and HCl in the presence of Lewis acid catalyst $AlCl_3$, furfural is obtained as final product.



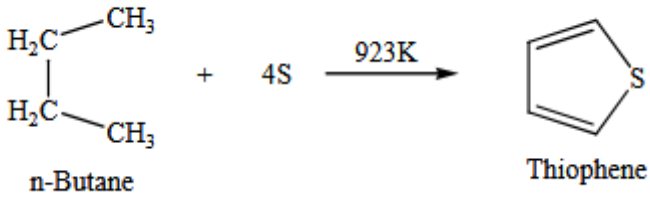
d) Diels-Elder Reaction: Furan is the only heterocyclic compound which undergoes Diels-Elder reaction. Diels-Elder reaction is a cycloaddtion reaction of 4π-system to 2π-system.



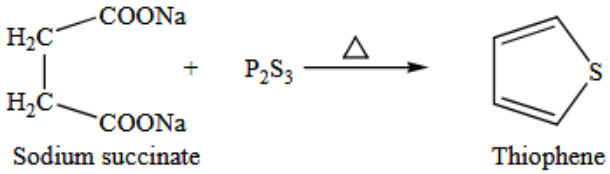
5.7.5 Methods of Preparation of Thiophene:

Following are the general methods of preparation of thiophene

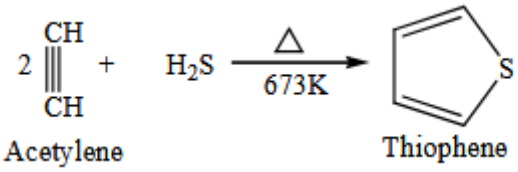
i. ***From n-Butane:*** Thiophene is obtained when n-butane is heated with elemental sulphur at very high temperature (923K).



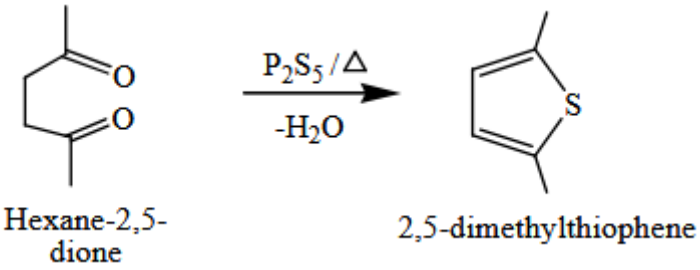
ii. Laboratory Method: When sodium succinate is heated with phosphorous sulphide, thiophene is obtained.



iv. **Industrial Method**: Industrially, thiophene is prepared by passing a mixture of acetylene and hydrogen sulphide through a tube containing alumina (Al_2O3) at 673K.



v. **Pall-Knorr synthesis of thiophene derivatives:** In this method, dehydration of 1,4- diketone with P2S5 (phosphorous Pentasulphide) gives derivatives of thiophene.



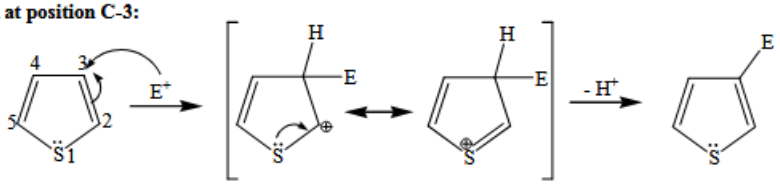
5.7.6 Properties of Thiophene:

i. Physical Properties of thiophene: Thiophene is colorless liquid. Boiling point of thiophene is 357 K. It smells like benzene. It is soluble in alcohol and ether but insoluble in water.

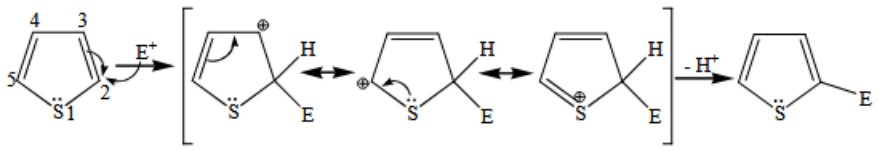
ii. Chemical Properties of thiophene: Thiophene is an aromatic compound and more reactive than benzene. Because of the aromatic nature, thiophene gives all characteristic reactions (electrophilic substitution reactions) of aromatic compounds such as halogenation, nitration, sulphonation, Friedel-Crafts reactions etc. Similar to pyrrole and furan; thiophene also undergoes electrophilic substitution at the position C-2. Approach of the electrophile at position C-2 leads the formation of three resonating structures; however, only two resonating structures are obtained when the electrophile.

approaches at position C-3. Thus, the intermediate obtained by the approach of electrophile at position C-2 is more stable than the intermediate obtained by the approach of electrophile at position C-3. This is the reason that electrophilic attack occurs at position C-2. Following mechanism is suggested for the electrophilic attack at position C-2.

Attack at position C-3:



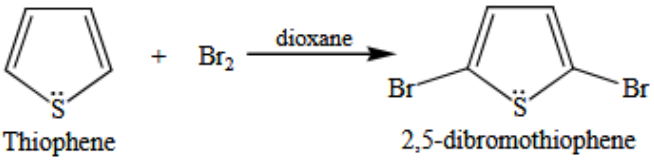
Attack at position C-2:



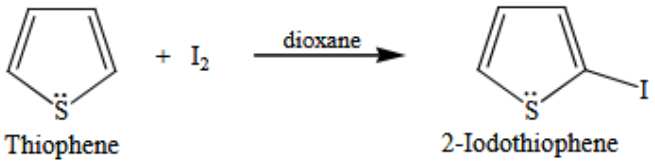
E= electrophile

a) **Electrophilic Substitution Reactions of Thiophene**: Thiophene undergoes electrophilic substitution reactions at position C-2.

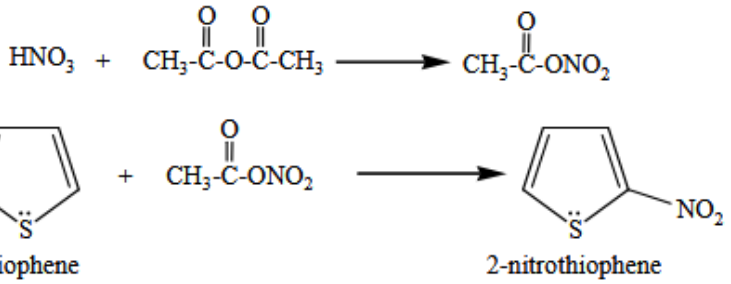
i. ***Halogenation:*** Thiophene reacts with halogens [X2 (X2 = Cl2, Br2 and I2)] to give 2-halofuran. For example, reaction of bromine with Thiophene in absence of any halogen carrier gives 2,5-dibromothiophene.



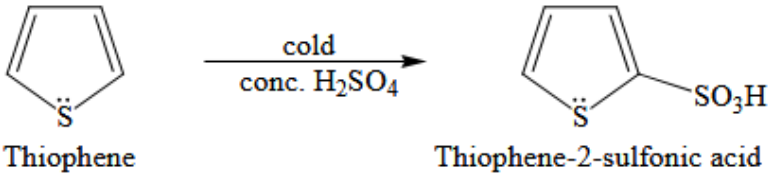
However, Iodination of thiophene in presence of yellow mercuric oxide gives 2-iodothiophene.



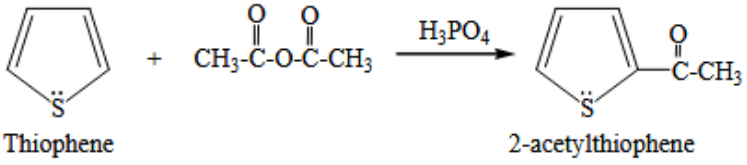
ii. ***Nitration:*** 2-Nitrothiophene is obtained when nitration of thiophene is performed by reacting it with fuming HNO_3 in acetic anhydride. The reaction of HNO_3 and acetic anhydride resulted acetyl nitrate in which $–NO_2$ acts as an electrophile.



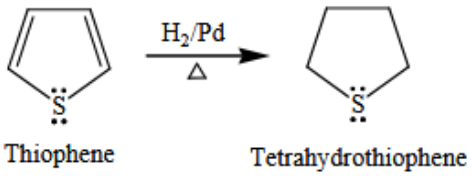
iii. ***Sulphonation:*** Sulphonation of thiophene is achieved by reacting it with cold Concentrated H_2SO_4. Thiophene-2-sulphonic acid is obtained as product.



iv. ***Friedel-Crafts Acylation:*** Reaction of thiophene with acetic anhydride in presence of H_3PO_4 gives 2-acetylthiophene.



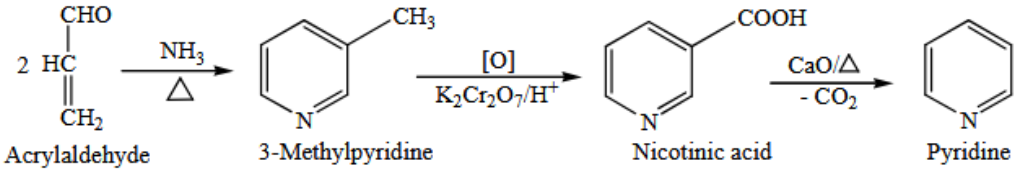
b) **Reduction:** On catalytic hydrogenation of thiophene, the tetrahydrothiophene (Thiophane) is obtained.



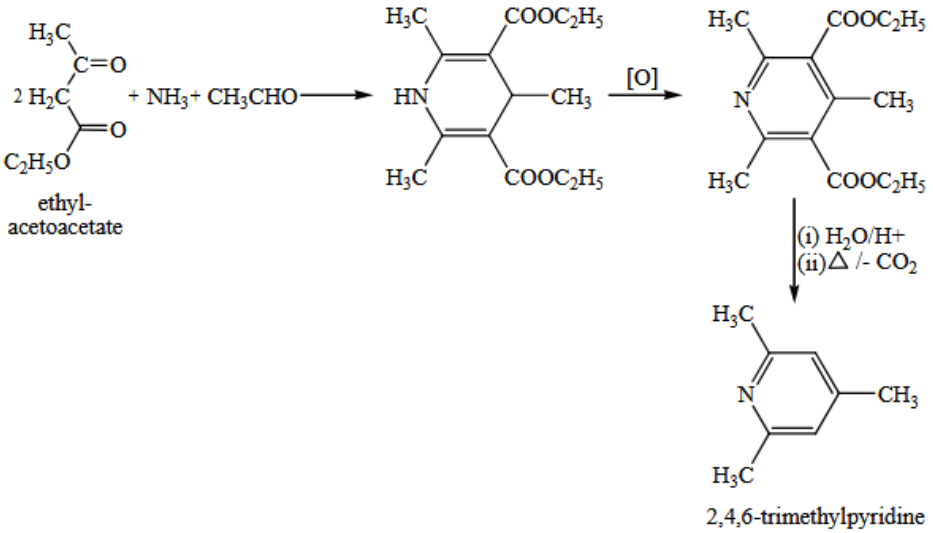
5.7.7 Methods of Preparation of Pyridine:

Following are the general methods of preparation of pyridine:

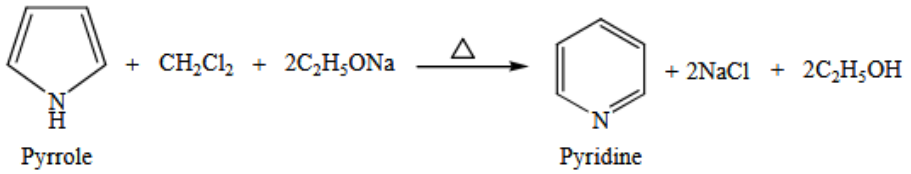
i. ***From acroline:*** Pyridine can be prepared by the reaction of acroline and ammonia according to following reaction steps.

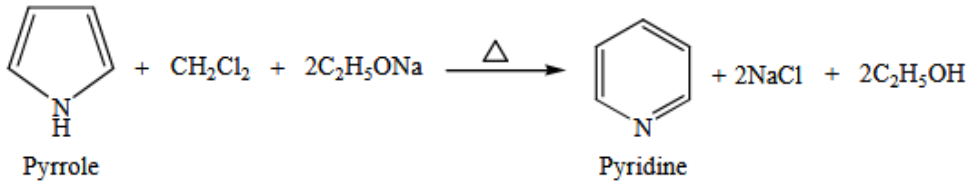


ii. **Hantzsch Synthesis (1882):** In this method, the condensation of a beta-dicarbonyl compound, ammonia and an aldehyde lead the formation of 1,4-dihydropyridine derivative. The 1,4-dihydro pyridine derivative on oxidation with HNO_3 yields the formation of pyridine derivative.

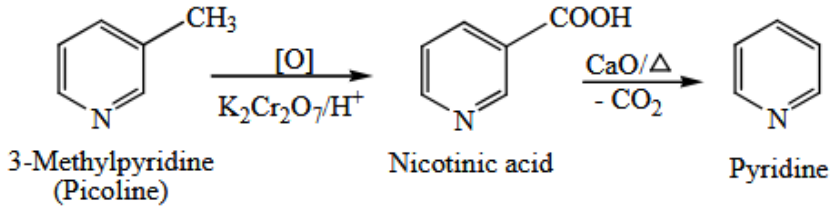


ii. ***From pyrrole:*** Pyrrole when heated with methylene chloride in presence of sodium ethoxide, pyridine is formed.

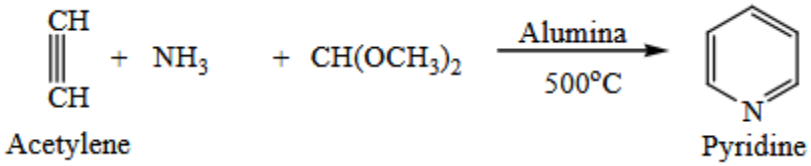




iv. **From Picoline:** Beta-picoline on oxidation with potassium dichromate and sulphuric acid gives nicotinic acid, which on decarboxylation with calcium oxide gives pyridine.



v. **Industrial Method:** Industrially pyridine is prepared by heating the acetylene, ammonia and formaldehyde dimethylacetal in the presence of alumina at 500° C.

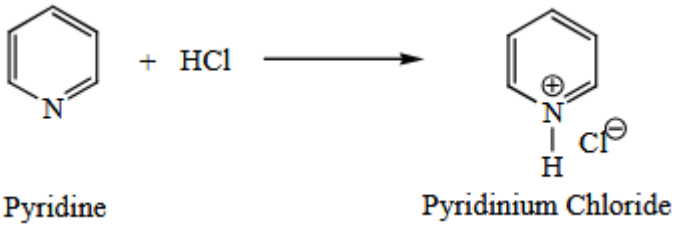


4.7.8 Properties of Pyridine:

i. **Physical Properties of Pyridine:** Pyridine is a colourless liquid. Its boiling point is 115.5° C. It has a characteristic unpleasant odor. It is soluble in water and most organic solvents.

ii. **Chemical properties of Pyridine:** Chemical properties of pyridine are discussed as follow:

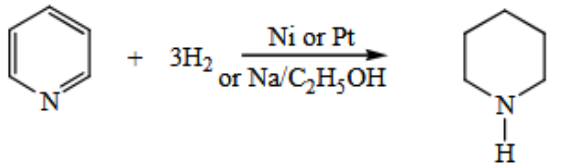
a. **Basic character of pyridine:** Pyridine is basic in nature. Its pKb is 8.75. It reacts with strong acids to form salts.



The basic nature of pyridine is due to the freely available lone pair of electrons in sp^2 hybridized orbital pyridine, which does not participate in the formation of delocalized π -molecular orbital. Pyridine is less basic in comparison to aliphatic amines whereas, it is more basic than aniline and pyrrole. This is because the lone pair of electrons in aliphatic amines exists in sp3

hybridized orbital, however, in case of pyridine the lone pairs of electrons exists in sp^2 hybridized orbital. Electrons are held more tightly by the nucleus in a sp^2 hybridized orbital than an sp^3 hybridized orbital. Hence the lone pair of electrons in pyridine is less available for protonation. The less basicity of pyrrole and aniline can be explained in terms of non-availability of these lone pair of electrons on nitrogen atom. These lone pair of electrons is involved in the formation of delocalized π -molecular orbital.

i. ***Reduction:*** Under catalytic hydrogenation of pyridine hexahydropyridine is formed. It is also known as Piperidine.

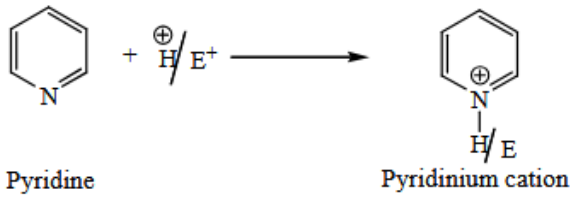


Pyridine Piperidine

ii. ***Electrophilic substitution Reactions:*** Pyridine is also an aromatic compound. It is less aromatic than benzene and pyrrole. Pyridine usually considered a highly deactivated aromatic nucleus towards electrophilic substitution reactions. Therefore, highly vigorous reaction conditions should be used for these reactions to take place. The low reactivity of pyridine towards the electrophilic substitution reactions is due to the following reasons:

- The higher electro negativity of nitrogen atom reduces electron density on the ring, thus deactivate the ring.
- Pyridine is highly sensitive to acidic medium; it readily forms pyridinium cation with a positive charge on nitrogen atom. Similarly, electrophile itself may also react with pyridine to form corresponding pyridinium ion. This positive charge on nitrogen atom decreases electron density on nitrogen atom, consequently, the electron density on ring also decreases.

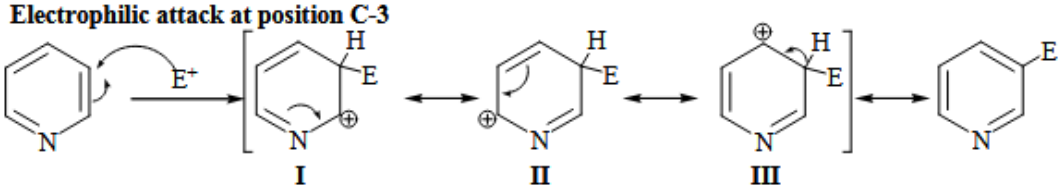
However, the effect of such deactivation is comparatively lower at position C-3. The position C-3 is thus, comparatively, the position of highest electron density in pyridine.



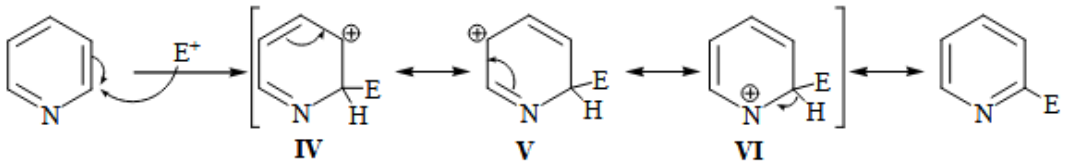
Pyridine Pyridinium cation

This is the reason that the pyridine undergoes electrophilic substitution at position C-3. Pyridine also gives electrophilic substitution like halogenation, nitration and sulphonation only under drastic conditions. Pyridine does not give Friedel-crafts reaction. Approach of the electrophile at position C-3 leads the formation of three resonating structures (I, II and III); similarly, approach of electrophile at position C-2 also leads the formation of three resonating structures (IV, V and VI). However, out of the three contributing resonating structures for the intermediate ion resulting from the attack of electrophile at position C-2, structures VI is considered as an unstable resonating form because in resonating structure VI the more electronegative nitrogen atom bears a +ve charge. Because of the unstable nature of one of the resonating structure of the intermediate ion formed during the attack of electrophile at position C-2 than that of the formed during the attack of electrophile at position C-3, the electrophilic substitution in pyridine at position C-3 is always favoured. Following mechanism is suggested for the electrophilic attack at position C-3.

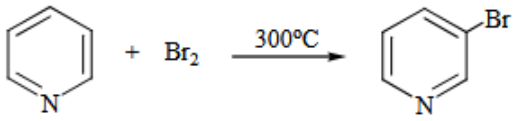
Electrophilic attack at position C-3



Electrophilic attack at position C-2

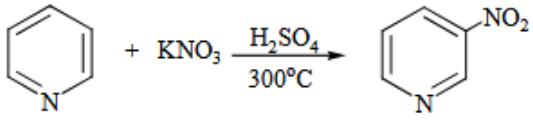


i. **Bromination:** Pyridine reacts with Bromine at high temperature to give 3-Bromopyridine.



Pyridine 3-Bromopyridine

ii. **Nitration:** 3-Nitropyridine is obtained when nitration of pyridine is performed by reacting it with KNO_3 in concentrated H_2SO_4 at 300°C. The reaction of KNO_3 and concentrated H_2SO_4 resulted–NO_2 which acts as an electrophile.

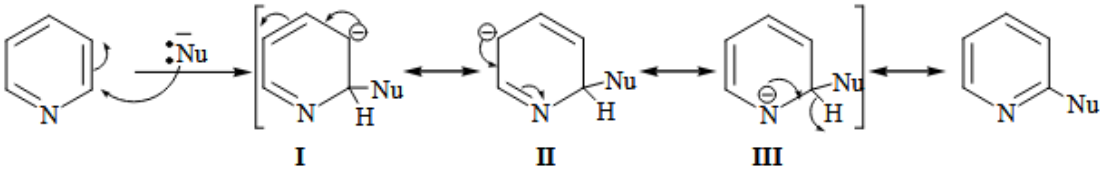


Pyridine 3-Nitropyridine

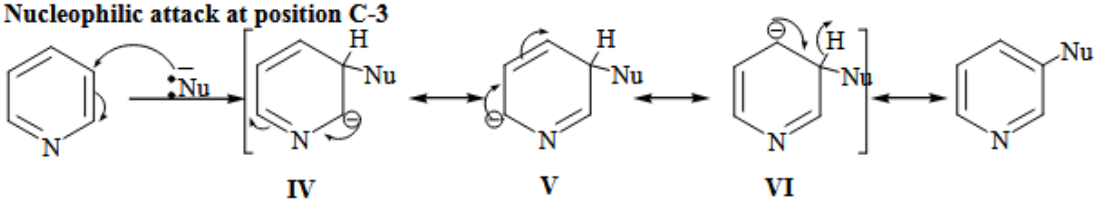
iii. **Sulphonation:** Sulphonation of pyridine is achieved by reacting it with fuming H_2SO_4 at 250°C. Pyridine-3-sulphonic acid is obtained as product.

d. Nucleophilic Substitution Reactions: As we have discussed in previous section that pyridine generally deactivated the aromatic ring towards electrophilic substitution reaction. The deactivation of aromatic ring towards electrophilic substitution resulted due to the electron withdrawing nature of nitrogen atom. Due to such deactivation, pyridine also gives nucleophilic substitution reaction. Nucleophilic substitution in pyridine ring occurs at position C-2. Approach of the nucleophilic at position C-2 leads the formation of three resonating structures (I, II and III); similarly, approach of nucleophilic at position C-3 also leads the formation of three resonating structures (IV, V and VI). The resonating structures for intermediate resulting from the attack of nucleophile at position C-2 are more stable than those of position C-3, since more electronegative nitrogen atom hold –ve charge in one of the resonating structure (III) obtained from the attack of nucleophile at position C-2. Hence, the nucleophilic substitution in pyridine at position C-2 is always favored. Following mechanism is suggested for the electrophilic attack at position C-2.

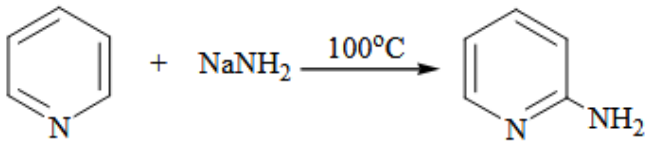
Nucleophilic attack at position C-2



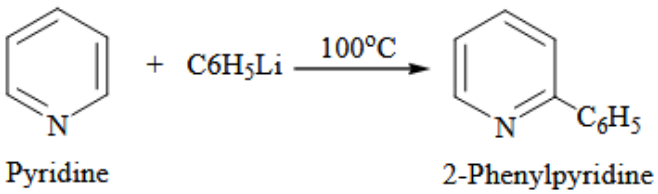
Nucleophilic attack at position C-3



i. **Reaction with Sodium amide:** Pyridine reacts with sodium amide to give 2-aminopyridine via nucleophilic substitution.



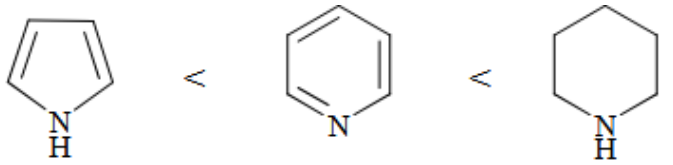
ii. **Reaction with Phenyllithium:** Pyridine reacts with phenyllithium (an organometallic compound) to give 2-phenylpyridine.



Pyridine 2-Phenylpyridine

5.8 COMPARISON OF BASICITY OF PYRROLE, PYRIDINE AND PIPERIDINE

From experimental studies it is observed that the pKb values of pyrrole, pyridine and Piperidine are ~14, ~8.7 and ~2.7, respectively. Based on the suggested pKb values the piperidine in found as a stronger base than pyridine and pyrrole. Pyrrole is the weakest base among these three heterocyclic bases. The order of basicity of pyrrole, pyridine and piperidine is as given below:



Pyrrole $pK_b = 14$ Pyridine $pK_b = 8.7$ Piperidine $pK_b = 2.7$

The above order of basicity of pyrrole, pyridine and piperidine can be justified in terms of the structure of these compounds. As we know that the basicity of nitrogen compounds depends upon the availability of lone pair of electrons on nitrogen atom. In pyrrole, the lone pair of electrons on nitrogen atom exists in the sp^2 hybridized orbital of nitrogen and participates in the delocalization, hence does not freely available to cause the basic character of pyrrole. Similar to pyrrole, the lone pair of electrons on nitrogen atom of pyridine also exists in the sp^2 hybridized orbital; however, it does not participate in the delocalization and available freely to cause the basic character. Although the lone pair of electrons on nitrogen atom of pyridine available freely but due to more electronegative character of sp^2 hybridized nitrogen atom (50% s-character) this lone pair is tightly bonded with nucleus, hence, less available for protonation. However, in piperidine, the lone pair of electrons of nitrogen atom lies in sp^3 hybridized orbital of nitrogen. These electrons are less tightly bonded with nucleus. Therefore, these electrons are readily available for protonation. Thus, piperidine is the strongest base among the three.

5.9 SUMMARY

Heterocyclic compounds are cyclic organic compounds that contain at least one atom other than carbon (commonly N, O, or S) in the ring. They occur widely in natural products such as alkaloids, vitamins, hormones, antibiotics, dyes, and biomolecules, and are important in pharmaceuticals, agrochemicals, and biochemical systems.

They are broadly classified as **aliphatic** and **aromatic heterocycles**. Aromatic heterocycles follow **Hückel's rule** and include five-membered rings like **pyrrole, furan, thiophene** and six-membered rings like **pyridine and piperidine**, along with fused systems such as **indole, quinoline, and purine**.

The nomenclature of heterocycles may follow **trivial names** or the **systematic Hantzsch-Widmann IUPAC system**, which identifies heteroatoms, ring size, saturation, and substitution pattern.

Molecular-orbital treatment explains the **aromaticity and electron distribution** in heterocycles such as pyrrole and pyridine. The unit further discusses **structure, aromatic character, preparation methods, physical and chemical properties**, and **electrophilic substitution behavior** of the major heterocyclic systems.

5.10 TERMINAL QUESTIONS

Short Answer / Conceptual Questions

1. What are heterocyclic compounds? Give two natural examples.
2. Differentiate between aliphatic and aromatic heterocyclic compounds.
3. State Hückel's rule and apply it to pyrrole and pyridine.
4. What is meant by fused heterocyclic compounds? Give two examples.
5. Write a note on the trivial and systematic nomenclature of heterocycles.

Long Answer / Descriptive Questions

1. Discuss the classification of heterocyclic compounds with suitable examples.
2. Explain the molecular orbital picture and aromaticity of pyrrole and pyridine.
3. Describe the structure, aromatic character, and reactivity of (a) Pyrrole, (b) Furan, and (c) Thiophene.
4. Explain the Hantzsch-Widmann system of nomenclature with examples.
5. Describe the methods of preparation and electrophilic substitution reactions of pyrrole.

Application / Analytical Questions

1. Why do pyrrole and furan undergo electrophilic substitution at the C-2 position?

2. Compare the basicity and aromatic character of pyridine and pyrrole.
3. Discuss the importance of heterocyclic compounds in pharmaceutical chemistry.

5.11 REFERENCES

1. Joule, J. A., & Mills, K. (2010). **Heterocyclic Chemistry** (5th ed.). Wiley-Blackwell.
2. Katritzky, A. R., Ramsden, C. A., Scriven, E. F. V., & Taylor, R. J. K. (Eds.). (2010). **Comprehensive Heterocyclic Chemistry III**. Elsevier.
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UNIT-6: HETEROCYCLIC COMPOUNDS-II

CONTENTS:

6.1 INTRODUCTION

In unit 5 we have discussed that the heterocyclic compound is a class of cyclic organic compounds those having at least one hetero atom (i.e. atom other than carbon) in the cyclic ring system. The most common heteroatoms are nitrogen (N), oxygen (O), and sulphur (S). Heterocyclic compounds are frequently abundant in plants and animal products, and they are one of the important constituents of almost one half of the natural organic compounds known. Alkaloids, natural dyes, drugs, proteins, enzymes etc. are some important class of natural heterocyclic compounds. Heterocyclic compounds can be easily classified based on their electronic structure. Heterocyclic compounds are primarily classified as saturated and unsaturated. The saturated heterocyclic compounds behave like the acyclic derivatives with modified steric properties. Piperidine and tetrahydrofuran are the conventional amines and ethers of this category. However, unsaturated heterocyclic compounds of 5- and 6- 6-member rings have been studied extensively because of their unstrained nature. The unstrained unsaturated heterocyclic compounds include Pyridine, Thiophene, Pyrrole, Furan and their benzo-fused derivatives. Heterocyclic ring systems that are formally derived by fusion with other rings, either carbocyclic or heterocyclic, have a variety of common and systematic names. For example, with the benzo-fused unsaturated nitrogen heterocycles, pyrrole provides Indole or isoindole depending on the orientation. Various other important examples of benzofused heterocyclic compounds are Quinoline, Isoquinoline, Benzothiophene, Benzazepine, Dibenzoazepine Carbazole, Acridine, and Benzofuran. Figure 1 shows the structural representation of various important 5 and 6-membered benzofused heterocyclic compounds.

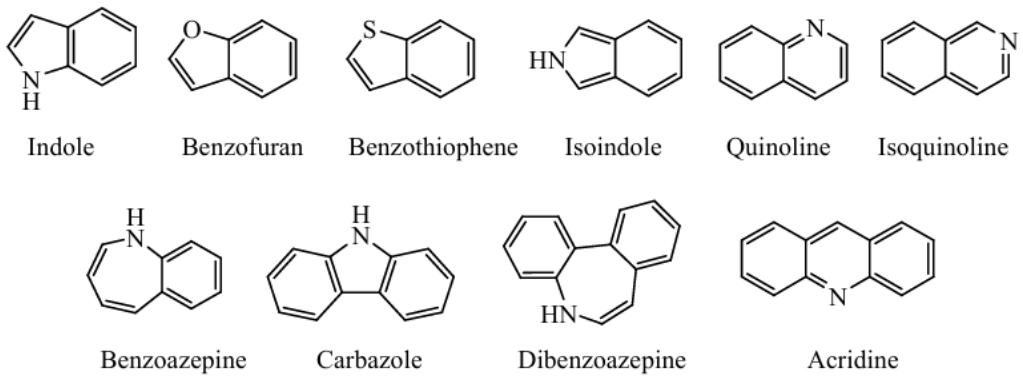


Figure 1: Examples of various important benzo-fused heterocyclic compounds

In the present unit, students would be able to learn about the most important five and six membered benzo fused heterocyclic compounds, such as Indole, Quinoline and Isoquinoline.

6.2 OBJECTIVES

In this unit learner will be able to

- Know about the most important condensed heterocyclic compounds containing five and six-membered fused rings.
- Understand and discuss the reactivity and stability of such bicyclic hetero aromatic compounds.
- Study the important synthetic routes and reactivity for five and six-membered benzo-fused hetero aromatic compounds.
- Understand the important physical and chemical properties of five and six-membered benzo-fused hetero aromatic compounds.
- Know about the applications of these five and six-membered benzo-fused hetero aromatic compounds in the synthesis of important industrial and pharmaceutical compounds.

6.3 PREPARATION AND REACTIONS OF INDOLE, QUINOLINE AND ISOQUINOLINE

"The preparation, properties, and reactions of indole, quinoline, and isoquinoline are discussed below."

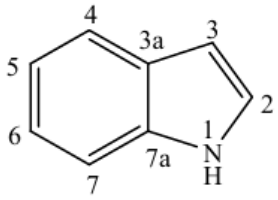
6.3.1 Indole

Indole is an aromatic heterocyclic organic compound with the formula C_8H_7N. It has a bicyclic structure, consisting of a six-membered benzene ring fused to a five-membered nitrogen-containing pyrrole ring. The chemistry of Indole was developed with the study of the dye indigo. Indigo can be converted to Isatin and then to Oxindole. Indole was first synthesised in 1866, when Adolf von Baeyer reduced Oxindole to Indole using zinc dust. The name Indole is a combined name of the words indigo and oleum, since Indole was first isolated by treatment of the indigo dye with oleum. Indole is widely distributed in the natural environment and can be produced by a variety of bacteria. As an intercellular signal molecule, it regulates various aspects of bacterial physiology, including spore formation, plasmid stability, drugs resistance, bio-film formation, and virulence. The amino acid tryptophan is an Indole derivative and the

precursor of the neurotransmitter serotonin. Certain Indole derivatives were important dyestuffs until the end of the 19th century. In the 1930s, interest in Indole intensified when it became known that the Indole substituent is present in many important alkaloids (e.g., tryptophan and auxins), and it remains an active area of research today. Indole is found in coal tar and in essential oils (jasmine oil, orange oil) of many plants. It also occurs in amino acids as a plant growth hormone in alkaloids.

6.3.1.1 Structure of Indole:

The IUPAC name of Indole is 1H-benzo[b] pyrrole, it is the b face benzo-fused isomer. The atoms are numbered as shown in the structure below. The numbering begins from the Nitrogen atom and goes counterclockwise around the two condensed rings.



All the ring atoms in Indole are sp2 hybridised. The sp2 orbitals of all carbon and nitrogen atoms overlap with each other and also with the s orbitals of hydrogen to form C-C, C-N, C-H and N-H σ bonds. Each ring atom also possesses a p orbital. These are perpendicular to the plane of the ring. Lateral overlap of these p-orbitals produces a π molecular orbital containing 10 electrons. Indole is an aromatic compound since it follows Huckel's rule (i.e. 4n+2π electron rule) for n=2. Indole is a resonance hybrid of several canonical forms. The different possible canonical forms of Indole are shown in Figure 2. Structures IV, V and VI involve the formation of a non-benzenoid system in which the aromaticity of the benzene ring dose not retained. Hence, these structures contribute less to the resonance.

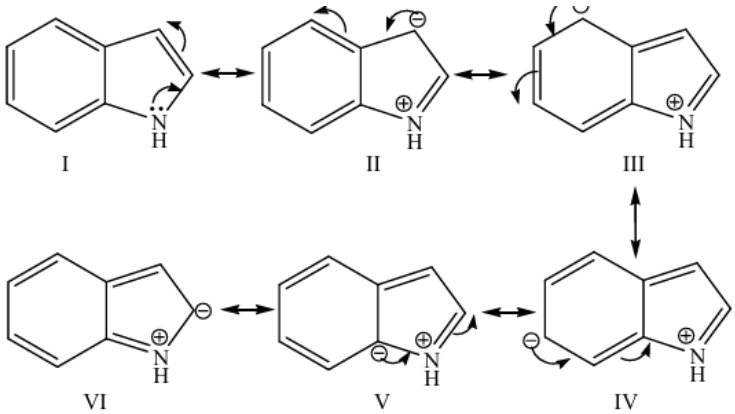
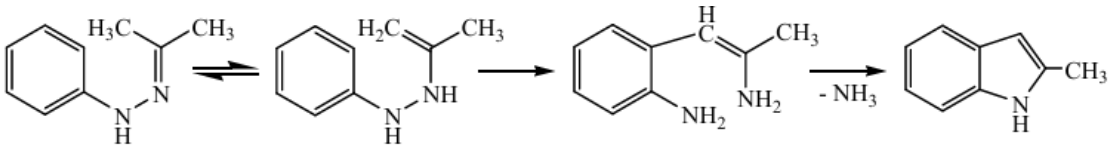


Figure 2: Different possible canonical forms of Indole

6.3.1.2 Synthesis or preparation of Indole

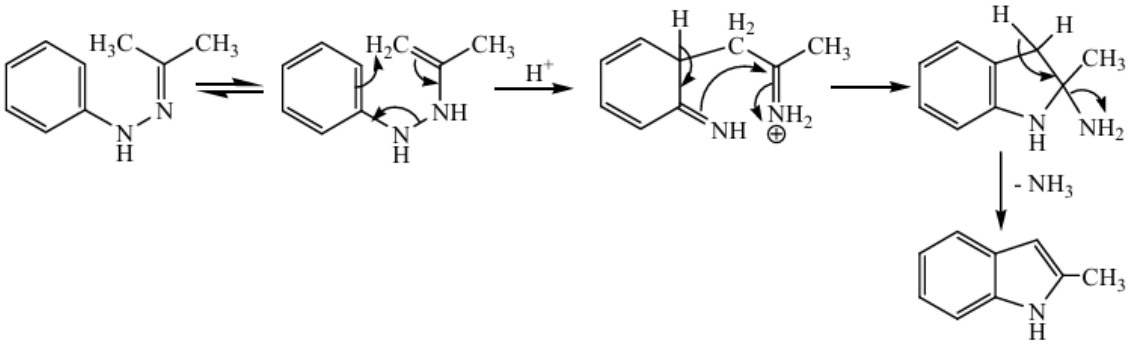
There are different methods available for the synthesis of Indole and its derivatives. These methods differ in their range of applicability. However, several general methods are also known in which the pyrrole ring is formed through the ring closure reactions. The important methods for the synthesis of Indole are discussed below.

1. ***The Fisher-Indole synthesis:*** This is the most widely used method for the synthesis of Indole. It involves an acid (Lewis acid) catalysed rearrangement of a phenylhydrazone of an aldehyde or ketone, with the elimination of a molecule of ammonia. The conventional catalysts used in this process are zinc chloride, polyphosphoric acid or a Lewis acid (BF3). Synthesis of 2-methyl indole can be achieved by taking the phenylhydrazone of acetone. The reaction is as shown below.

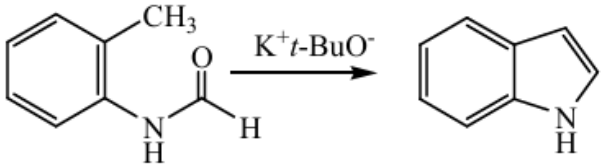


2-methyl-1*H*-indole

Mechanism: Fisher–Indole synthesis is supposed to take place through the acid-catalysed rearrangement of the tautomeric form of the starting phenylhydrazone, as shown below.

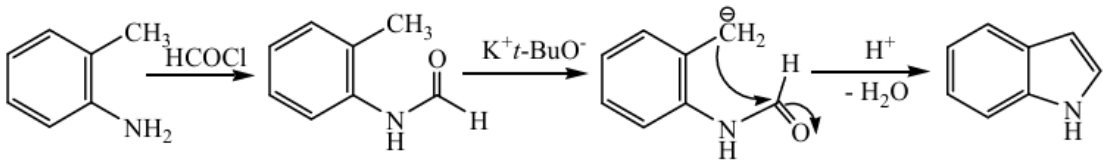


2. ***The Madelung Synthesis:*** This involves the cyclic dehydration of an acyl o-toluidine in the presence of a strong base and at high temperature. Indole itself can be prepared by this method. 2-alkylindole can be synthesised by the cyclodehydration of o-acyl aminotoluene by treatment with a strong base such as potassium tertiary butoxide or sodamide. The reaction is shown as below.

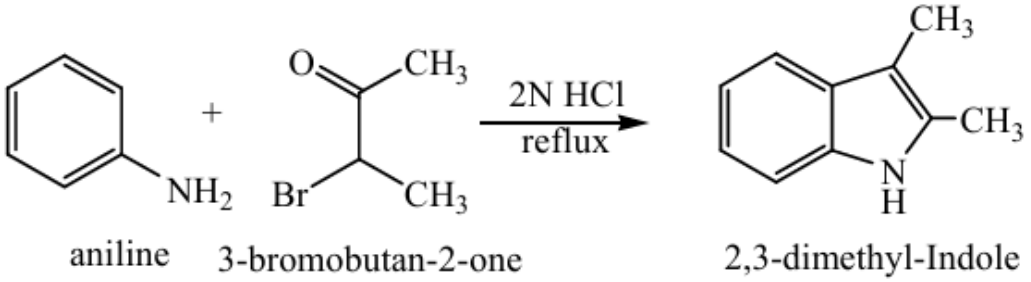


N-*o*-tolylformamide Indole

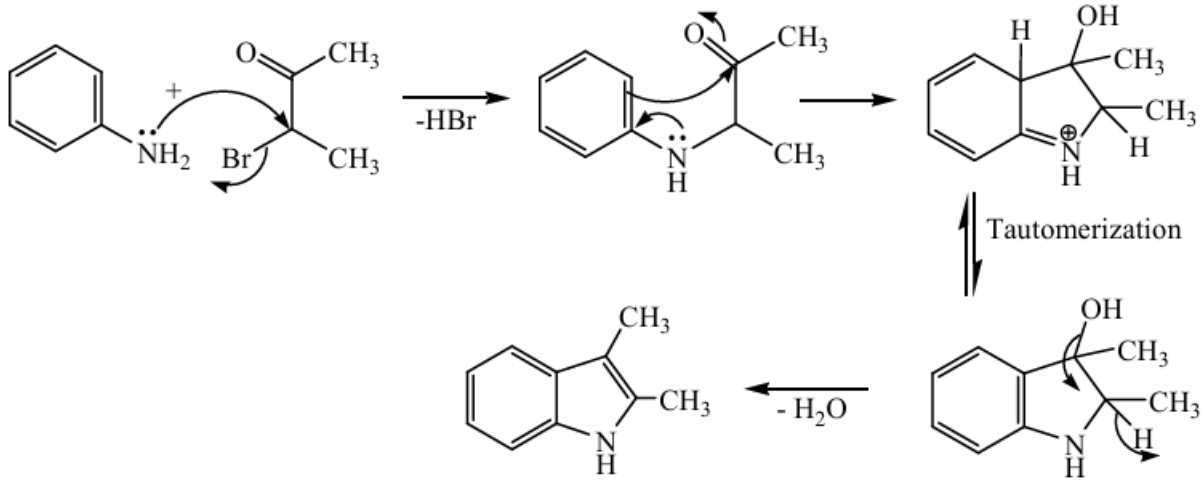
Mechanism: o-amino toluene forms o-acyl aminotoluene on treatment with formyl chloride. The o-acyl aminotoluene, on reaction with a strong base, gives the corresponding carbanion. The subsequent protonation, followed by elimination of a water molecule, leads to the formation of Indole. The overall mechanism is shown as follows.



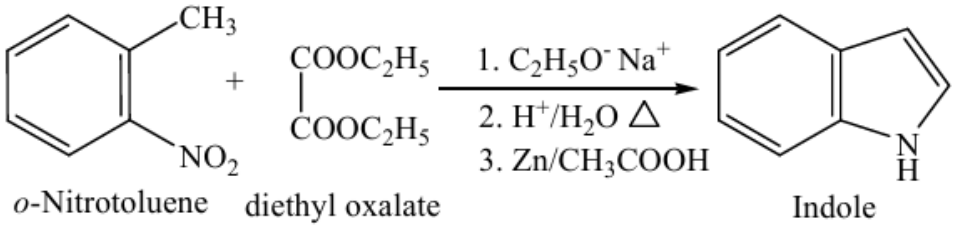
3. **The Bischler's synthesis:** This method involves the reaction of an aryl amine and α-haloketone or α-haloaldehyde in presence of zinc chloride under thermal or heating conditions. The reaction is shown as follows.



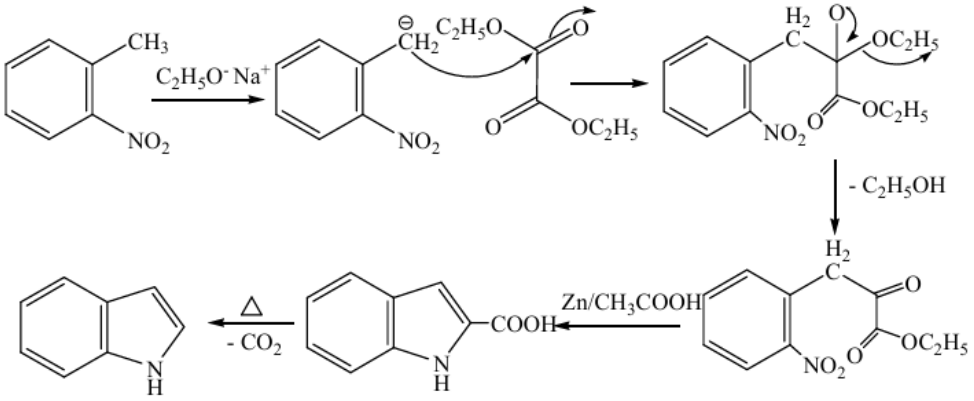
Mechanism: The mechanism of Bischler's Indole synthesis involves the following steps. Reaction of aniline with α-bromoketone (3-Bromo-2-butanone) in the presence of acid under reflux conditions gives the condensed product with elimination of the HBr molecule. Which, on thermal cyclisation and subsequent aromatisation, leads to the formation of 2,3-dimethyl Indole.



4. **The Reissert Synthesis:** This method also provides a very simple and convenient procedure for the synthesis of Indole and its derivatives. This method involves the base-catalysed condensation of o-nitrotoluene with oxalic acid ethyl ester (diethyl oxalate) in the presence of a strong base like sodium ethoxide. This condensation leads to the formation of o-nitro-phenylpyruvate, which on hydrolysis gives the corresponding acid. The resultant acid on reductive cyclisation in the presence of Zn/CH_3COOH yields the Indole. The reaction is shown as follows.



Mechanism: o-Nitrotoluene, on reaction with sodium ethoxide, produces a carbanion which, on condensation with diethyl oxalate, yields the o-nitro-phenylpyruvate. The acidic hydrolysis converts the o-nitro-phenylpyruvate in to corresponding acid. The reductive cyclisation followed by the decarboxylation gives the formation of Indole.



6.3.2 Physical Properties of Indole:

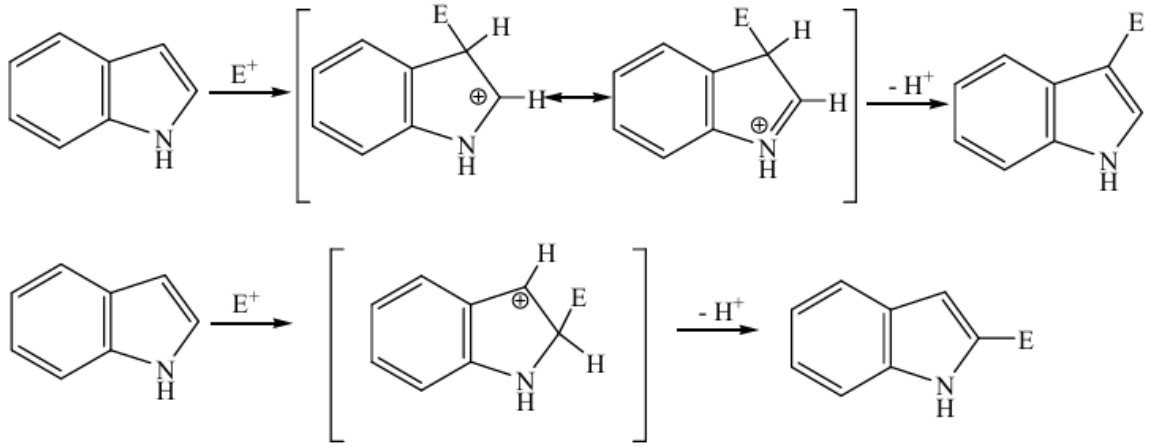
Indoles and simple alkyl Indoles are colourless crystalline solids. The melting point of Indole is 52°C, and the boiling point is 254°C. Indole is soluble in most organic solvents. The pure form of Indole has a very pleasant smell, and this is the reason it is used as a perfumery base; however, the impure Indole has a very unpleasant smell. The main commercial source of Indole comes from the 220-260°C fraction of coal tar distillation.

The 1H NMR spectra of Indole feature all the resonances for the hydrogen in the aromatic region. The upfield shift observed for H3 and C3 in the 1H and 13C NMR indicates the higher electron density around C3.

6.3.3 Chemical Properties of Indole

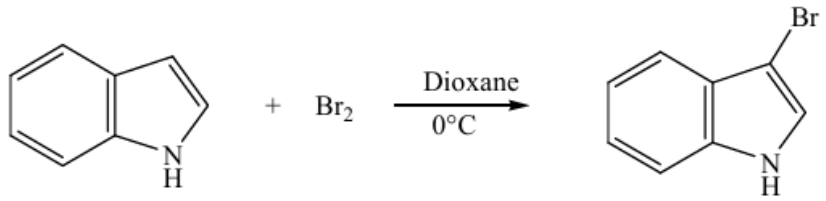
6.3.3.1 Electrophilic substitution reactions

Indole is a π-excessive aromatic heterocycle with ten π electrons. Indole is an aromatic compound. It involves the 4n+2 π electrons and hence follows the Huckel rule of aromaticity. The lone pair of the sp^2-hybridised nitrogen atom participates in the delocalisation process and thus helps to complete the ten π-electrons across the ring. Like pyrrole, the π-excessive nature of the aromatic ring governs the reactivity and chemical properties of Indole. Indole is a weak base (pKa=-2.4). In the presence of a strong acid, protonation of the nitrogen atom would disrupt the aromaticity of the five-membered ring. Like other aromatic compounds, Indole also gives the electrophilic substitution (the characteristic reactions of aromatic compounds). However, unlike pyrrole, electrophilic substitution in Indole takes place preferentially at C3. A simple explanation for this can be made by analysis of the Wheland intermediates resulting from the attack of an electrophile at C3 and C2 positions. For a reaction at C-3, the energy of activation of the intermediate is lowered because it is possible to delocalize the positive charge through resonance involving the nitrogen lone pair of electrons. This favourable situation is not possible in the corresponding intermediate for attack at C-2.



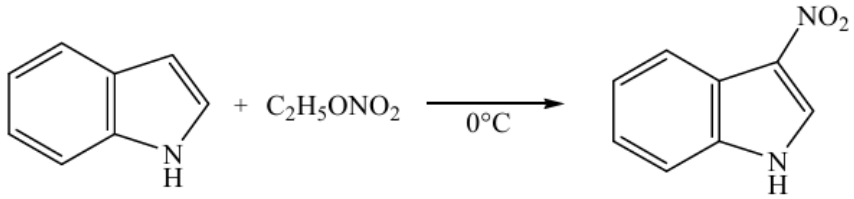
The intermediate of the attack at C3 is stabilised by delocalisation of the positive charge. However, no delocalisation is possible in the intermediate derived from attack at C2 position without disrupting the aromaticity of the six-membered rings. The common electrophilic substitution reactions of Indole are discussed as follows.

1. ***Bromination:*** Indole undergoes bromination at very low temperature (0°C) in dioxane. The bromination occurs at C3 position.

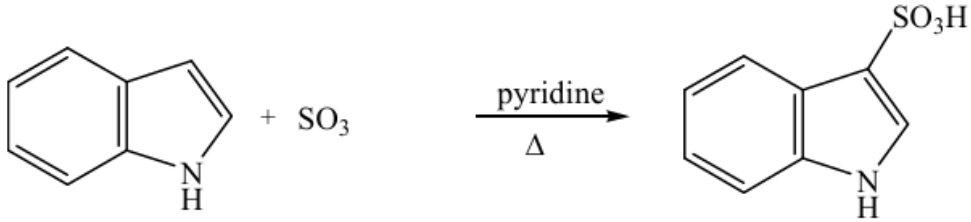


The mechanism of bromination is similar as discussed above the general mechanism of electrophilic substitution. In the above mechanism, the E can be replaced by Br.

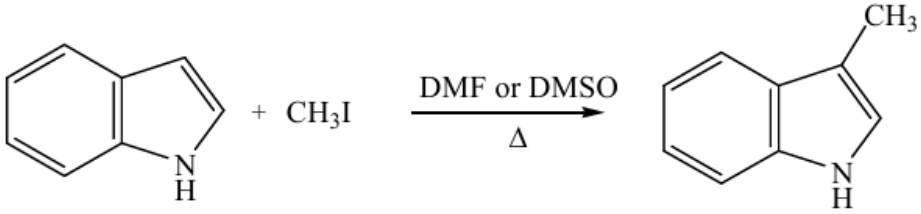
2. ***Nitration:*** Indole undergoes nitration in the presence of ethyl nitrate at low temperature (0 - 5°C). Nitration of Indole also occurs at C3 with a similar mechanism as discussed above.



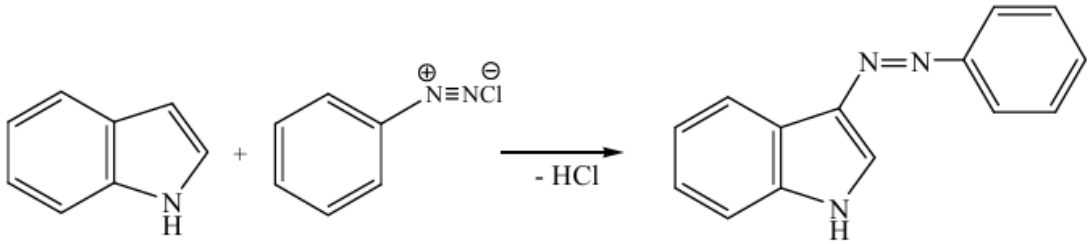
3. ***Sulphonation:*** Sulphonation of Indole is carried out only under milder conditions using pyridine-sulphur trioxide complex to minimise the acidity of the reagent.



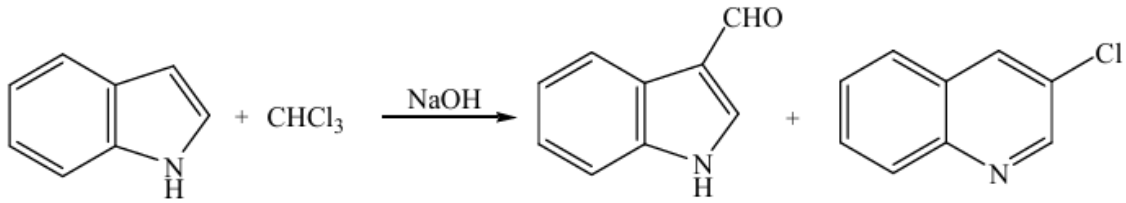
4. ***Friedel crafts alkylation:*** Indole undergoes alkylation at C3 position with alkyl iodide in N, N-dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO) as solvent.



5. ***Diazocoupling or Diazotisation reaction:*** Indole reacts with benzene diazonium chloride to give 3-phenylazoindole, a diazotised coupled product.



6. ***Reimer Tiemann formylation:*** Indole, like other aromatic compounds, reacts with Chloroform (CHCl3) in presence of alkali to give formylated product at C3 position. This reaction proceeds via carbine intermediate. In general, two products are obtained in this reaction, first, the C3 formylated product (Indole-3-cabaldehyde) and second, the rearranged product (3-Chloroquinoline).



Indole-3-carbaldehyde 3-Chloroquinoline

6.3.4 Applications of Indole and its Derivatives

Indole and its derivatives are being extensively used in medicinal and pharmaceutical industry. Indole derivative Indigo is also used as a dyestuff called in Textile industry.

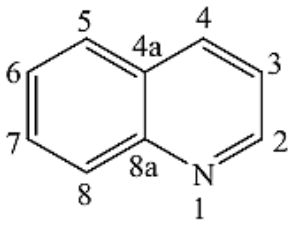
6.3.5 Quinoline

Quinoline is a heterocyclic aromatic organic compound with the chemical formula C_9H_7N. It is a colourless hygroscopic liquid with a strong odor. It is a bicyclic heterocycle having a benzene ring fused with a pyridine ring at 2, 3-positions. It is also called 1-azanaphthalene or benzo[b]pyridine. Quinoline was first extracted from coal tar in 1834 by German chemist Friedlieb Ferdinand Runge; he called quinoline leukol ("white oil" in Greek). Coal tar remains the principal source of commercial quinoline. In 1842, French chemist Charles Gerhardt obtained a compound by dry distilling quinine, strychnine, or cinchonine with potassium hydroxide; he called the compound Chinoilin or Chinolein. Runge's and Gephardt's compounds seemed to be distinct isomers because they reacted differently. However, the German chemist August Hoffmann eventually recognized that the differences in behaviors were due to the presence of contaminants and that the two compounds were actually identical. Like other nitrogen heterocyclic compounds, such as pyridine derivatives, quinoline is often reported as an environmental contaminant associated with facilities processing oil shale or coal, and has also been found at legacy wood treatment sites. Owing to its relatively high solubility in water quinoline has significant potential for mobility in the environment, which may promote water contamination. Quinoline is readily degradable by certain microorganisms, such as Rhodococcus species Strain Q1, which was isolated from soil and paper mill sludge. Quinolines are present in small amounts in crude oil within the virgin diesel fraction. It can be removed by

the process called hydrodenitrification. Quinoline is only slightly soluble in cold water but dissolves readily in hot water and most organic solvents. Quinoline itself has few applications, but many of its derivatives are useful in diverse applications. A prominent example is quinine; an alkaloid found in plants. 4-Hydroxy-2-alkylquinolines (HAQs) are involved in antibiotic resistance.

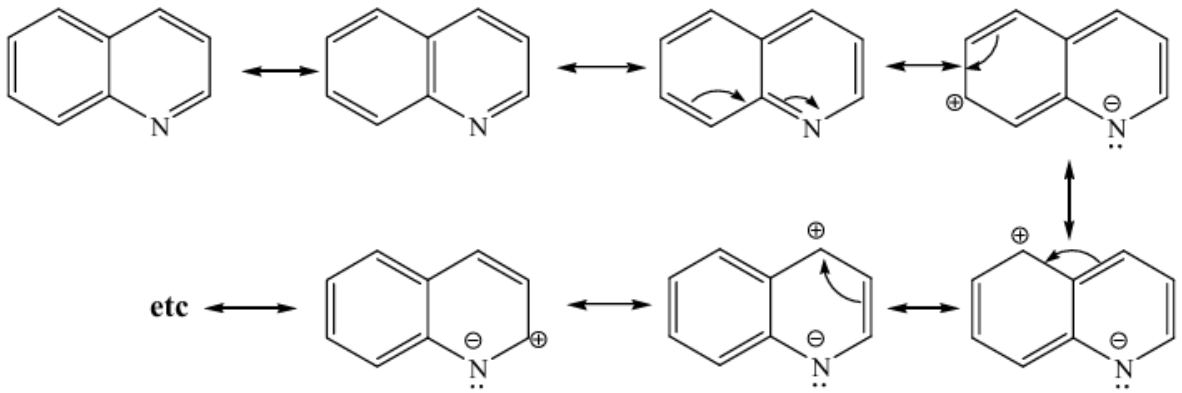
6.3.5.1 Structure of Quinoline

The IUPAC name of quinoline is benzo[b] pyridine, it is being the b-face benzo-fused isomer. The atoms are numbered as shown in structure below. The numbering begins from the Nitrogen atom and going counter clock wise around the two condensed rings. The structure of quinoline is shown as follows.



Quinoline

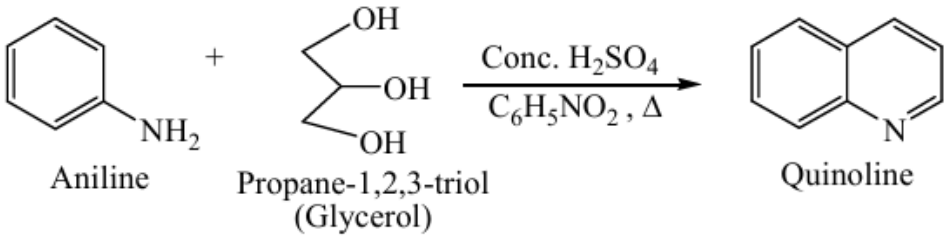
All the ring atoms in Quinoline are sp^2 hybridised. The sp^2 orbitals of all carbon and nitrogen atom overlap with each other and also with the s orbitals of hydrogen to form C-C, C-N, and C-H π bonds. Each ring atom also possesses a p orbital. These p orbitals are perpendicular to the plane of the ring. Lateral overlap of these p-orbitals produces a π molecular orbital containing 10 electrons. Quinoline is an aromatic compound since it follows Huckel's rule (i.e. 4n+2 π electron rule) for n=2. Unlike Indole, the lone pair of nitrogen of quinoline does not participate in the delocalisation. Quinoline is a resonance hybrid of several canonical forms, as shown below.



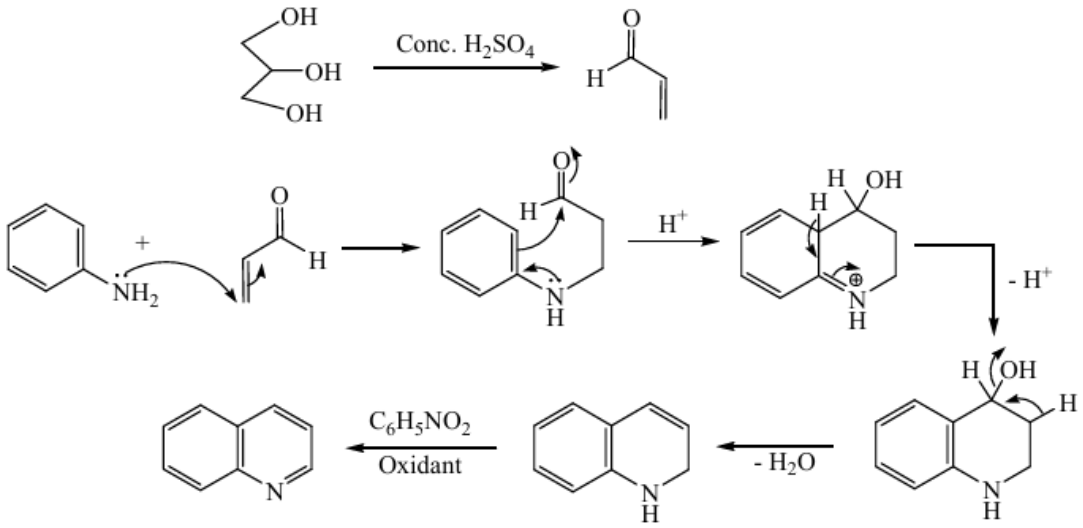
6.3.5.2 Synthesis or preparation of Quinoline

There are different methods available for the synthesis of quinoline and its derivatives. These methods may differ in their range of applicability. However, a number of general well known methods have been used for the preparation of quinoline. The important methods for the synthesis of quinoline are discussed below.

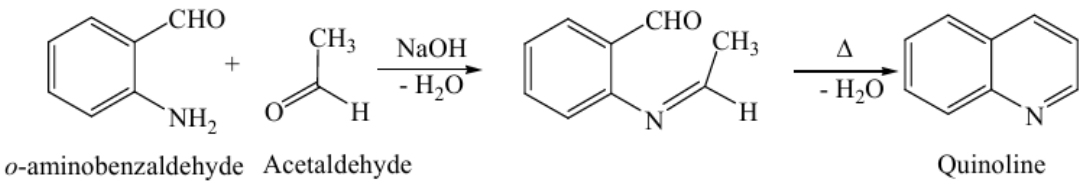
1. ***The Skraup synthesis:*** This is one of the most important methods for the preparation of quinoline. In this method, the aniline and its derivatives having a vacant ortho position is when heated with glycerol, concentrated H_2SO_4 and an oxidising agent the resultant product is obtained as quinoline or its derivatives. The nitrobenzene is generally used as mild oxidising agent in Skraup synthesis. Glycerol, when heated with concentrated H_2SO_4, gives acrolein after dehydration. Condensation of acroline thus obtained with aniline or its derivatives, followed by oxidation, gives the quinoline. The reaction is shown as follows.



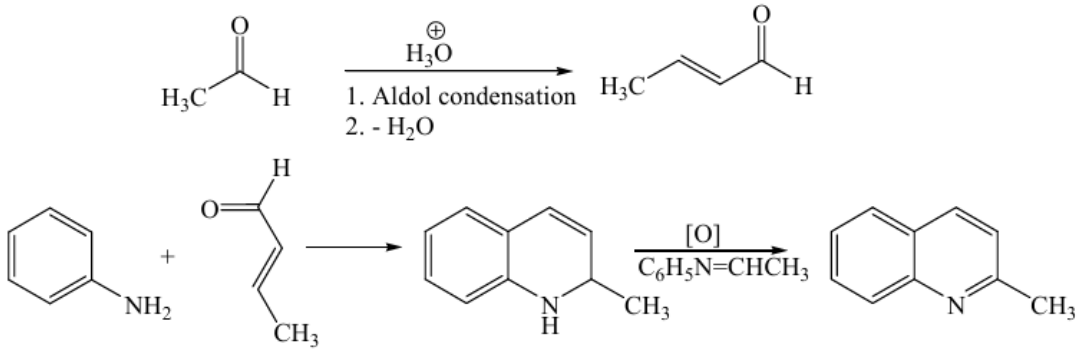
Mechanism: The stepwise mechanism of the Skraup synthesis of quinoline is given as follows.



2. ***The Friedlander's synthesis:*** Quinoline can also be prepared by the condensation of o-aminobenzaldehyde with acetaldehyde in sodium hydroxide solution. The reaction mechanism is shown as follow.



3. ***The Dobner-Miller Synthesis:*** This is a modified form of the Skraup synthesis. In this reaction, the simple aldehydes and ketones act as precursors of α, β-unsaturated carbonyl compounds. The reaction follows a similar reaction course as in the Skraup synthesis to produce derivatives of quinoline. When acetaldehyde is used as a precursor of α, β-unsaturated carbonyl compound, 2-methylquinoline is formed. The reaction mechanism is shown as follows.



6.3.5.3 Physical Properties of Quinoline:

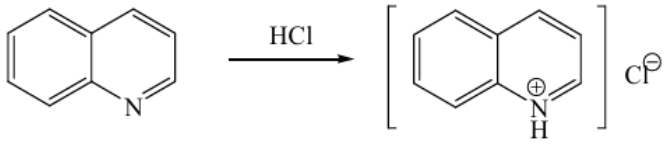
Quinoline is a colourless, hygroscopic liquid. Its boiling point is 237 °C. It has a characteristic smell similar to that of pyridine. On exposure to air quinoline turns in to yellow coloured. It is miscible in organic solvents. Quinoline is highly aromatic in nature and it has a resonance energy 47.3 kcal/mole. Quinoline is a weak base with having pKa 4.94. The basicity of quinoline is intermediate between aniline (pKa 4.58) and pyridine (pKa 5.17).

6.3.5.4 Chemical Properties of Quinoline:

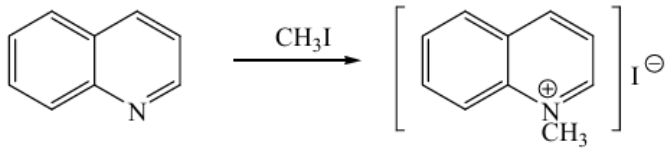
The important chemical properties of quinoline are discussed as follows.

1. ***Basicity:*** Due to the availability of a lone pair of electrons on nitrogen, quinoline acts as a base and forms salts with acids and quaternary salts with alkyl halides.

a. Reaction with acids:

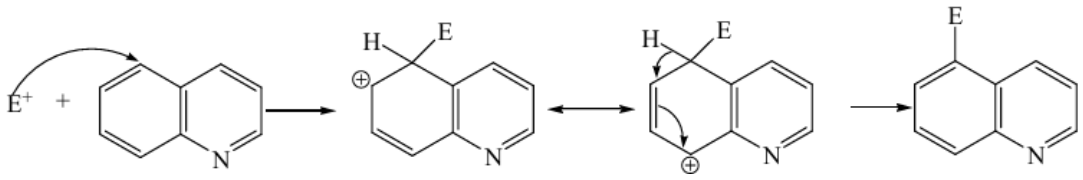


b. Reaction with methyl iodide:

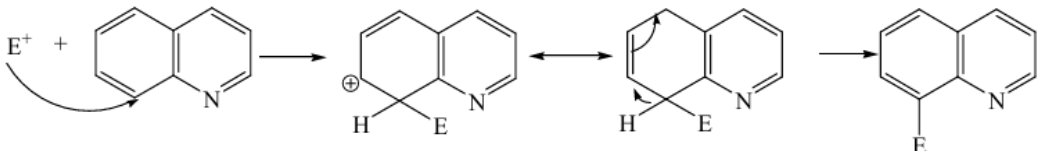


2. Electrophilic substitution: Out of the two fused rings in quinoline, the carbocyclic (benzene) ring is relatively more electron-rich and resembles benzene ring while the nitrogen-containing ring (less electron rich) resembles with pyridine ring. Therefore, the electrophilic substitution in quinoline takes place more readily at benzene ring (at position 5 and 8 of benzene ring) rather than the pyridine ring. Thus, if both the positions in benzene ring are vacant than mixture of substituted product is obtained. The general mechanism of electrophilic substitution on quinoline is shown below.

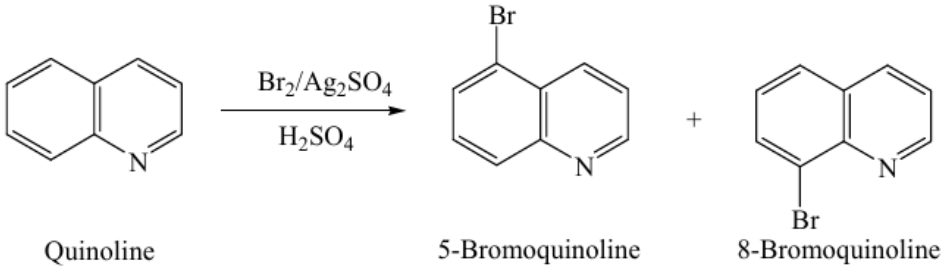
a. At position 5



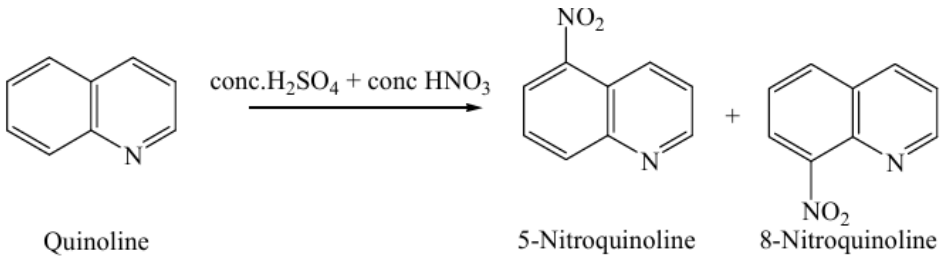
b. At position 8



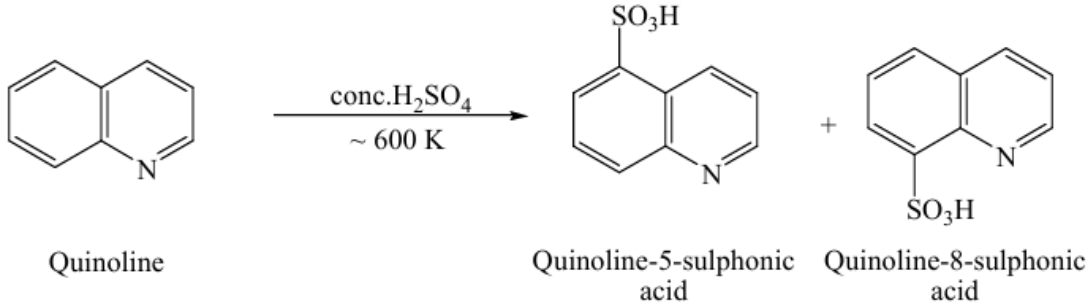
i. Bromination: Quinoline undergoes bromination with Br2 in presence of silver sulphate (Ag_2SO_4) and H_2SO_4. Bromination occurs at positions 5 and 8 hence mixture of products is formed.



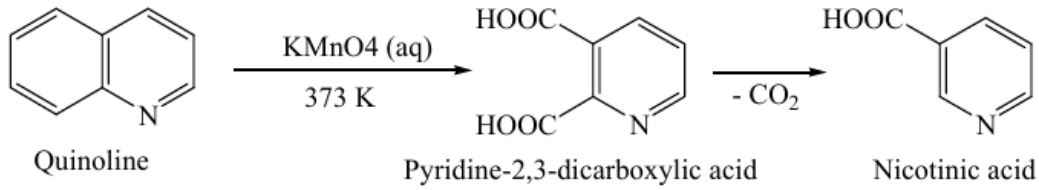
ii. Nitration: Quinoline can undergo nitration by reacting with the well-known nitrating agent (Conc. H_2SO_4 + conc. HNO_3). Nitration of quinoline occurs at positions 5 and 8.



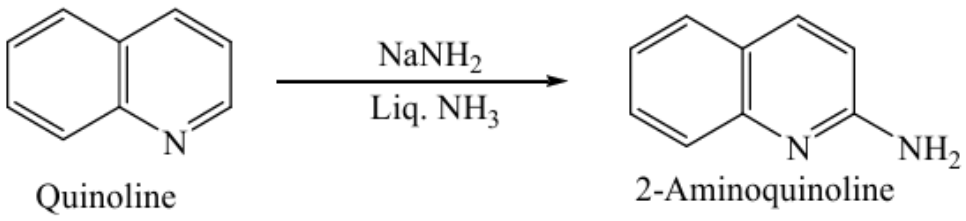
iii. Sulphonation: In the presence of Conc. H_2SO_4 at high temperature (~600K), sulphonation of quinoline takes place. Like nitration or bromination, the sulphonation of quinoline occurs at positions 5 and 8.



iv. Oxidation: In the presence of $KMnO_4$, quinoline get oxidised to pyridine-2,3 dicarboxylic acid, which on decarboxylation gives nicotinic acid.



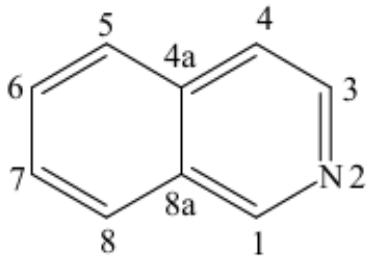
3. Nucleophilic substitution: Quinoline also gives nucleophilic substitution reactions. Since, pyridine ring of quinoline is comparatively lesser electron-rich in comparison to the benzene ring, therefore, nucleophilic substitution in quinoline takes place on the pyridine ring. The nucleophilic substitution on the pyridine ring takes place at position 2 of the pyridine ring. If position 2 is occupied, then the substitution takes place at position 4. Reaction of quinoline with strong base sodium amide (sodamide, $NaNH_2$) in liquid ammonia gives 2 aminoquinoline.



6.3.5.5 Applications of Quinoline:

- As a high-boiling basic solvent in organic reactions
- Quinoline is used in the manufacture of dyes, the preparation of hydroxyquinoline sulfate and niacin. It is also used as a solvent for resins and terpenes.
- Quinoline is mainly used as in the production of other speciality chemicals.
- Its principal use is as a precursor to 8-hydroxyquinoline, which is a versatile chelating agent and precursor to pesticides.
- Its 2- and 4-methyl derivatives are precursors to cyanine dyes. Oxidation of quinoline affords quinolinic acid (pyridine-2,3-dicarboxylic acid), a precursor to the herbicide sold under the name "Assert".
- The reduction of quinoline with sodium borohydride in the presence of acetic acid is known to produce Kairoline A.
- The piperazine antidepressant quipazine is also leucoline-based.

6.3.6 Isoquinoline



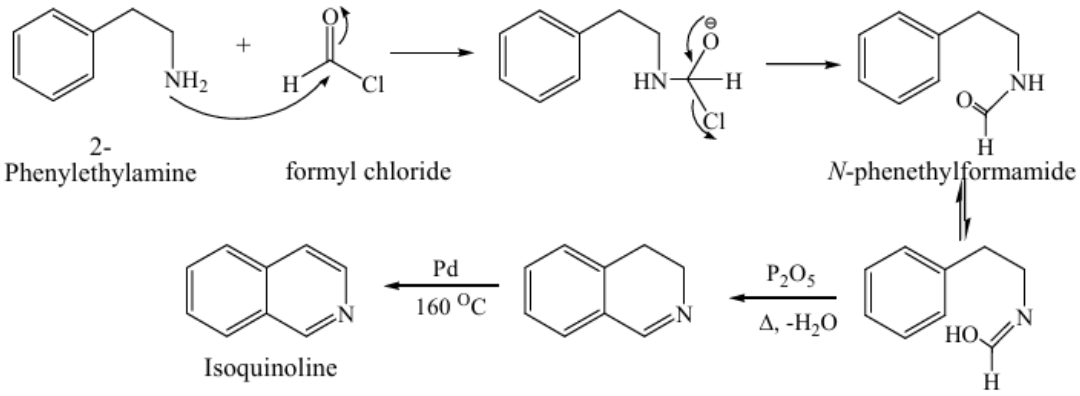
Isoquinoline

Isoquinoline is a heterocyclic aromatic organic compound. It is a structural isomer of quinoline. Isoquinoline is also obtained by ring fusion of pyridine and with a benzene ring. It was first isolated by Hoogewerff and Drop from the quinoline fraction of coal tar in 1885. Several derivatives of Isoquinoline also occur in coal tar. Isoquinoline does not occur free in nature but is founds frequently in several alkaloids. It is called 2-azanaphthalene or benzo[b]pyridine. The numbering of the atoms in Isoquinoline is similar as followed in quinoline; however, the nitrogen atom is assigned position-2. Isoquinoline has close similarities in the structure with quinoline; therefore, both have a close relationship in their physical and chemical properties.

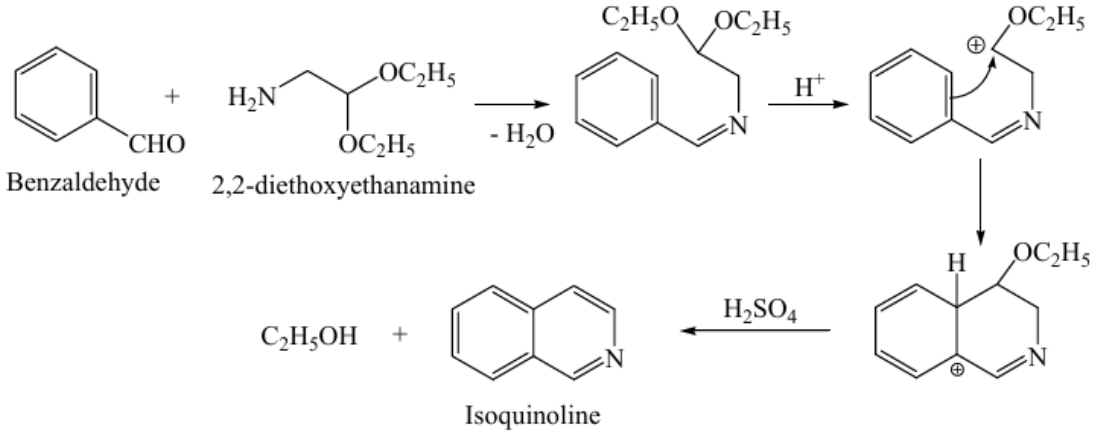
6.3.6.1 Synthetic Methods of Isoquinoline:

Following are the important synthetic methods for the preparation of Isoquinoline.

1. ***The Bischler Napieralski synthesis:*** This synthesis was first suggested by Bischler and Napieralski and has been subjected to several improvements later on. This method involves the cyclodehydration of an acyl derivative of B-phenylethylamine to give 3,4-dihydroisoquinoline, in the presence of Lewis acids such as polyphosphoric acid, zinc chloride or phosphorous pentoxide. The 3,4-dihydroisoquinoline is then dehydrogenated by Pd at 160 °C to Isoquinoline. It must be noted that the yields of this reaction are excellent if electron-donating groups are present on the benzene ring however, if the electron-withdrawing groups are present on the benzene ring, the yields are very poor. This is because of the electrophilic ring closure nature of the ring.



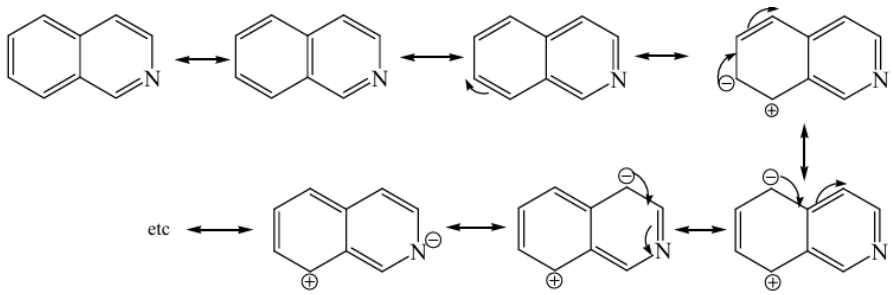
2. ***The Pomeranz Fritsch synthesis:*** In this synthesis, an aromatic aldehyde or a substituted Benzaldehyde is condensed with an aminoacetal to give Schiff's base. The Schiff's base thus formed is cyclized in the presence of H2SO4 or P2O5. The last step of this reaction is similar to the Skraup synthesis of quinoline.



6.3.6.2 Physical Properties of Isoquinoline:

Isoquinoline is a colourless solid with a melting point 243 °C. It has a smell resembling that of Benzaldehyde. It is a stem volatile and sparingly soluble in water but soluble in most of the

organic solvents such as ethanol, acetone, diethyl ether, carbon disulfide, and other common organic solvents. It is also soluble in dilute acids as the protonated derivative. Isoquinoline is highly aromatic and may be considered a resonance hybrid of the following structures. Similar to pyridine, the lone pair of electrons on the nitrogen atom is not conjugated with the ring and therefore, Isoquinoline behaves as a weak base.

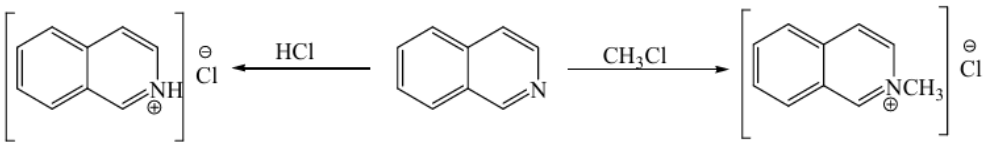


The pKa of Isoquinoline is 5.14 in comparison to quinoline (pKa 4.94). It gets protonated to form salts upon treatment with strong acids, such as HCl. It forms adducts with Lewis acids, such as BF_3.

6.3.6.3 Chemical Properties of Isoquinoline:

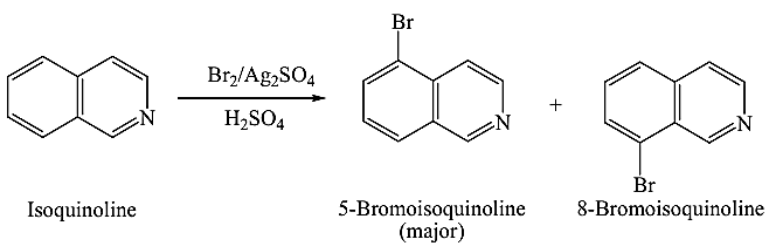
The important chemical properties of Isoquinoline are discussed as follows.

1. ***Basicity***: Isoquinoline is a moderately basic compound. It reacts with protic acid to form salts, and with alkyl halides to form quaternary ammonium salt.

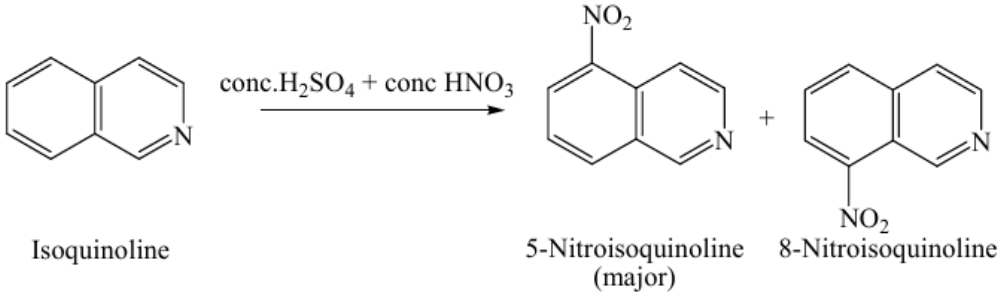


2. **Electrophilic substitution:** Isoquinoline also gives electrophilic substitution like quinoline. Electrophilic substitution on Isoquinoline takes place more preferentially at position 5 however small amount of substitution also occurs at position 8. The different types of electrophilic substitution reactions of Isoquinoline are discussed as follows.

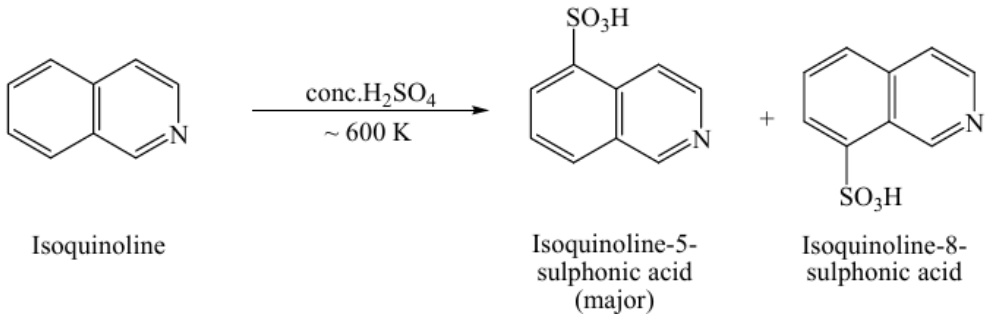
   i. Bromination: Isoquinoline undergoes bromination with Br_2 in the presence of silver sulphate (Ag_2SO_4) and H_2SO_4. Bromination occurs preferentially at position 5; a small amount of product is also formed with substitution at position 8.



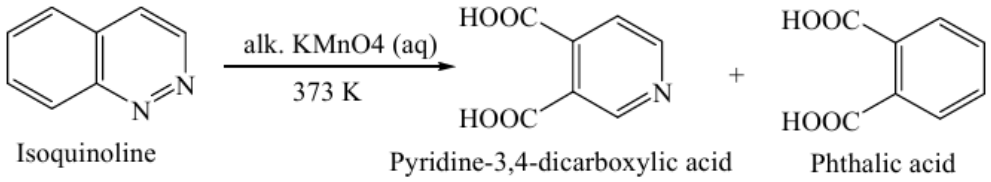
ii. ***Nitration:*** Isoquinoline can undergo nitration by reacting with the well-known nitrating agent (Conc. H_2SO_4 + conc. HNO_3). Nitration of Isoquinoline occurs preferentially at position 5; a small amount of product is also formed with substitution at position 8.



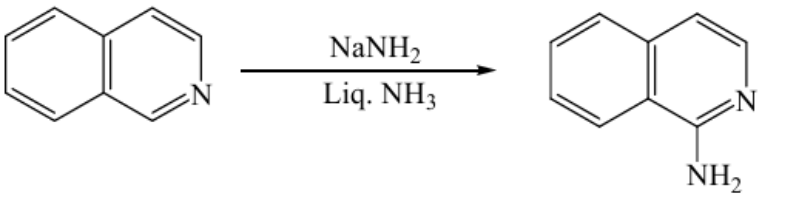
iii. ***Sulphonation:*** In the presence of Conc. H_2SO_4 at high temperature (~600K), sulphonation of Isoquinoline takes place. Like nitration or bromination, the sulphonation of Isoquinoline occurs preferentially at position 5; a small amount of product is also formed with substitution at position 8.



vi. Oxidation: In the presence of alkaline $KMnO_4$, Isoquinoline get oxidised to equimolar mixture of phthalic acid and pyridine-3,4-dicarboxylic acid.



3. ***Nucleophilic substitution***: Like Quinoline, Isoquinoline also gives nucleophilic substitution reactions. Since, pyridine ring of Isoquinoline is comparatively lesser electron-rich in comparison to the benzene ring, therefore, nucleophilic substitution in Isoquinoline takes place on the pyridine ring. The nucleophilic substitution on pyridine ring takes place at position 1 of the pyridine ring. Reaction of Isoquinoline with strong base sodium amide (sodamide, $NaNH_2$) in liquid ammonia gives 1-aminoisoquinoline.



Isoquinoline 1-Aminoisoquinoline

6.3.6.4 Applications of Isoquinoline:

Isoquinolines have various applications as:

- Isoquinoline and its derivatives are used in the manufacture of dyes, paints, insecticides, disinfectants, anaesthetics, antihypertension agents and antifungal agents.
- It is also used as a solvent for the extraction of resins and terpenes, and as a corrosion inhibitor.

6.4 SUMMARY

This unit focuses on condensed heterocyclic compounds containing five- and six-membered benzo-fused rings, with emphasis on Indole, Quinoline, and Isoquinoline. It explains their structure, aromaticity, resonance behavior, physical properties, and chemical reactivity. The unit discusses major synthetic methods such as Fischer-Indole, Skraup, Friedländer, Madelung, Reissert, and Bischler-Napieralski syntheses.

Indole is described as a benzopyrrole system showing high reactivity at the C-3 position in electrophilic substitution reactions and having significant biological and industrial applications. Quinoline and Isoquinoline, which are benzopyridine isomers, exhibit electrophilic substitution mainly on the benzene ring and nucleophilic substitution on the pyridine ring, and serve as precursors for dyes, pharmaceuticals, and speciality chemicals. The unit highlights their environmental occurrence, industrial relevance, and role in medicinal chemistry.

6.5 TERMINAL QUESTIONS

1. What are benzo-fused heterocyclic compounds? Give examples discussed in this unit.

2. Explain the structure and aromaticity of Indole with reference to Huckel's rule.
3. Describe the Fischer-Indole synthesis with a mechanism.
4. Why does electrophilic substitution in Indole occur preferentially at the C-3 position?
5. Discuss the Skraup synthesis of Quinoline and write its mechanism.
6. Compare the electrophilic and nucleophilic substitution reactions in Quinoline.
7. What are the major physical and chemical properties of Quinoline?
8. Write short notes on Bischler-Napieralski synthesis of Isoquinoline.
9. Mention at least four industrial or pharmaceutical applications of Indole or Quinoline derivatives.
10. Differentiate between Quinoline and Isoquinoline based on structure and reactivity.

6.6 REFERENCES

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Unit-7 NATURAL PRODUCTS

CONTENTS:

7.1 INTRODUCTION

Natural products are organic compounds produced by living organisms such as plants, animals, and microorganisms. They form an important class of naturally occurring biomolecules that play significant roles in biological systems and human life. Many natural products possess medicinal, pharmacological, and industrial importance and serve as the basis for numerous modern drugs, flavours, fragrances, and essential oils.

Among natural products, **terpenoids and alkaloids** are two major groups of great structural diversity and chemical interest. Terpenoids are widely distributed in plants and are responsible for characteristic aromas, resins, and essential oils. Alkaloids, on the other hand, are nitrogen-containing compounds commonly found in medicinal plants and exhibit strong physiological and therapeutic activities.

This unit focuses on the basic concepts related to natural products, with special emphasis on the **classification, properties, extraction techniques, and structural elucidation** of selected terpenoids and alkaloids such as **limonene, citral, nicotine, and cocaine**. The study of these compounds helps in understanding their chemical nature, biological significance, and practical applications in pharmaceutical and chemical industries.

7.2 OBJECTIVES

After completing this unit, the learner will be able to:

1. Understand the meaning and importance of natural products in chemistry and biological systems.
2. Explain the classification of natural products, especially terpenoids and alkaloids.
3. Describe the general properties and characteristics of terpenoids.
4. Understand the methods of extraction and general approaches to structure determination of terpenoids.
5. Study the structure and important features of selected terpenoids such as limonene and citral.
6. Explain the nature, occurrence, and general properties of alkaloids.
7. Discuss the structures and basic characteristics of important alkaloids such as nicotine and cocaine.

7.3 CLASSIFICATION

Terpenoid polyhydrocarbons, with few exceptions, have the molecular formula $(C_5H_8)n$ and the value of n has been used as a basis for the classification of terpenoids.

S.No.	Value of n	formula	classes
1.	2	$C_{10}H_{16}$	monoterpenoid
2.	3	$C_{15}H_{24}$	sesquiterpenoid
3.	4	$C_{20}H_{32}$	diterpenoid
4.	5	$C_{25}H_{40}$	sester terpenoid
5.	6	$C_{30}H_{48}$	triterpenoid
6.	8	$C_{40}H_{64}$	tera terpenoid (carotenoids)
7.	>8	$(C_5H_8)_n$	Polyterpenoids

The simpler mono-and sesqui-terpenoids and the related oxygen-containing substances are highly widespread in the plant kingdom. Volatile oils contained in different parts of the plants are separated by steam distillation. These are called essential oils and have a strong and. pleasant odour. This oil is responsible for the odour and flavour associated with plants. Essential oils are mixtures of terpenoid hydrocarbons and their oxygenated derivatives. Some essential oil, for e.g. lemon, orange and turpentine oil, are almost exclusive mixtures of terpenoids. Terpenoids are most widespread, chemically interesting and provide structures of great diversity. Although the majority of terpenoids occur in the plant kingdom, a few of them have also been obtained from other sources.

7.4 GENERAL PROPERTIES OF TERPENOIDS

Terpenoids are lighter than water and boil between 410K and 460K. A few of them are solids these are usually lighter than water, volatile in steam, usually high refractive index. These are insoluble in water but soluble in organic solvents. Most of the terpenoids are optically active. The various general chemical properties of terpenoids are as follows: 1. They are unsaturated compounds (open chain or cycles) with one or more carbon atom rings having one or more double bonds. Consequently, terpenoids undergo addition reaction with hydrogen, halogens, halogen acids etc. Some of them form hydrates. They also form characteristic addition products with NO2, NOCl and NOBr. These additional proudest are found to be useful in the

identification of terpenoids. A number of additional products have antiseptic properties. 2. They undergo polymerisation, also dehydrogenation in the ring. 3. As they have olefinic bonds, they are very easily oxidised by nearly the entire oxidising agent. 4. Several terpenoids are labile and hence readily isomerised in the presence of and into more stable forms. 5. On thermal decomposition, most of the terpenoids yield isoprene as one of the products. Isoprene Rule: Wallach, in 1887 enunciated the famous isoprene rule, which stated as follows: "The skeleton structures of all naturally occurring terpenoids are built up of isoprene units."

From the above rule it follows that the divisibility into isoprene units is regarded as a necessary condition to be satisfied by every naturally occurring terpenoid. The isoprene rule has been deduced from the following facts.

a) The empirical formula of almost all the naturally occurring terpenoid is C_5H_8

$$(C_5H_8)_n \xrightarrow[distilation]{distructive} nC_5H_8\ isoprene$$

b) The thermal decomposition of almost all terpenoids gives isoprene as one of the products. For example rubber on destructive distillation field isoprene as one of the decomposition products.

$$(C_5H_8)_n \xrightarrow[distilation]{distructive} nC_5H_8\ isoprene$$

The isoprene rule has been confirmed by the fact that under special experimental conditions, isoprene undergoes polymerisation to yield various terpenoids. For example.

i) Isoprene, when heated to 280^0C gets dimerised to yield a widely distributed terpenoid called dipentene.

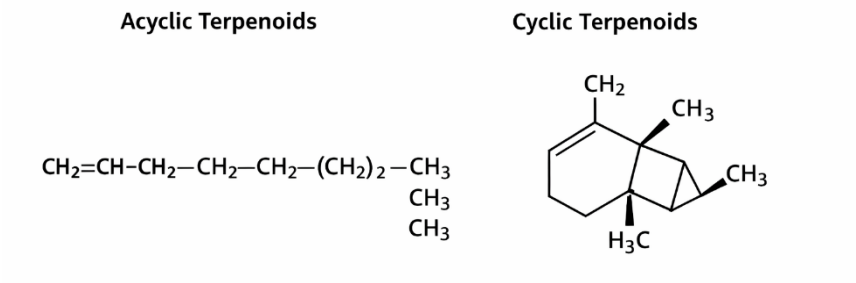
$$2C_5H_8 \xrightarrow[280^0C]{Heat} C_{10}H_{16}$$

ii) Isoprene may be polymerised to yield a rubber-like product.

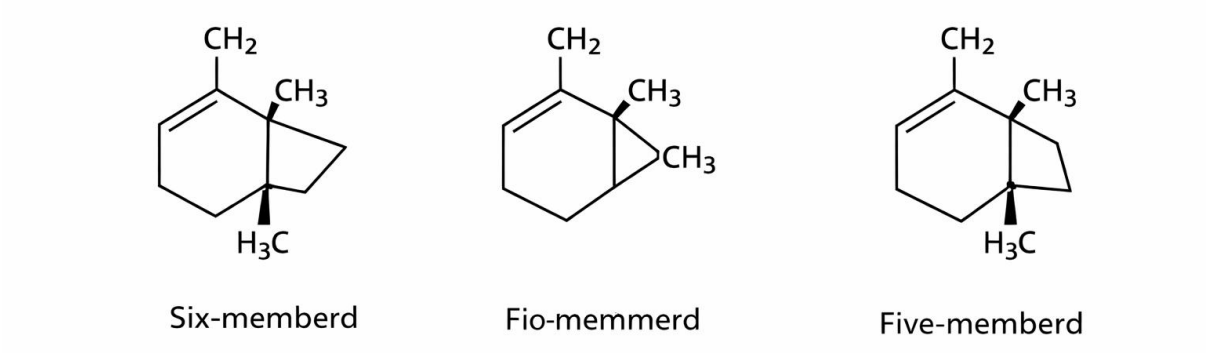
$$nC_5H_8 \xrightarrow{Polymerisation} (C_5H_8)_n$$

Special isoprene rule: - According to Ingold (925), molecules of terpenoids are built of isoprene units joined head to tail. The branched and of the isoprene molecule is termed the head, and the other end is called the tail.

This divisibility of terpenoids into isoprene units and their head-to-tail union is referred to as Ingold's special isoprene rule: this rule is a very suitable tool to limit the number of carbon skeletons of the structure of unknown terpenoids. Monocyclic monoterpenoids contain a six-membered ring. Inglod point out that the presence of a gem-dialkyl group renders the cyclohexane ring more stable. This gem-dialkyl rule, stated by Inglod, limits the number of possible structures obtained by classing the open chain as a cyclohexane ring. Thus, the monoterpenoid open chains give rise to only one monocyclic monoterpenoid like p-cymene structure. Most of to the monoterpenoids are derivatives of P-cymene.



Bicyclic monoterpenoids contain a six-member ring along with another three, four or five-member ring. The presence of a gem-dimethyl group in these cyclopropanes and cyclobutane rings is essential to render them sufficiently stable for occurrence in nature. Three possible skeletons of a bicyclic montoerpoid are:



Terpenoids with all three types of skeletons given above are known. Thus gem dialkyl group tends to render the cyclohexane ring unstable, whereas it stabilises the three, four and five-membered rings.

7.5 EXTRACTION AND GENERAL METHODS OF STRUCTURE DETERMINATION OF TERPENOIDS

Due to their wide occurrence in nature, all the terpenoids could not be isolated and separated by a general method. However, mono-and sesqui-terpenoids have a common source, i.e.,

essential oils and, therefore, their isolation has been generalised. This is carried out in two steps as follows:

1. Isolation of essential oils.

a) Extraction by means of volatile solvents. This method is widely used in the perfume industry. This method is generally used for such plants that yield an oil or give low quantities of oil on steam distillation due to the decomposition of essential oils. In such cases, the plant material is directly treated with light petrol at 50^0C. Under these conditions, the oil is taken up by the solvent along with the soluble colouring materials. The essential oils from this extract are separated by removing the solvent by distillation under reduced pressure.

(b) Adsorption in purified fats. This method is also known as the enfleurage method and is widely employed in France. By this method, the yield of the essential oil is generally higher. This method is used to extract a large number of essential oils, like rose and jasmine. In this method, the fat is warmed to 50^0C in glass plates. Then, the surface of the fat is covered with flower petals, and it is allowed to be kept as such for several days until it becomes saturated with essential oils. Then, the old petals are replaced by fresh petals, and this process is repeated. After removing the petals, the fat is digested with ethyl alcohol when all the oil present in the fat is dissolved in alcohol. Some quantity of fat is also dissolved in alcohol. This can be removed by cooling the alcohol extract to 200 °C, when the fat separates out. The alcoholic distillate is then finally fractionally distilled under reduced pressure to remove the solvent. Recently, the fat has been replaced by coconut charcoal due to its greater stability and higher adsorptive capacity. After keeping the coconut charcoal in contact with petals for several days, the charcoal is submitted to steam to get essential oils. This method is superior to the enfleurage method.

2. Separation of Terpenoids from Essential Oils.

The essential oils 1 generally contain several terpenoids and are obtained from the step where these are separated by various physical and chemical methods.

a) Physical methods. The various physical methods are as follows:

(i) Fractional distillation methods. The various terpenoids present in essential oils are separated by the fraction distillation method. The terpenoid hydrocarbons distil first, followed by the oxygenated derivatives. Distillation of the residue under reduced pressure yields the sesquiterpenoids and these are separated by fractional distillation. On an industrial scale, specially designed stills are employed and an efficient condensing system is necessary to minimise loss of more volatile hydrocarbons.

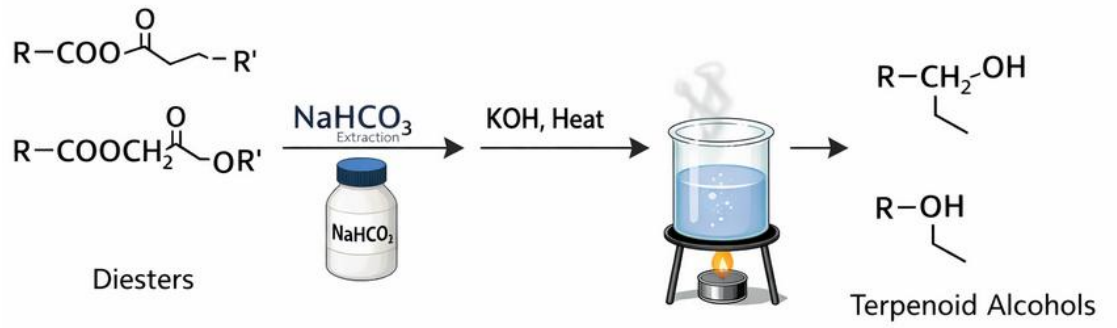
(ii) Chromatography More recently, chromatography in its various forms has been widely used both for the isolation and separation of terpenoids. In adsorption chromatography, the essential oil is made to flow through a particular adsorbent when the different types of terpenoids are adsorbed at different places on the adsorbent to form different chromatograms. Then, the various chromatograms are eluted by different solvent systems to get different eluates (each eluate has terpenoids of a single group). Each eluate is then subjected separately to adsorption separately to adsorption chromatography when different subjected chromatography when different bands due to the various terpenoids present in the eluate are obtained, which are then eluted to yield different terpenoids. In the adsorption chromatographic method, alumina and silica gel are generally adsorbents for separating the terpenoids, particularly triterpenoids. used as Gas chromatography has been particularly useful for isolating pure configurationally forms of a given terpenoid from mixtures produced by synthesis.

b) Chemical methods. These methods are not used these days to separate various from essential oils. However, the various chemical methods are as follows:

i) When essential oils containing terpenoid hydrocarbons are treated with nitrosyl chloride in chloroform, crystalline adducts of hydrocarbons having sharp melting points are obtained. These are separated and decomposed into their corresponding hydrocarbons.

ii)When essential oils containing alcohols are treated with phthalic anhydride to form diesters, the primary alcohols react with phthalic anhydride readily, secondary alcohols less readily and tertiary alcohols do not react at all.

After extracting with sodium bicarbonate, diesters are decomposed by alkali to the parent terpenoid alcohols.

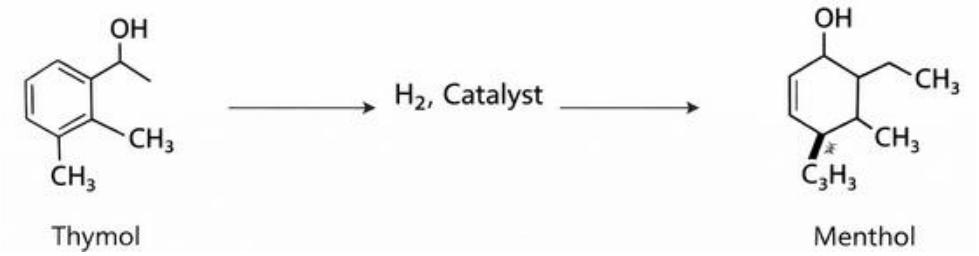


iii)Terpenoid aldehydes and ketones are separated from essential oils by forming their adducts with the common carbonyl reagents like NaHSO3, 2-dinitrophenylhydrazine, phenylhydrazine, semicarbazide, etc. After separation, these are decomposed to regenerate terpenoid aldehydes and ketones.

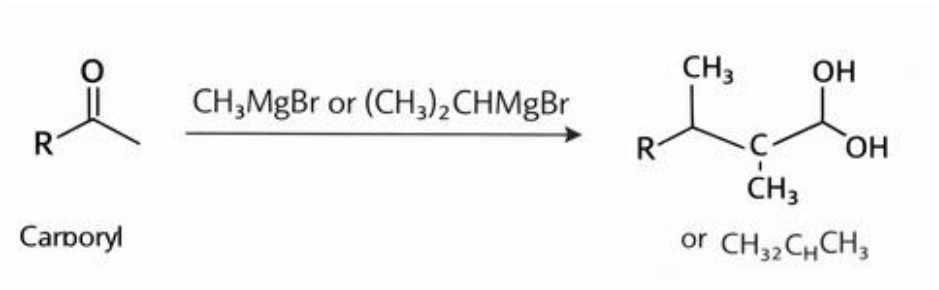
3. General methods for the determination of the structure of terpenoids.

The fundamental research done by Wallach, Baeyer, Perkin, Semmler, Simonson, Ruzicka, etc. are of great importance in elucidating the complicated structures of terpenoids. All the methods used for these have been grouped into four classes: 1. Analytical methods. 2. 3. 4. 5. Synthetical methods. Physical methods. Knowledge of a molecular rearrangement. Synthesis. We will discuss some methods.

1. **Synthetic Method:** The following synthetic reactions are of great value in elucidating the structure of terpenoids.
   a) **Catalytic hydrogenation:** When aromatic compounds are hydrogenated catalytically under suitable conditions, it is possible to obtain synthetic terpenoids. For example, a terpenoid alcohol, menthol, may be prepared from thymol, an aromatic compound, by catalytic hydrogenation.



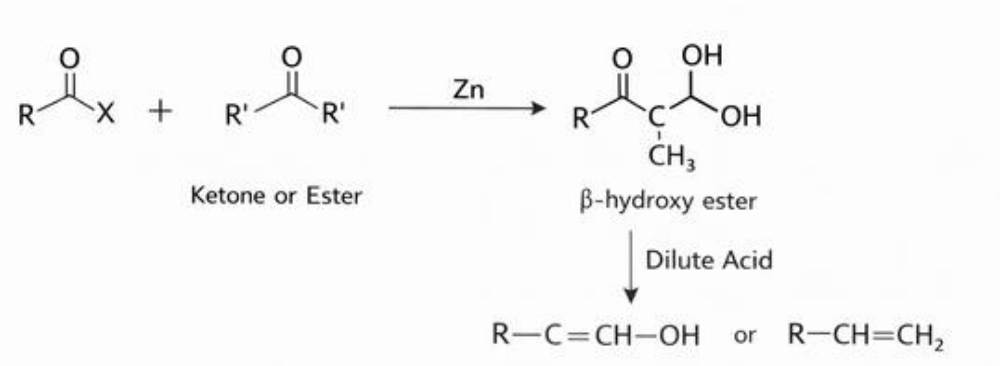
   b) **Grignard's reaction.** This reaction is of wide importance in the chemistry of terpenoids. This reaction was successfully employed by Perkin et al. to synthesise a large number of compounds which are related to terpenoids. By Grignard's reagent, methyl or isopropyl groups can be introduced into a compound having a carbonyl group.



   By the direct application of Grignard's reaction, tertiary alcohol, can be readily prepared. − α terpineol, a naturally occurring

   c) **Reformatsky reaction**. The Reformatsky reaction, similar to the Grignard reaction, is highly important in the chemistry of terpenoids and is widely used for the synthesis of many terpenoid compounds. In this reaction, an α-halo carbonyl compound (such as an aldehyde or a halogen-substituted ester) is treated with a

ketone or an ester in the presence of zinc. This results in the formation of a **β-hydroxy ester**. The β-hydroxy ester obtained in this reaction, when treated with dilute acid, undergoes further transformation to yield an **unsaturated acid** or, in some cases, a **hydrocarbon**.



2. **Physical Methods:** Physical methods play a major role in determining the structures of natural terpenoids. They help in solving many complex structural problems and are also useful for confirming the results obtained from degradative (chemical) studies. Among these methods, ultraviolet (UV) spectroscopy is especially important for detecting conjugated double-bond systems in terpenoids.

- Used for structure elucidation of terpenoids
- Help in solving complex structural problems
- Support and confirm results of chemical degradation studies

Ultraviolet (UV) Spectroscopy

This technique is widely applied in terpenoid chemistry to detect conjugation. The values of λmax provide important information about the nature of double bonds.

- For conjugated dienes
    - Acyclic dienes: 217–228 nm
    - Heteroannular dienes (double bonds in different rings): 230–240 nm
    - Homoannular dienes (double bonds in the same ring): 256–265 nm
- For β-unsaturated carbonyl systems
    - λmax range: 220–250 nm
    - Show an additional weak band at 315–330 nm

These λmax values, along with correlation tables and substituent increment data, help chemists in interpreting and confirming terpenoid structures.

Absorption value for Various Polyenes and the increment values for substituent's

S.No.	Polyenes	Absorption value
1	Basic value of homoannular dienes	253 nm
2	Basic value of heteroannular (and acyclic) dienes	214 nm
3	Increment for each C-substituent	5 nm
4	Increment for each exocyclic double bond	5 nm
5	Increment for each double bond that extends conjugation	30 nm

The general formula of β α, unsaturated ketenes is

Where R is an alkyl group or a ring residue and the parent system. The various values of these systems are given in the Table.

Absorption Values of Unsaturated Ketones and Incremental Absorption Values for Various Substituents'

S.No.	Polyenes	Absorption value
1	Basic value of homoannular dienes	215 nm
2	Basic value of heteroannular (and acyclic) dienes	10 nm
3	Increment for each C-substituent	12 nm
4	Increment for each exocyclic double bond	5 nm
5	Increment for each double bond that extends conjugation	30 nm

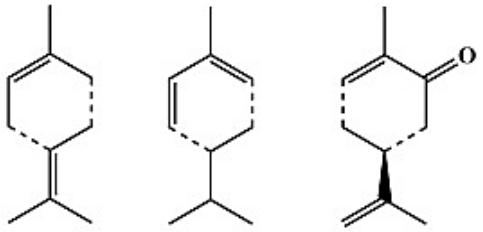
The above-mentioned rules have been successfully applied to various terpenoids. For example,

i)The observed max λ value for mycrene is 224 nm, whereas the calculated max λ cyclic diene with one C-substituent is 214+5-219 nm.

ii)The observed max λ value (an value for phellandrene is 232 nm whereas the calculate max λ heteroannular diene with two substituents and value (a one exocyclic double bond) is 214+2×5+5 or 229 nm.

iii)The observed max λ value for carvone is 235 nm, whereas the calculated max λ nm which is obtained as follows:

Parent system	215 nm
C-substituent at $\alpha - c$	10 nm
C-substituent at $\beta - c$	12 nm
	λ max 237 nm

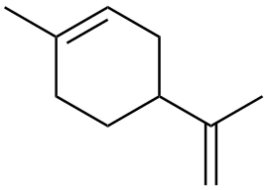


Terpinolene **Phellandrene** **Carvone**

Ultraviolet spectroscopy has also been used to recognise unsaturated acids, esters and lactones. These compounds have in a region of 220 nm.

7.5.1 Limonene

Introduction: It is the most important monoterpenoid which is widely distributed in nature. Its +). form occurs in lemon and orange oils the (-). form occurs in peppermint oil where as the (+). form occurs in turpentine oil. The racemic modification of limonene is known as dependence. This name was given to the inactive form before its relation to the active form (limonene) was established.

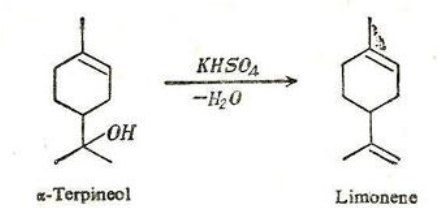


Limonene

Preparation

(i) From Essential Oils. (+) - Limonene is obtained from oranges. Dipentene is extracted from turpentine oil.

(ii) (ii) By dehydration of α- terpineol with $KHSO_4$.

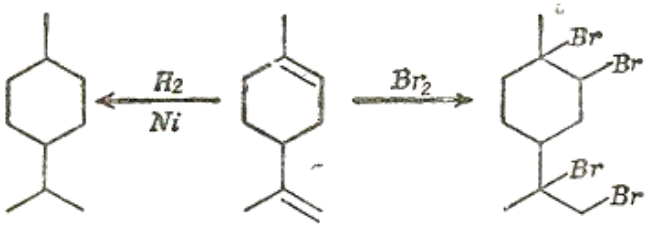


α-Terpineol Limonene

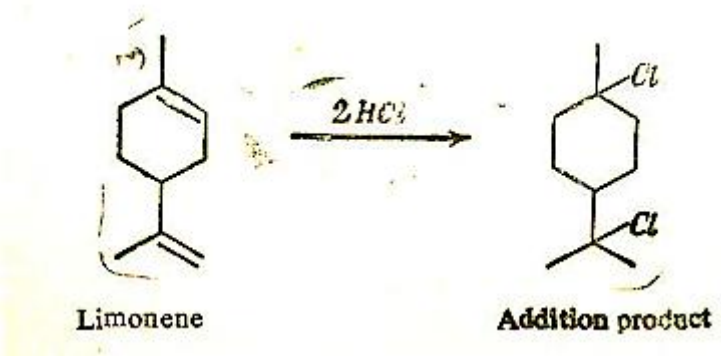
Properties:

Limonene is a pleasant-smelling liquid with citrus-like odour (b.p. 450K). It is insoluble in water. Chemically, it gives the reactions of a diolefin. For example,

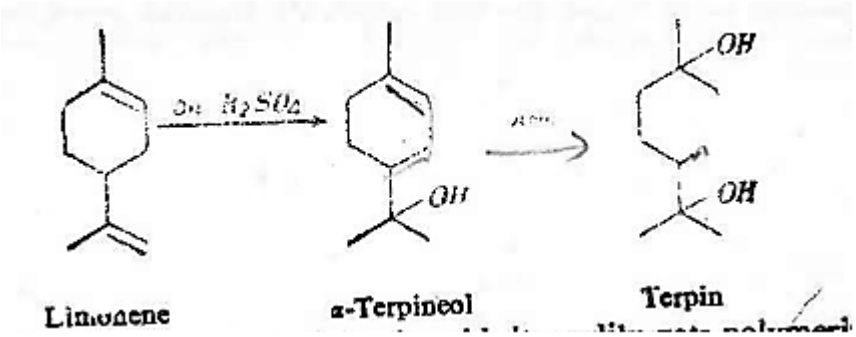
(i) It forms addition products with hydrogen and bromine to give p-menthane and its crystalline tetrabromide, respectively.



(ii) It gives an addition product with two molecules of halogen acid.



(iii) With dilute sulphuric acid, it gives α-terpineol and terpin hydrate.



Uses:

(i) Limonene is used as a flavouring agent in beverages and foods.

(ii) Dipentene is used in medicine and in making synthetic resins and high-pressure lubricating oil additives.

(iii) It is also used in the synthesis of isoprene, cymene and menthane.

7.5.1.1 Constitution of limonene

This has been elucidated on the basis of the following analytical and synthetic evidence.

1. Molecular formula. From analytical data, the molecular formula of limonene has been found to be $C_{10}H_{16}$.

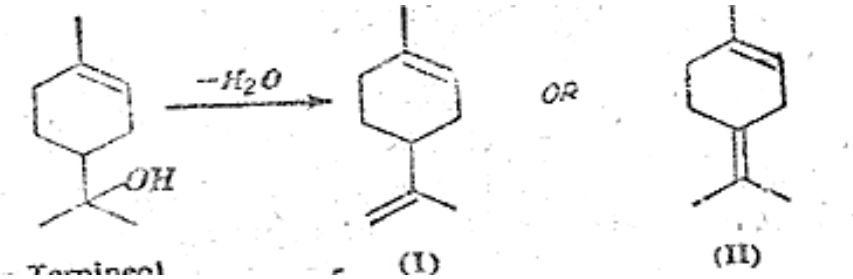
2. Presence of two olefinic bonds. This has been revealed on the basis of the following facts.

(a) It adds four bromine atoms to form a tetra bromide.

(b) On catalytic reduction, it adds four atoms of hydrogen to form a tetrahydro derivative.

c) With hydrochloric acid, a dihydrochloride is formed.

d) With hydrobromic acid, it yields a dihydrobromide.

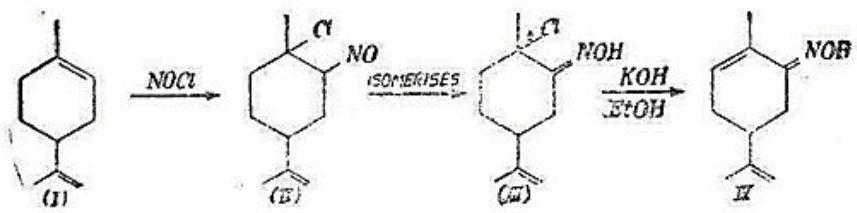


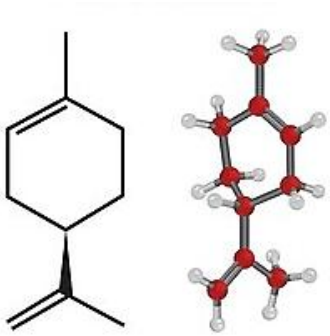
3. As a monocyclic derivative. The molecular formula of the saturated parenthy drocarbon corresponding to limonene is $C_{10}H_{20}$, which corresponds to the general formula CnH_2n (n=10) for the monocyclic compound. Hence, the limonene contains a monocyclic system.

4. Position of the double bonds. Chemical proof for double bond at position-8(9) is afforded by the following reactions.

$$\underset{(I)}{\text{Limonene}} \xrightarrow{NOCl} \underset{(III)}{\text{Limonene nitrosochloride}} \xrightarrow[EtOH]{KOH} \underset{(IV)}{\text{Carvoxime}}$$

The structure of carvoxime is known, and it has a double bond in Position 8(9). It, therefore, follows that limonene must have the structure I with a double bond in position 8(9). Thus, the above reaction may be written as follows:





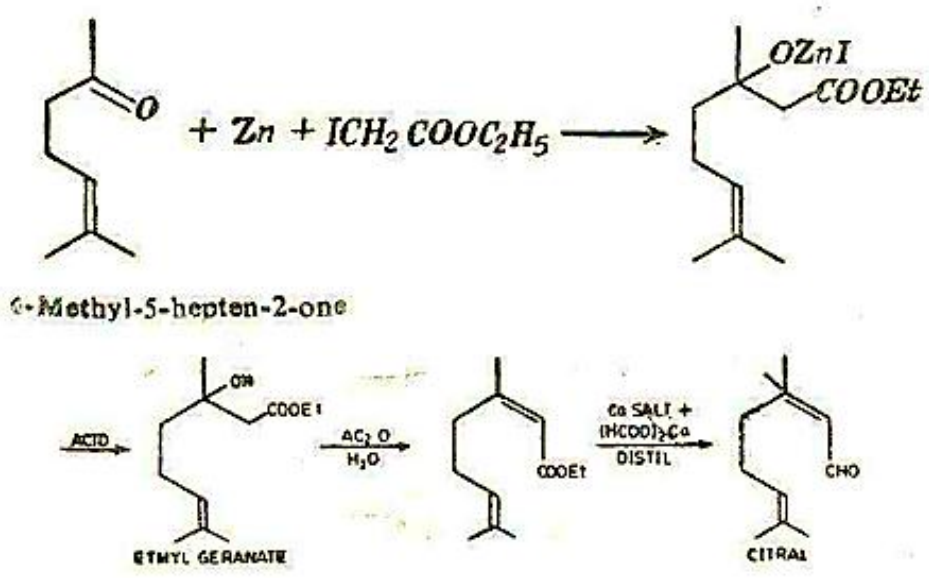
Thus Structure of limonene is 1, 8(9) menthadiene (I).

7.5.2 Citral ($C_{10}H_{16}O$):

This is the most important acyclic terpenoid since the structures of most of the other monoterprenoids are based on the structure of citral. It occurs in oil of lemon grass (70-80%) and oils of lime, lemon, citronella, etc.

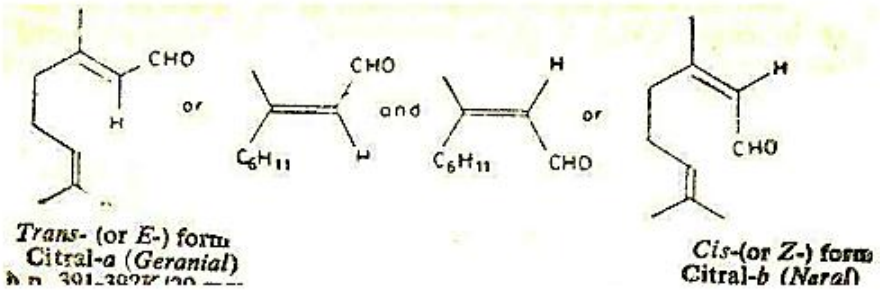
Extraction: It is obtained from lemon-grass oil by fractional distillation under reduced pressure and purified through the formation of bisulfite compound, which is decomposed with sodium carbonate to get free citral.

Synthesis: Citral may be synthesied from 6-methyl-5- hepten 2 one by Reformatsky reaction using $Zn+ICH_2COOEt$, as follows:



Properties:

Citral is a pale-yellow oily liquid (b.p. 497-501 K) with a pleasant odour of lemons. Chemical formula of citral is.

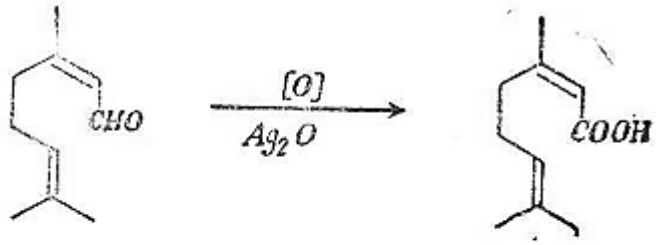


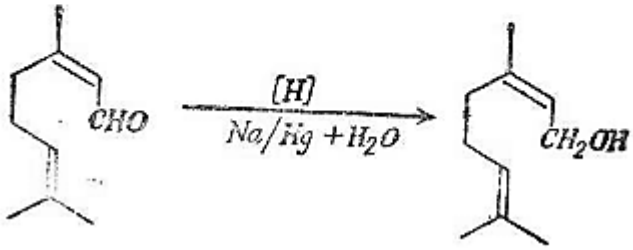
Chemical Properties:

Some chemical reactions of citral are:

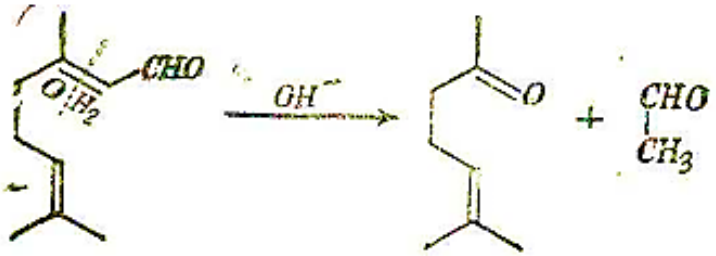
(i) **Reduction.** Citral on reduction with sodium amalgam and water gives geranial.

(ii) **Oxidation.** On oxidation with silver oxide, it gives geranic acid.

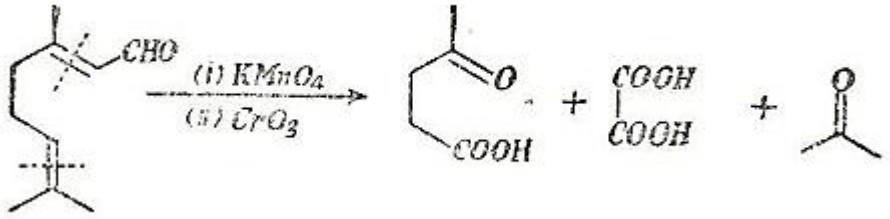




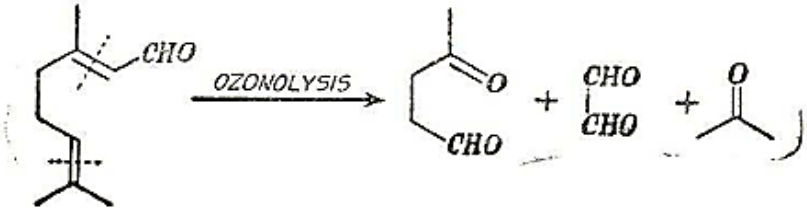
iii) **Hydrolysis.** When heated with potassium carbonate solution, citral undergoes hydrolysis and yields 6-methyl-5 hepten-2-one and acetaldehyde. During this reaction, citral undergoes cleavage at the double bond. This cleavage by alkaline reagents is a general reaction of unsaturated carbonyl compounds.



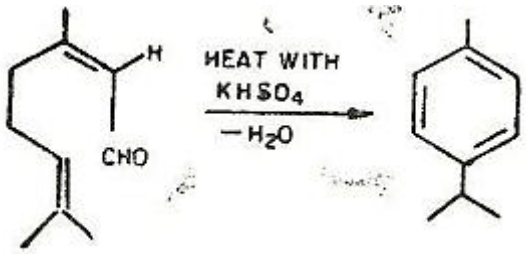
(iii) **Oxidation with alkaline $KMnO_4$** followed by chromic acid oxidation gives acetone, oxalic acid and laevulic acid.



(iv) **Ozonolysis.** On ozonolysis it gives acetone, laevula dehyde and glyxol.



(v) **Dehydration:** One heating with KHSO4 citral lose two molecules of water and gives p cymene.



These reactions confirm the structure assigned to citral.

Uses: It is widely used as a flavouring agent and in preparing synthetic perfumes e.g., and ionone. It is also employed for the manufacture of geraniol.

7.5.2.1 Constitution of Citral:

a) **Molecular formula** of citral as deduced from its analytical data is $C_{10}H_{16}O$.

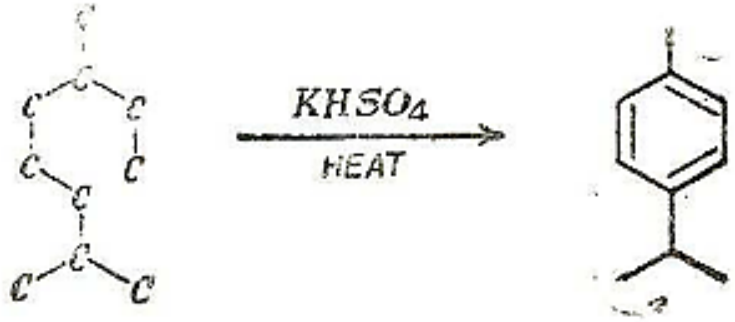
b) Presence of the CHO group it gives the typical reaction of an aldehyde function e.g.,

i) It gives a bisulfite compound and an oxime.

ii) On oxidation with silver oxide, it gives geranic acid, an acid with the same number of carbon atoms as citral.

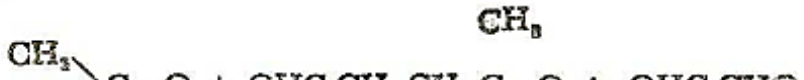
c) Positions of methyl and isopropyl groups. On beating with potassium hydrogen sulphate, citral forms p-cymene (II), (p-methyl isopropylbenzene). It is concluded from this that citral

molecule was acyclic and assigned it the structure (I), having two isoprene units joined head to tail.

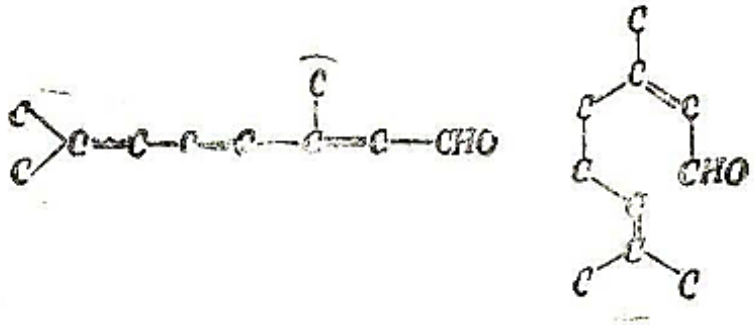


(d) Presence of two double bonds. On ozonolysis, it gives accons, laevuladehyde and glyoxal, i.e., the chain breaks at two points. This suggests the presence of two double bonds.

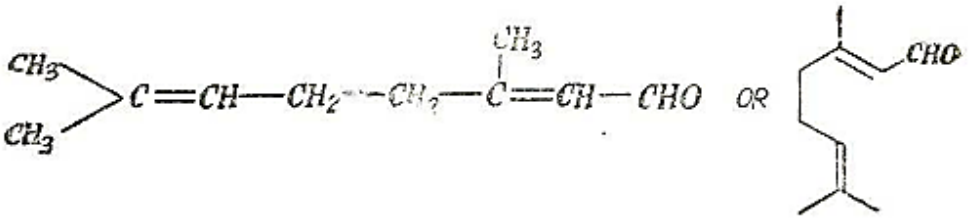
(e) Location of two double bonds. The carbon atoms in the molecule are arranged as in the above three products and with CHO group at one end.



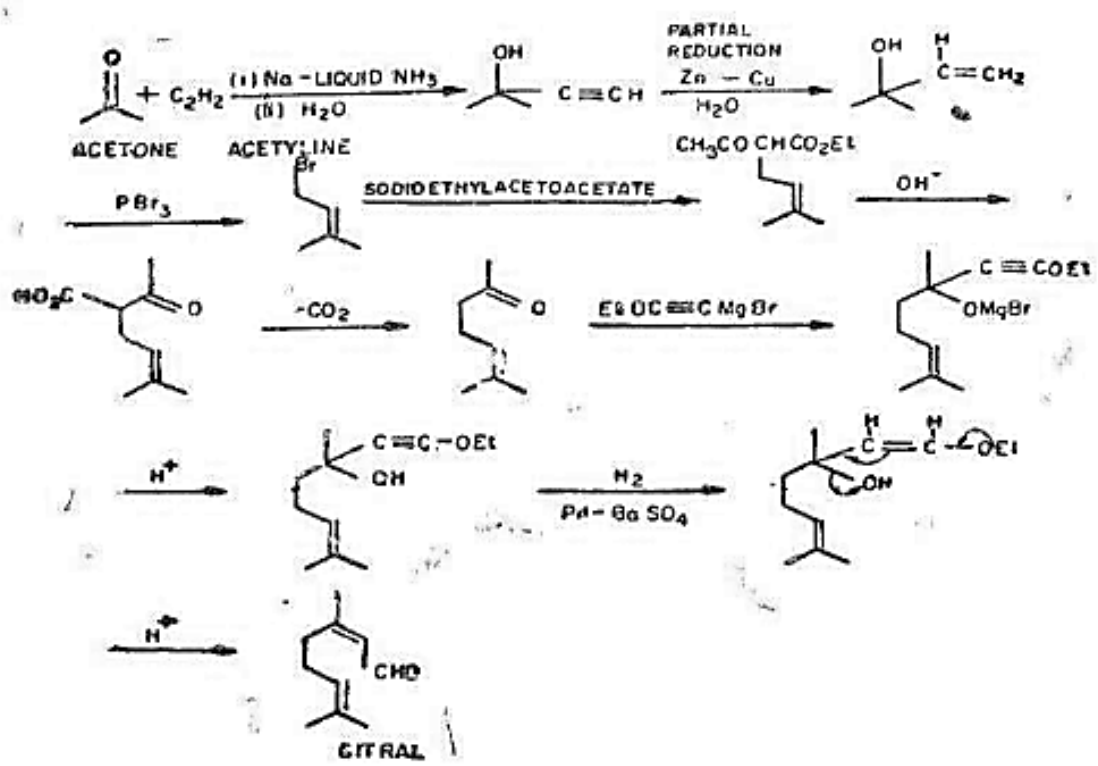
Hence the skeleton structure for citral is



(f) Structural formula. From this we can write the structural formula of as



(g) Final confirmation. The structure of citral was finally confirmed by its synthesis from methytehptemone, whose synthesis is given below:



7.5.3 Alkaloids:

Introduction: These are the basic nitrogenous compounds of vegetable usually having a marked physiological action and which may be regarded divided form parole, pyridine quinoline, isoquinoline or similar cyclic nitrogenous nuclei. Many of them possess curative properties and are of great value in medicine.

Occurrence: Generally they are usually found in plants in the form of their salts- in which they are either combined with organic acids such as lactic, citric, malic, oxalic commonly found plants or with certain characteristic acid such as quinic acid and meconic acid. In some case they exist glycoside. Generally they accumulate in the first and seeds and some times in the break of the trees.

Isolation of Alkaloids Plants: Alkaloids are extracted form plarite the plant material is finally powdered and treated with water acidified with HCL, when alkaloids form salts with HCL dissolve in water. The water extract contains the hydrochlorides of the Alkaloids together with Carbohydrates and other products form the plant tissue and free alkaloids are obtained from the acidified water extract which when treated with alkali precipitate out the alkaloids (being sparingly soluble in water) in the case of volatile alkaloids, the acidulated water extract is treated with alkali and stream - distilled.

Purification of the crude product obtained above is carried out by special methods or frequently by crystallization of the freed compounds or their salts.

General Properties:

(i) ***State***: Most of the alkaloids are crystalline solids which cannot be distilled. Only a few of them are liquids and can volatilize without decomposition, e.g., coniine and nicotine.

(ii) ***Physiological action:*** Most of them are bitter in taste and often exert a marked physiological action.

(iii) ***Solubility*****:** Almost all of them are either insoluble or sparingly soluble in water. Liquids alkaloids (coniine and nicotine are notable exceptions (being readily soluble in water and appreciably volatile in steam.) Alkaloids are generally less soluble in chloroform, either and benzene but are readily soluble in alcohol.

(iv) ***Optical activity:*** Most of them are optically active and usually laevo- rotatory.

(v) ***Basic nature:*** In a number of cases their solutions give a strong alkaline reaction. All of them form salts with acids, among these salts the chlorides, sulphates and oxalates crystallize well, there chlorides give double salts with chlorides of gold, platinum and mercury.

(vi) ***Precipitation :*** Alkaloids are precipitated form their aqueous or acid solution by a number of substances such as picric acid, tannic acid, perchloric acid, potassium mercuric iodide, potassium bismuth iodide, potassium bismuth iodide, phosphomolybedic acid and phosphotungstic acid. Precipitation with these reagents is often employed for the isolation and purification of alkaloids. This procedure cannot, however, be used for quantitative analysis since the resulting compounds are not sufficiently insoluble and because the reagents precipitate some other organic substances as well.

Determination of the Chemical constitution of Alkaloids: Different steps involved in the determination of constitution of an alkaloid are:

(a) ***Determination of Molecular Formula:*** The sample is purified and subjected to qualitative analysis. Carbon, hydrogen and nitrogen are invariably present while oxygen is rarely is rarely absent. This is followed by quantitative analysis, determination of molecular weight and then calculation of empirical and molecular formula.

(b) ***Ditection of Groups:*** Knowing the presence of nitrogen and/or oxygen in the alkaloid, the functional nature of these elements is determined.

7.5.3.1 Functional Nature of Oxygen

(1) Hydroxyl Group: The alkaloid is treated with acetic anhydride, acetyl chloride or benzoyl chloride to detect the presence of hydroxyl group. The hydroxyl group present may be phenolic or alcoholic. It is phenolic if the alkaloid –

(i) Gives a colour with ferric chloride:

(ii) Is soluble in sodium 'hydroxide and is reprecipitated by carbon dioxide.

If the hydroxyl group is not phenolic, it must be alcoholic this is confirmed by treatment with dehydrating agents (eg. H_2SO_4 or O_4O10) or by oxidation.

(**2) Carboxyl group:** Presence of a carboxyl group is indicated by the solubility of the alkaloid in aqueous sodium carbonate or formation of esters.

(3) Ester group: Identification of the products of hydrolysis of alkaloid indicates the presence or absence of an ester group.

(4) Methoxy group: The presence of methoxy groups and their number is determined by Zeisel method which is described under Estimation of groups.

7.5.3.2 FUNCTIONAL NATURE OF NITROGEN

(1) Amino Group.

(i) The reactions of the alkaloid with acetic anhydride, benzoyl chloride, nitrous methyl iodide show whether the amino group is primary, secondary or tertiary.

(ii) Formation of methylamine, dimethylamine, trimethylamine (volatile products) acid and on distillation with aqueous potassium hydroxide indicates the nature and number of methyl groups attached to nitrogen atom.

(2) Amide group: Products of hydrolysis (acid and ammonia) of the alkaloid will show the presence of an amide group.

(3) Presence of Unsaturation: It's in an alkaloid sample is indicated by the treatment with bromine water or dilute alkaline permanganate.

(c) Estimation of Groups: The estimation of various groups, detected as above, is carried out as follows.

(1) Hydroxyl groups: The number of hydroxyl groups is determined by acetylating the alkaloid followed by hydrolysis of the acetyl derivative with a known volume of N-NaOH. The excess of the alkali left unused is estimated by back titration with a standard acid.

$$\underset{\text{Hydroxy Compound}}{ROH} \xrightarrow{CH_3COCl} \underset{\text{Acetyl derivative}}{RO.OCCH_3} \xrightarrow{NaOH} ROH + CH_3COONa$$

From the volume of N-NaOH used, the number of acetyl groups or hydroxyl groups can be calculated.

(2) Carboxyl groups. The number of carboxyl groups in a given sample may be determined volumetrically by titration against standard barium hydroxide solution using phenolphthalein as an indicator or gravimetrically by the silver self-method.

(3) Methoxy groups: The presence of methoxy groups and their number many are determined by the Zeisel's method. The alkaloid is treated with concentrated hydroiodic acid at 399 K (boiling point of HI). The methoxy groups present in the molecule are thereby changed into methyl iodide which is absorbed in alcoholic silver nitrate when silver iodide precipitated.

$$R(OCH_3)x + xHI \longrightarrow R(OH)x + xCH_3I$$

$$xCH_3I + xAgNO_3 \longrightarrow xAgI + xCH_3NO_3$$

The precipitate of AgI is boiled with HNO_3, filtered, washed, dried and weighed. From the weight of silver iodide, we calculate the number of methoxy groups as illustrated in the solved example given below:

Example: When treated according to Zeisel's method 0.226 gram of an alkoloid $C_{20}H_{21}O_4N$ yielded 0.626 gram of silver iodide. Calculate the number of methoxy groups present in the molecule of the alkaloid.

SOLUTION

Mol. mass of the alkaloid, $C_{20}H_{21}O_4N$ =240+21+64+14=339

Wt of alkaloid taken = 0.226 g

Wt of AgI obtained = 0.626 g

The wt of AgI that will be produced by I mole, i.e., 339g of alkaloid= $\frac{0626}{0.226}$ X 339=939 gm.

Mol. mass of AgI = 107.88+127=234.88

It is clear from the equations given above that corresponding to each methoxy group present, one melecule of AgI is obtained at the end. Hence the number of methoxy group in the molecule of the alkaloid = $\frac{939}{234.88}$ =4

(d) Degradation: The complex molecule is broken into relatively simple fragments whose nature gives useful information about the type of nuclei present in the molecule. Various methods employed for degradation of an alkaloid are:

(i) Hydrolysis: Molecules containing an ester or amide group break on hydrolysis into simpler products. For example, piperine on hydrolysis splits up to give piperic acid and piperidine. From this we infer that piperine is a piperidinamide of piperic acid.

$$\underset{\text{Piperine}}{C_{11}H_9O_2CO\text{-}NC_5H_{10}} + H_20 \longrightarrow \underset{\text{Piperic Acid}}{C_{11}H_9O_2COOH} + \underset{\text{Piperidine}}{C_5H_{10}NH}$$

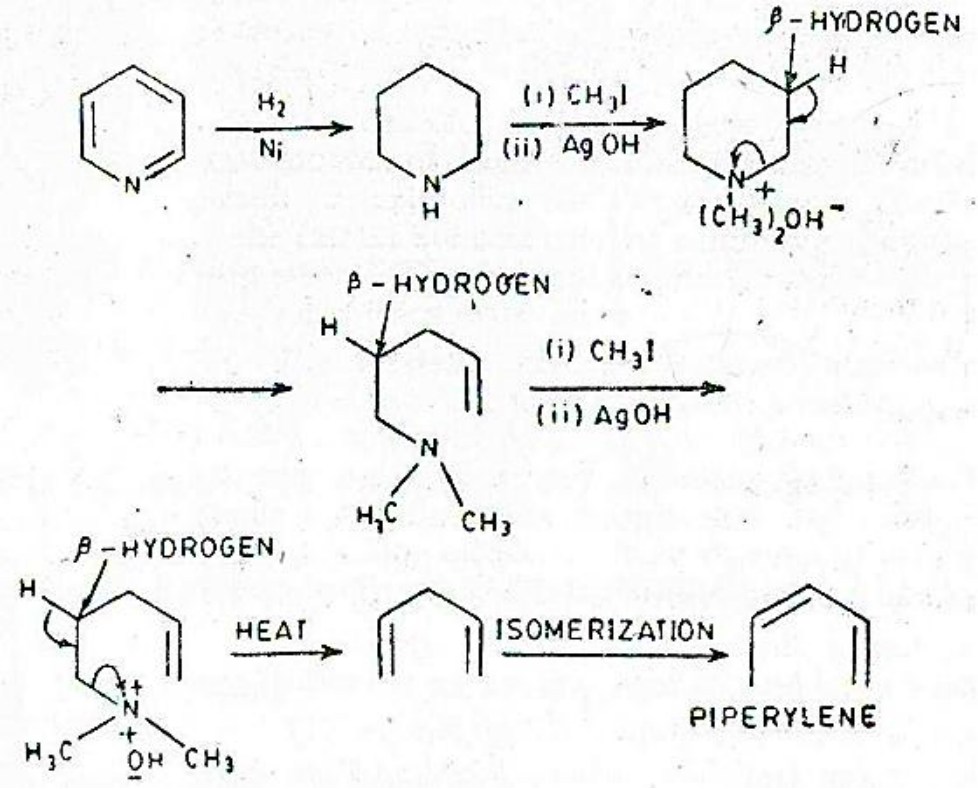
(ii)Oxidation: Alkaloids on oxidation give a variety of products depending the nature of oxidizing agents-mild (H_2O_2 or alkaline potassium ferricyanide), moderate (acid or alkaloid $KMnO_4$) or vigorous (K_2Cr_2O H_2SO_4; conc. HNO_3 or MnO_2 + H_2SO_4)

(iii) Distillation with Zinc dust: This brings about degradation or dehydrogenation of the alkaloid under study. When the alkaloid contains oxygen it is removed during distillation. For example, on distillation with zine dust morphine yields phenanthrene (parent compound) while coniine undergoes dehydrogenation to give conyrine.

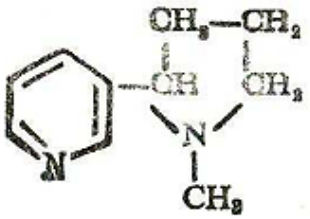
(iv) Hofmann Exhaustive Methytation: Heterocyclic rings containing nitrogenare opened with the elimination of nitrogen when subjected to exhaustive methylation. It thus helps us in knowing the nature of the carbon skeleton.

The heterocyclic, if unsaturated, is hydrogenated, and converted to the quaternary methylammonium hydroxide. This on heating loses a molecule of water by combination of -OH group with a hydrogen atom in B-position with respect to the nitrogen atom and the ring is opened at the nitrogen atom. On repeating the process with the product, nitrogen atom is

completely removed and an unsaturated hydrocarbon is left behind which generally isomerises to a conjugated diene. For example, starting with pyridine we have:



(e) Synthesis. The alkaloid under investigation is assigned a tentative structure on the basis of the foregoing analytical data. This is finally proved only if it could be synthesised by a suitable unambiguous method.



7.5.4 NICOTINE ($C_{10}H_{14}N_2$)

It is the chief alkaloid of the tobacco plant (Nicotiana tobacco) where in it is present as a salt of malic or citric acid. In leaves of tobacco its concentration is the highest. It varies from 0.6 to 8% depending upon the kind of tobacco. The alkaloids are conveniently prepared from tobacco leaves. Raw tobacco of high nicotine is crushed and its soluble constituent extracted with cold water. The hydrocarbons present in the extract are removed by acidifying the solution

and extracting with ether. The residual solution is made alkaline and nicotine sec free is extracted with other.

Properties:

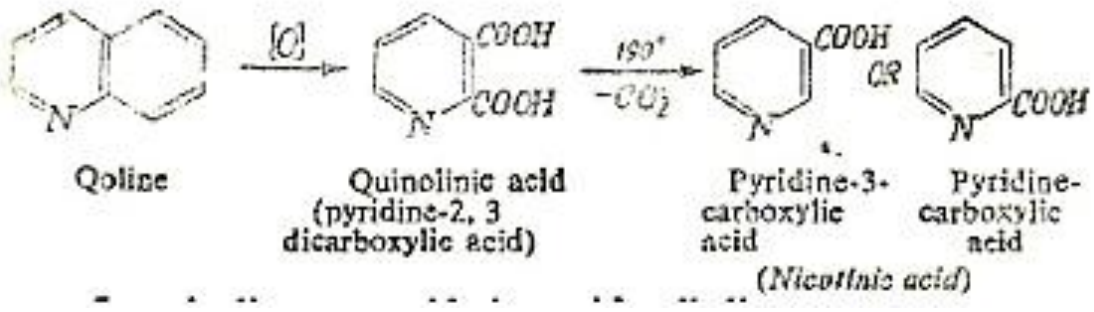
Freshly prepared nicotine is a colourless oily liquid. (b.p. 519.K under 730 mm pressure) readily soluble in water. Unlike tobacco, pure nicotine has an unpleasant smell. It has a burning taste and is very poisonous (lethal dose being 30 to 50 mg). In air it rapidly turns brown and resinifies and cab be distilled without decomposition only in vacuum or in a current of hydrogen. The natural alkaloid is laevo-rotatory and has [x] of - 169°. In a mixture with soap solution it is one of the most effective exterminating agents for green fly and other insect pests.

Constitution:

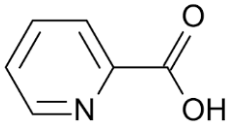
(1) Molecular formula of nicotine as deduced from its analytical data and molecular mass determination is $C_{13}H_{14}N_2$.

(2) Nicotine reacts with methyl iodide to form dimethiodide and two monomethiodidis but it does not form an acetyl or benzyl derivative. This show hat the two nitrogen atoms in nicotine are tertiary.

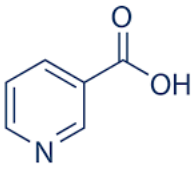
(3) Nicotine on oxidation with chromic acid or permanganate gives nicotinic acid ($C_6H_4N_2COOH$). Three pyridine carboxylic acids are known with COOH group in 2-,3- or 4-position. These are named picolinic acid, nicotinic acid. Their orlentation was proved as follows: Quinoline on oxidation with alkaline permanganate gives quinolinic acid which must be pyridine-2, 3-dicarboxylic acid. Quinolinic acid on being heated to 360K loses one carboxyl group and gives nicotinic acid. Hence nicotinic acid must be either pyridine-2-carboxylic acid or pyridins-3-carboxylic acid.



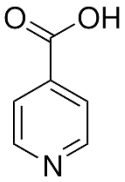
By elimination, therefore, picolinic acid is pyridine-2-carboxylic acid.



Picolinic Acid

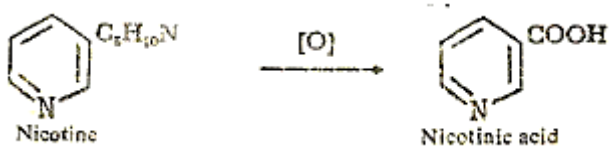


Nicotinic acid

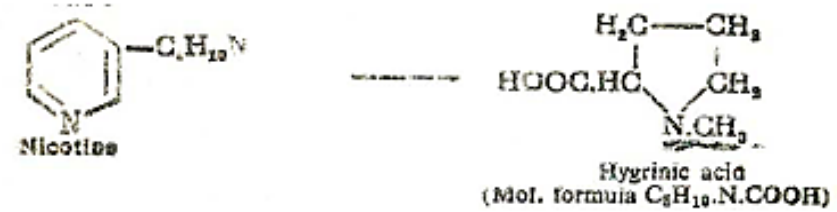


Isonicotinic acid

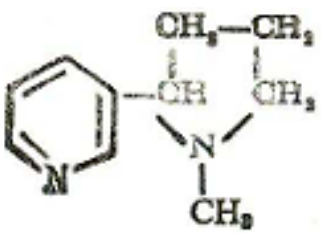
Now since nicotine on oxidation followed by heating at 460K, yields nicotinic acid (pyridine-3-carboxylic acid), it suggests that nicotine contains a pyridine ring with some sort of group attached to it at the ß-position. This group attached to the pyridine ring is $C_5H_{10}N$ and the oxidation can be formulated as follows:



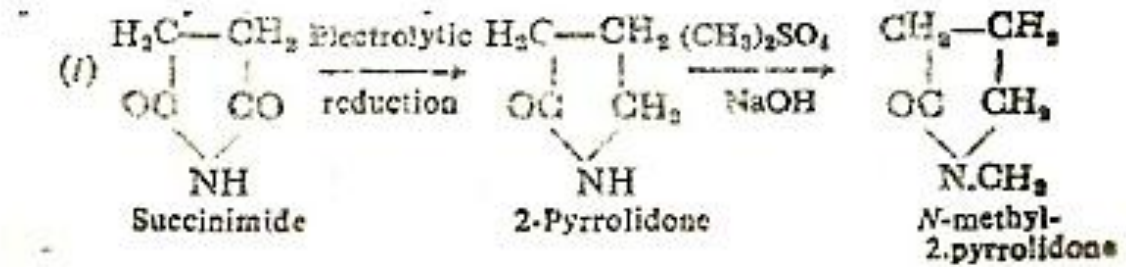
Nicotine hydriodide on treatment with methyl iodide gives a methiodide. This on oxidation yields hygrinic acid (N-methylpyr- rolidine-α-carboxylic acid.

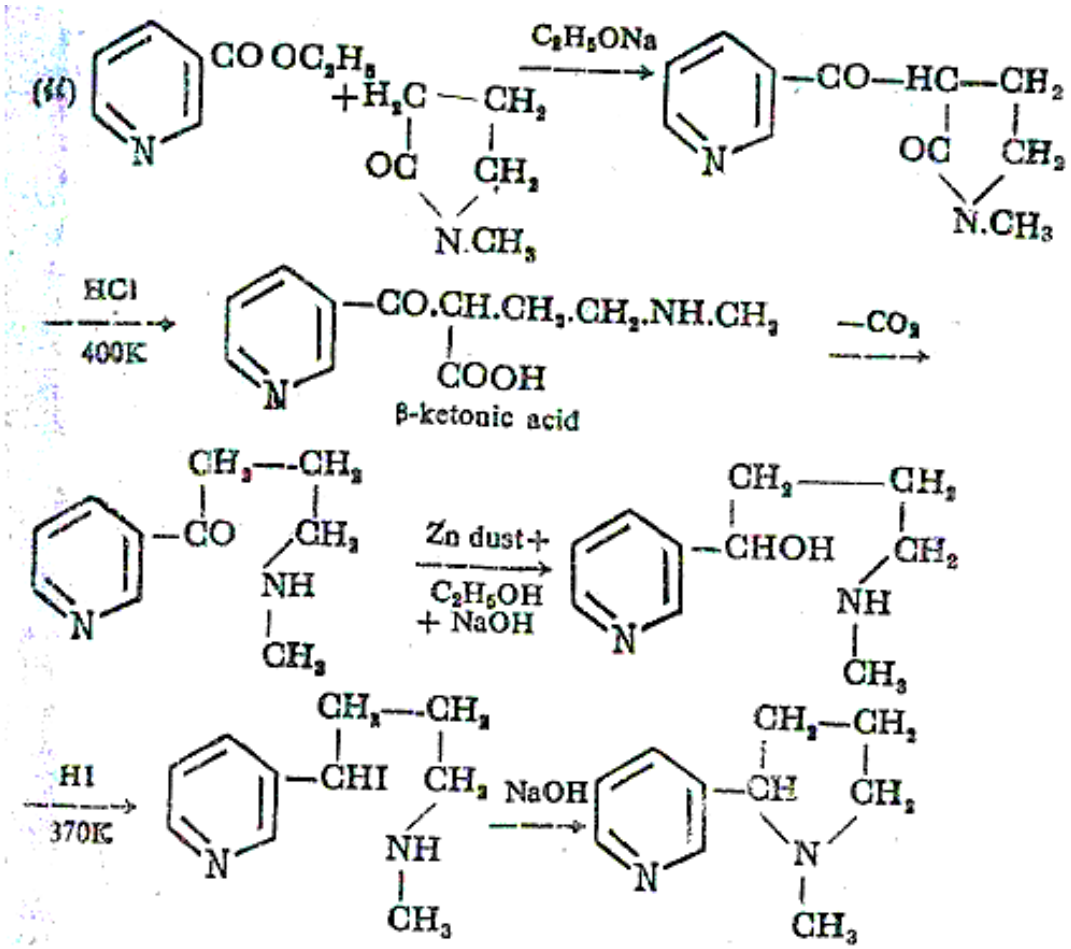


This indicates that pyridine ring has been destroyed during the above transformation and the group-$C_5H_{10}N$ attached to the pyridine ring in ß-position is N methylpyrrolidine. Pyridine and pyrrolidine nuclei are joined through carbon atoms at ß-position in pyridine and 2 position in pyrrolidine. This gives the structure of nicotine as:



This formula has been further confirmed by its synthesis by Spath and (1928): Bpetshneider.



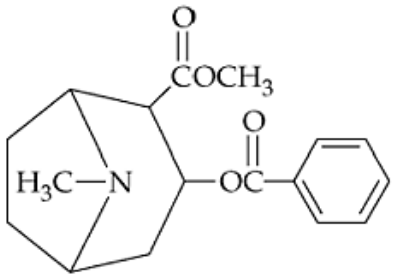


The (+/-) - mixture of nicotine obtained by the above synthesis was resolved by forming salts with (+/-) -tartaric acid and (-) - nicotine thus obtained was found to be identical with the natural product.

7.5.5 Cocaine

It was first isolated in 1860 from the leaves of Erythroxylon coca L., (Coca Plant) which is mainly grown in South America, particularly in Peru and Bolivin and now grown in java and

Ceylon. However, the plant from which cocaine is obtained (i.e. coca plant) should not be confused with Theobroma cacao, the beans of which are the source of cocoa and chocolate.



Cocaine

Isolation: To obtain the crude cocaine, the Peruvian leaves are powdered and thoroughly digested with lime or sodium carbonate and a little water. The digested solution is then extracted with light petroleum, when the alkaloids get dissolved in the light petroleum layer. From the organic layer, the alkaloids are removed by shaking with a controlled amount of dilute sulphuric acid (avoiding excess). This acid solution, when evaporated, yields a crystalline precipitate of a larger portion of the cocaine, which can be further purified by crystallisation of its hydrochloride.

Cocaine can also be extracted directly from the leaves with high-boiling petroleum.

Properties:

1. It forms colourless crystals (m.p. 98 °C). It is sparingly soluble in water, but its hydrochloride is quite soluble. It is a strong tertiary base (pka 8.7).

2. The hydrochloride of cocaine is used as a local anaesthetic in eye surgery and dentistry. Usually, cocaine is injected along with adrenaline.

3. Cocaine is a habit-forming drug and is, therefore, used with great care. Taken internally, it increases physical and mental power but the after-effects is deep depression.

Constitution:

1. **Molecular Formula.** From analytical data and molecular weight determination, it follows that the empirical and molecular formula of cocaine i.e., $C_{17}H_{21}NO_4$.

2. **Nature of the Nitrogen Atom.** It is a strong tertiary base (pka 8.7) and adds on one molecule of methyl iodide to form a methiodide. It also reacts with cyanogen bromide to give methyl bromide and cyanonorcocaine and thus contains an N-methyl group.

$$C_{17}H_{21}NO_4 + CH_3I \longrightarrow C_{17}H_{21}NO_4.CH_3I$$

3. **Hydrolysis.** When cocaine is heated with water, it is hydrolysed to methanol and benzoylecgonine.

$$\underset{\text{Cocaine}}{C_{17}H_{21}NO_4} + H_2O \longrightarrow \underset{\text{Benzoylecgonine}}{C_{16}H_{19}NO_4} + CH_3OH$$

But benzoylecgonine contains a carboxyl group. Therefore, cocaine is the methyl ester of benzoylecgonine, which is also proved by the fact that benzoylecgonine, when heated with methyl alcohol in the presence of hydrochloric acid, yields cocaine.

When benzoylegonine is boiled with barium hydroxide solution. It undergoes further hydrolysis, yielding benzoic acid and ecognine.

$$\underset{\text{Benzoylecgonine}}{C_{16}H_{19}NO_4} + H_2O \xrightarrow{Ba(OH)_2} \underset{\text{(-)-Ecgonine}}{C_9H_{15}NO_3} + \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

From the above reactions, it is evident that the constitution of cocaine depends on the constitution of ecgonine.

4. **Constitution of Ecgonine**. It is established as follows:

a) Its ***molecular formula*** is $C_9H_{15}NO_3$.

b) It is a tertiary base because it gives the crystalline additive compound $C_9H_{15}NO_3.CH_3I$ with methyl iodide. This reaction shows that ecgonine contains tertiary nitrogen atom.

c) As ecognine forms ester and salt with alcohol and alkali respectively, it means that it contains one carboxyl group.

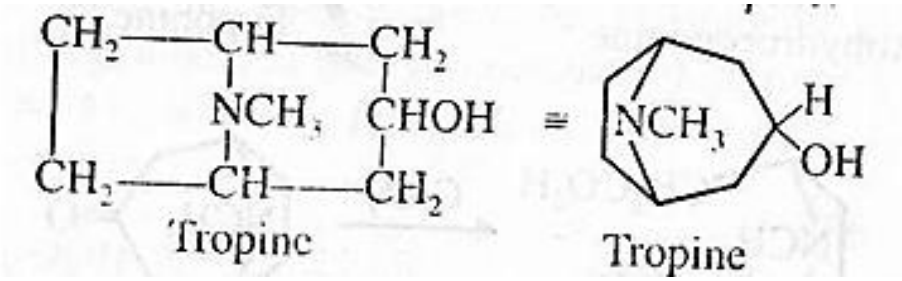
d) The presence of - OH group is indicated by the fact that it reacts with acid chloride and anhydride to form acyl derivatives. Since this acyl derivative can be further esterified, it shows that ecgonine is both an alcohol and an acid.

e) Ecgonine when oxidised with CrO_3 yields a ketone ecgoninone which soon loses a molecule of carbon dioxide to yield tropinone. The latter compound when further oxidised, yields a mixture of tropinic acid and ecgoninic acid, former of which is also obtained from tropine.

$$\underset{\text{Ecgonine acid}}{C_9H_{15}NO_3} \xrightarrow{CrO_3} \underset{\text{Ecgoninone}}{C_9H_{13}NO_3} \xrightarrow{-CO_2} \underset{\text{Tropinone}}{C_8H_{13}NO} \xrightarrow{CrO_3} \underset{\text{Tropinic acid}}{C_8H_{13}NO_4} + \underset{\text{Ecgoninic}}{C_7H_{11}NO_3}$$

From the nature of products obtained by oxidation of ecgonine, the following conclusions are drawn:

(i) The reaction, which involves the oxidation of ecgonine first to tropinone and then to tropinic acid, reveals that ecgonine contains the tropane skeleton and the position of the secondary alcoholic group in ecgonine remains the same as in tropine.

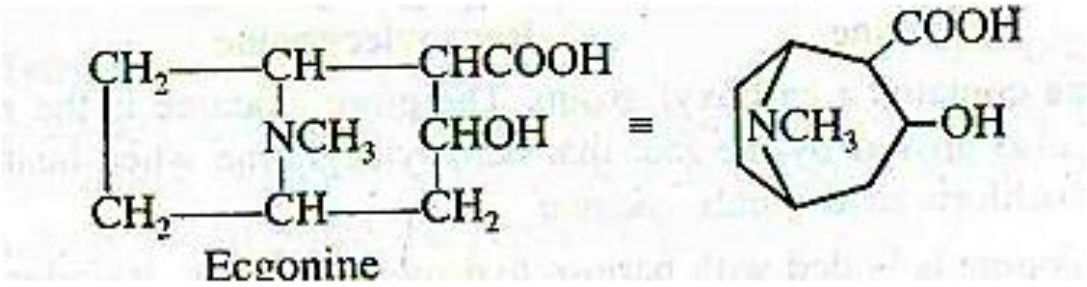


The close similarity between the structures of ecgonine and tropine is further demonstrated by the fact that the dehydration of ecgonine yields anhydroecgonine, which, upon decarboxylation, yields tropidine. The dehydration of tropine also forms the latter compound.

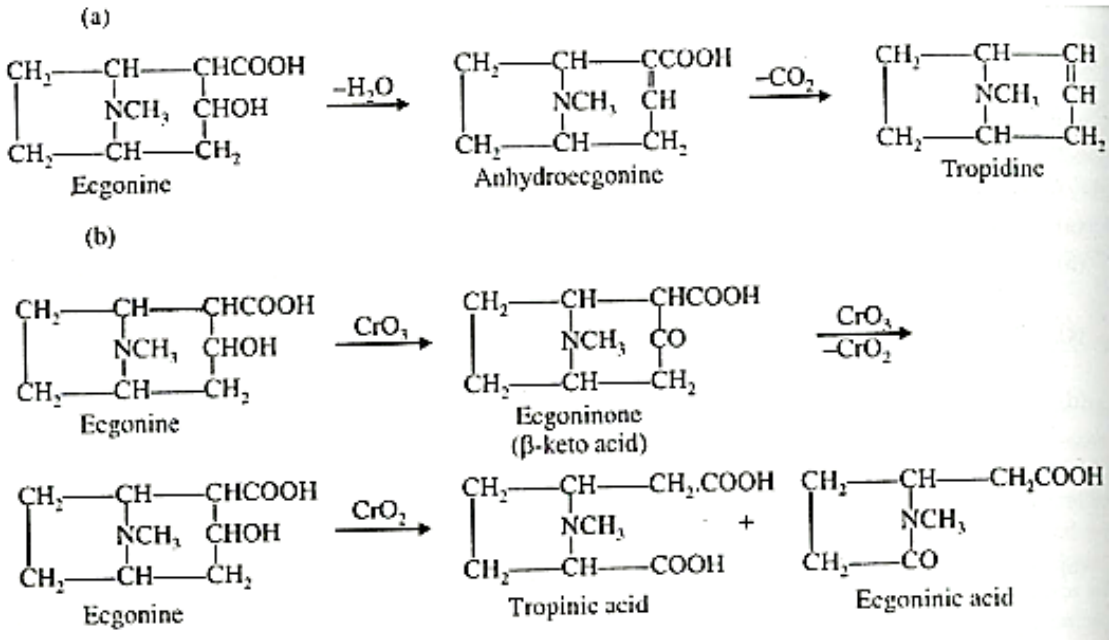
$$\text{Ecgonine} \xrightarrow{-H_2O} \text{Anhydroecgonine} \xrightarrow{-CO_2} \text{Tropidine}$$

$$\text{Tropine} \xrightarrow{-H_2O} \text{Tropidine}$$

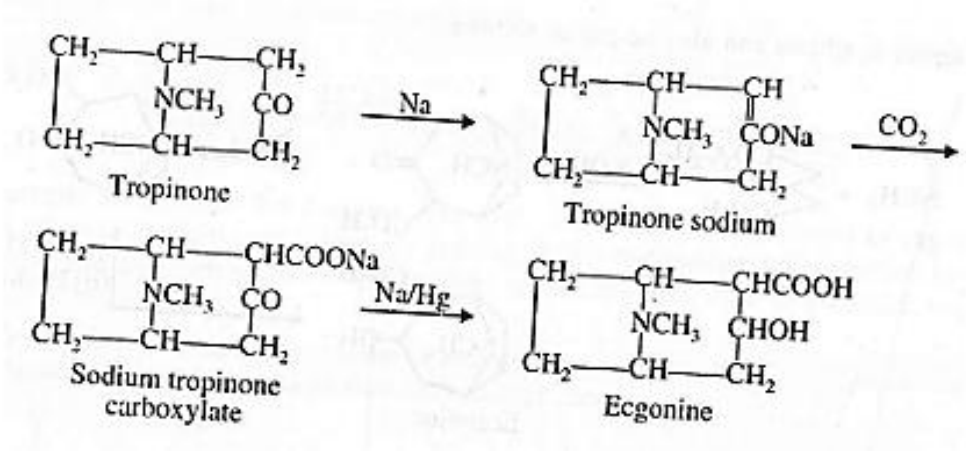
(ii) The easy decarboxylation of the ecogonine reveals that it is a B-keto acid. This interpretation is confirmed by the fact that Willstatter actually observed the formation of an unstable ketonic acid, which lost carbon dioxide to yield tropinone. Thus, ecgonine is:



f) The above structure of ecgonine explains all its reactions:

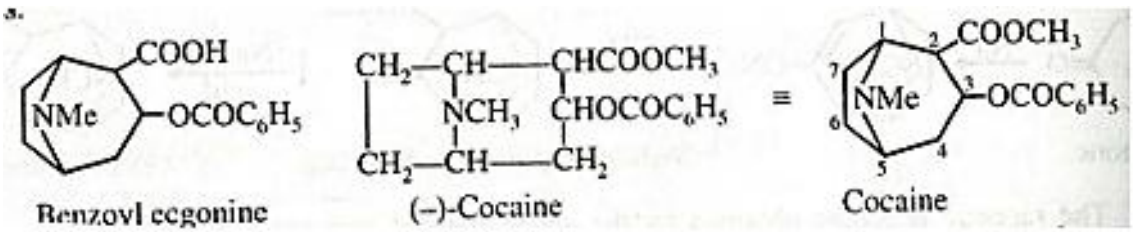


g) Finally, the structure of ecgonine is proved by its synthesis: The starting material is tropinone.

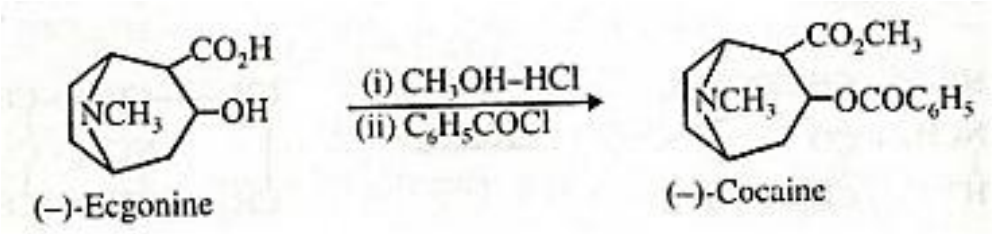


The racemic ecgonine obtained by the above method was not identical with (-) ecgonine obtained from (-). cocaine. However, its chemical properties were the same.

5. **Constitution of Cocaine.** Now, since we know that cocaine is the methyl ester of benzoyl ecgonine, having a free carboxylic group, the benzoyl ecgonine and cocaine will have the following structures.



The above structure of cocaine has been proved by its synthesis, which consists of the resolution of the racemic ecgonine, esterification of (-). ecgonine followed by benzoylation to give cocaine identical to natural (-). form.



Similarly, (+) and (-) cocaine were obtained from the corresponding - ecgonines.

7.6 SUMMARY

Natural products are organic compounds produced by plants, animals, and microorganisms, many of which possess medicinal, biological, and industrial importance. Among them, terpenoids and alkaloids are two major groups of significant structural diversity.

Terpenoids are widely found in essential oils and exhibit characteristic aromas and physiological activities. They follow the isoprene rule, occur as mono-, sesqui, and bicyclic structures, and show typical physical and chemical properties such as unsaturation, optical activity, and ease of oxidation. Their extraction is mainly carried out from essential oils by solvent extraction, steam distillation, adsorption, chromatography, and fractional distillation. Structural elucidation involves synthetic reactions, physical methods (especially UV spectroscopy), and degradative studies. Important examples discussed include limonene and citral, along with their preparation, reactions, and constitution.

Alkaloids are basic nitrogen-containing natural compounds found in plants, usually as salts. They exhibit strong physiological actions and are extracted by acid–base methods followed by purification. They commonly occur as crystalline solids and show optical activity, characteristic solubility, and basic behavior. Examples include nicotine and cocaine.

7.7 TERMINAL QUESTIONS

1. Define natural products and explain their significance in biological and industrial systems.

2. What are terpenoids? Discuss their classification based on the isoprene rule.
3. Write the general physical and chemical properties of terpenoids.
4. Describe different methods used for the extraction and separation of terpenoids from essential oils.
5. Explain the role of UV spectroscopy in the structural elucidation of terpenoids.
6. Discuss the preparation, properties, and constitution of limonene.
7. Describe the structure, reactions, and confirmation of citral.
8. What are alkaloids? Explain their occurrence, extraction, and general properties.
9. Differentiate between terpenoids and alkaloids with suitable examples.
10. Explain the importance of terpenoids and alkaloids in the pharmaceutical industry.

7.8 REFERENCES

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UNIT 8: UV-VISIBLE SPECTROSCOPY

CONTENTS:

8.1 INTRODUCTION

The chemical structure of the unknown material was determined by using physical, chemical and spectroscopy techniques. Most common spectroscopy techniques, such as UV, IR, NMR and Raman have been used to identify the chemical structure of compounds. Ultraviolet-Visible (UV-Vis) spectroscopy is one of the most commonly used analytical techniques in both research and industrial laboratories. It is primarily employed to study the absorption of ultraviolet (UV) and visible light by molecules, providing insights into molecular structure, concentration, and the dynamics of chemical reactions. Whether it's identifying organic compounds, determining protein concentrations, or studying the kinetics of a reaction, UV-Vis spectroscopy plays an essential role in various scientific fields, including chemistry, biology, pharmacology, and environmental science. In this unit, we will explore the principles behind UV-Vis spectroscopy, its instrumentation, and its other aspects.

8.2 OBJECTIVES

After studying this unit, you shall be able to:

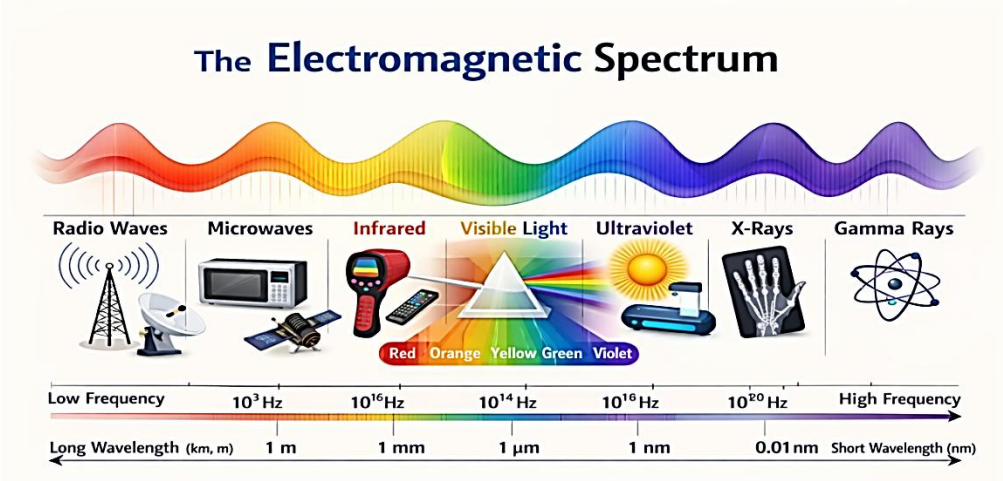
- Understand about electromagnetic radiation.
- Understand the basic concepts of UV-Visible spectroscopy.
- Know the absorption law (Beer-Lambert law).
- Learn about the electronic transitions occurs in UV-Visible spectroscopy.
- Know the different types of shift.
- Learn about the UV- Visible spectrophotometer.

8.3 ELECTROMAGNETIC RADIATION

Electromagnetic radiation (EMR) is a form of energy that propagates through space as oscillating electric and magnetic fields, travelling at the speed of light. It covers a wide range of wavelengths and frequencies known as the electromagnetic spectrum, which includes gamma rays, X-rays, ultraviolet, visible, infrared, microwave, and radio waves. Each region of the spectrum interacts differently with matter, depending on the energy of the radiation (Fig.8.1).

The energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength, as described by Planck's equation, $E = h\nu$, where h is Planck's constant and ν is frequency.

Spectroscopy is the scientific study of the interaction between electromagnetic radiation and matter. When EMR interacts with atoms or molecules, it can be absorbed, emitted, or scattered, leading to transitions between different energy levels.



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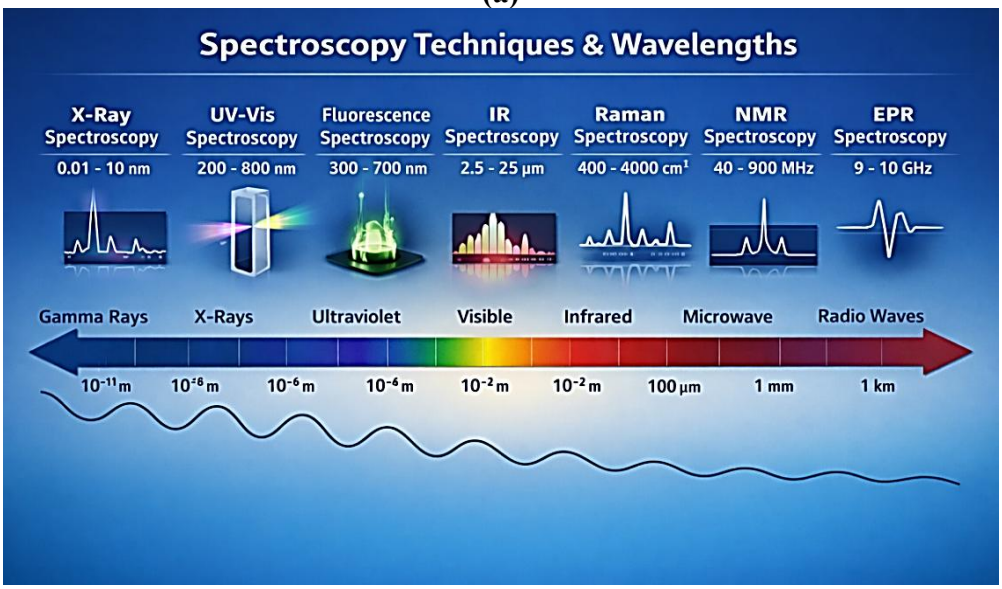


(b)

Fig. 8.1: Electromagnetic radiation and spectroscopy

These interactions produce characteristic spectra that serve as fingerprints for chemical species. Different spectroscopic techniques are associated with specific regions of the electromagnetic spectrum. For example, ultraviolet-visible (UV-Vis) spectroscopy involves electronic transitions, infrared (IR) spectroscopy is related to molecular vibrations, and microwave spectroscopy is associated with rotational transitions. Nuclear magnetic resonance (NMR) and X-ray spectroscopy further extend the applications of electromagnetic radiation in structural elucidation. Thus, electromagnetic radiation provides the fundamental basis for spectroscopy, enabling the identification, characterisation, and understanding of the structure and behaviour of matter at the atomic and molecular levels.

8.4 UV-VISIBLE SPECTROSCOPY

UV-Visible spectroscopy is an analytical technique based on the absorption of ultraviolet (200–400 nm) and visible (400–800 nm) radiation by molecules. The absorption of radiation occurs when the energy of the incident light matches the energy difference between two electronic states of a molecule, resulting in electronic transitions. In organic molecules, these transitions mainly involve promotion of electrons from bonding or non-bonding molecular orbitals to antibonding orbitals, such as $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ transitions.

The amount of radiation absorbed depends on the molecular structure, particularly the presence of chromophores-functional groups capable of absorbing UV–Visible radiation, such as double bonds, aromatic rings, and carbonyl groups. Auxochromes, like –OH, $–NH_2$, and –OR groups, do not absorb strongly themselves but modify the absorption characteristics of chromophores by shifting the absorption wavelength and increasing intensity. Quantitative analysis in UV-Visible spectroscopy is governed by the Beer–Lambert law, which states that absorbance is directly proportional to the concentration of the absorbing species and the path length of the sample cell. Mathematically, it is expressed as $A = \varepsilon cl$, where A is absorbance, ε is molar absorptivity, c is concentration, and l is path length. This principle allows UV-Visible spectroscopy to be widely used for concentration determination.

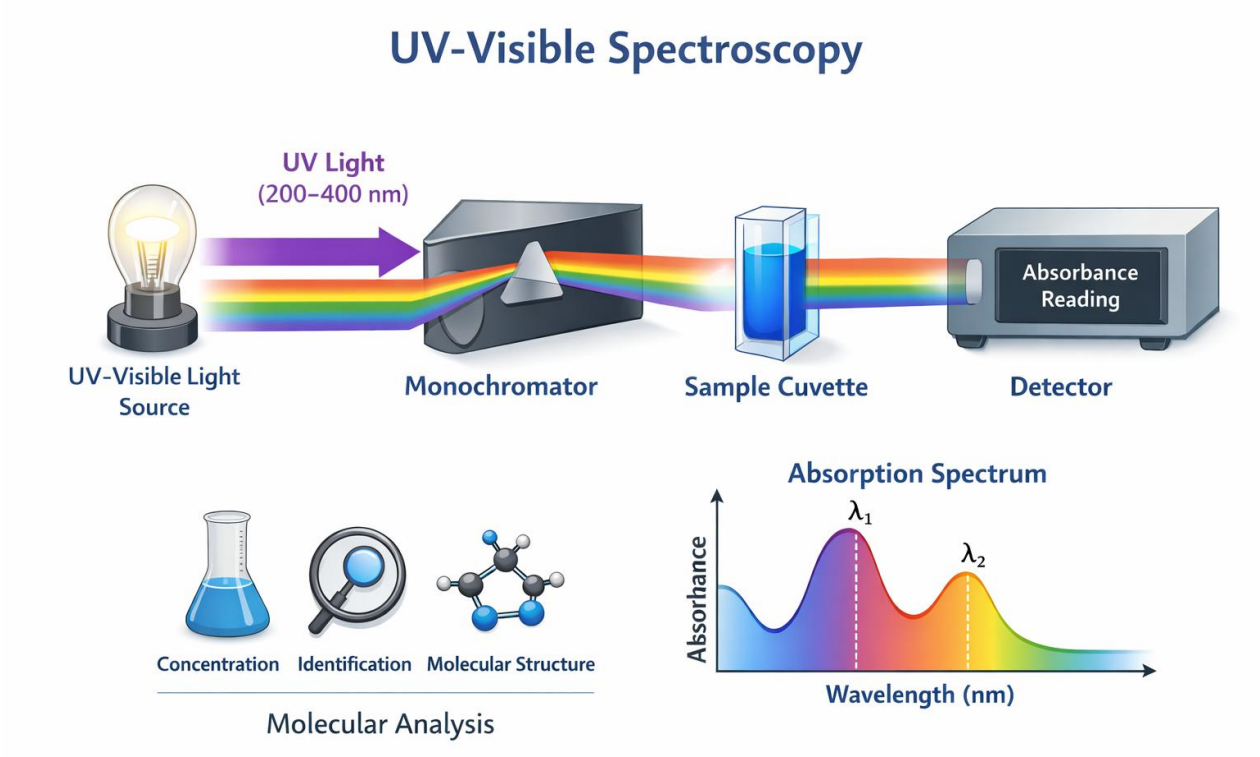


Fig. 8.2: UV-Visible spectroscopy technique

Instrumentation consists of a radiation source (deuterium lamp for UV and tungsten lamp for visible region), a monochromator to select a specific wavelength, a sample cell (usually quartz or glass), and a detector to measure transmitted light (Fig. 8.2). UV-Visible spectroscopy is extensively applied in chemical analysis, pharmaceutical quality control, environmental monitoring, and biochemical studies due to its simplicity, sensitivity, and reliability.

8.5 ABSORPTION LAWS (BEER-LAMBERT LAW)

The Beer-Lambert law is a fundamental principle in absorption spectroscopy that relates the absorption of electromagnetic radiation by a substance to its concentration and the path length of the absorbing medium. It combines two empirical laws: Beer's law and Lambert's law.

- According to Lambert's law, when a beam of monochromatic light passes through a homogeneous absorbing medium, the decrease in intensity is directly proportional to the thickness (path length) of the medium.
- Beer's law states that the absorption of light is directly proportional to the concentration of the absorbing species in the solution.
- Mathematically, the Beer–Lambert law is expressed as:

$$A = \varepsilon cl$$

Where:

A = Absorbance (no units, because it is a logarithmic ratio)

ε = Molar absorptivity (also called molar absorption coefficient) ($L \cdot mol^{-1} \cdot cm^{-1}$)

i = Path length of the sample cell (in cm)

c = Concentration of the solute/ absorbing species (in mol/L)

- Absorbance is a logarithmic measure defined as $A = \log_{10} (I_o/I)$, where I_o is the intensity of incident light and I is the intensity of transmitted light.
- The Beer-Lambert law is widely used in UV-Visible spectroscopy for quantitative analysis because absorbance is directly proportional to concentration within certain limits. It enables the determination of unknown concentrations by measuring absorbance and using calibration curves. However, the law is strictly valid only under ideal conditions, such as dilute solutions, monochromatic radiation, and the absence of chemical interactions or scattering effects.

- Deviations from the Beer-Lambert law may occur due to high concentrations, polychromatic light, stray radiation, or changes in refractive index. Despite these limitations, the Beer-Lambert law remains a cornerstone of analytical chemistry and spectroscopy for routine qualitative and quantitative measurements.

8.5.1 Molar absorptivity

Molar absorptivity, also known as molar extinction coefficient (ε), is a fundamental parameter in UV–Visible spectroscopy that measures how strongly a substance absorbs light at a particular wavelength. It is a constant characteristic of a given substance at a specified wavelength and solvent. According to the Beer–Lambert law:

$$A = \varepsilon cl$$

Where:

A = Absorbance (no units, because it is a logarithmic ratio)

ε = Molar absorptivity (also called molar absorption coefficient) ($L \cdot mol^{-1} \cdot cm^{-1}$)

i = Path length of the sample cell (in cm)

c = Concentration of the solute/ absorbing species (in mol/L)

(i) Significance of Molar Absorptivity

- It indicates the probability of an electronic transition occurring in a molecule.
- Higher ε values correspond to allowed transitions (e.g., $\pi \rightarrow \pi^*$), whereas lower ε values indicate forbidden or weak transitions (e.g., $n \rightarrow \pi^*$).
- It helps in quantitative analysis, allowing determination of unknown concentrations.
- It is useful for comparing the absorbing power of different compounds at the same wavelength.

(ii) Typical ε Values

- $\sigma \rightarrow \sigma^*$ transitions: $\varepsilon \approx 10^5$ (very strong, rarely observed in UV–Vis)
- $\pi \rightarrow \pi^*$ transitions: $\varepsilon \approx 10^4 - 10^5$
- $n \rightarrow \pi^*$ transitions: $\varepsilon \approx 10 - 10^2$

(iii) Factors Affecting ε

- Nature of chromophore
- Degree of conjugation
- Solvent polarity

- Molecular structure and symmetry

8.6 TYPES OF ELECTRONIC TRANSITIONS

In UV-Visible spectroscopy, the absorption of ultraviolet and visible light by molecules leads to electronic transitions, where electrons are excited from lower-energy molecular orbitals to higher-energy orbitals. The type of electronic transition depends on the nature of the molecule, particularly its molecular structure, functional groups, and the arrangement of electrons. Understanding the different types of electronic transitions helps in interpreting UV-Vis spectra and provides insights into the molecular characteristics of a substance.

8.6.1. Types of Electronic Transitions

Several common types of electronic transitions can occur when a molecule absorbs light in the UV-Vis spectrum. These transitions are primarily classified based on the nature of the molecular orbitals involved in the excitation of electrons (Fig. 8.3).

(i) $\pi \rightarrow \pi^*$ Transitions (Pi to Pi-Star Transitions)

- This transition occurs in molecules containing double bonds or aromatic rings, where electrons in bonding π orbitals are excited to anti-bonding π* orbitals. The π orbitals are associated with the electrons in double bonds, such as those in alkenes or aromatic rings.
- Compounds with conjugated systems, especially aromatic compounds (like benzene), alkenes, and polyenes.

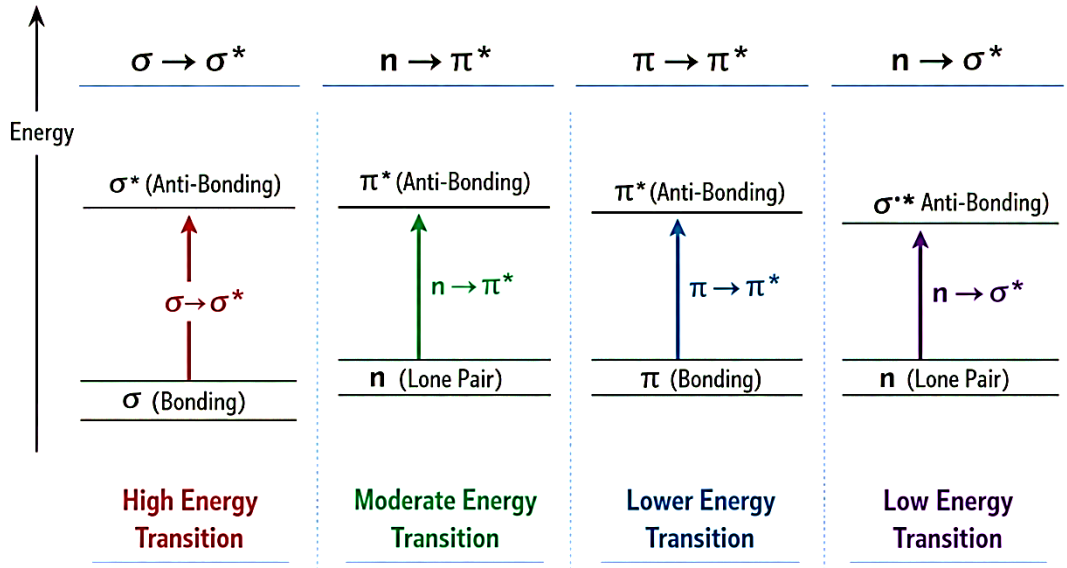


Fig. 8.3: Types of electronic transitions in UV-Visible spectroscopy

- These transitions typically require moderate energy and absorb light in the UV region, usually between 170 nm and 220 nm. For conjugated systems, the absorption may shift to longer wavelengths (near the visible spectrum).

Example: Benzene (C_6H_6): The absorption peak of benzene occurs around 254 nm due to π → π* transitions in the aromatic ring

(ii) n → π* Transitions (Non-Bonding to Pi-Star Transitions)

- This type of transition occurs when an electron from a non-bonding orbital (n) is excited to an anti-bonding π* orbital. Non-bonding electrons are typically found in lone pairs on heteroatoms such as oxygen, nitrogen, or halogens.
- Molecules containing heteroatoms (e.g., carbonyl groups (C=O), nitriles (C≡N), amines, alcohols, etc.). These transitions are often seen in polar functional groups.
- The n → π* transitions require less energy than π → π* transitions and typically absorb light in the UV range (around 200 nm to 250 nm). They usually result in weaker absorption compared to π → π* transitions.
- Example: Aldehydes and Ketones: The carbonyl group (C=O) exhibits an n → π* transition that absorbs light around 280–320 nm.

(iii) σ → σ* Transitions (Sigma to Sigma-Star Transitions)

- The σ → σ* transitions occur when an electron in a σ-bonding orbital (usually associated with single bonds) is excited to an anti-bonding σ* orbital. These transitions involve the promotion of electrons in bonds such as C-H, C-C, N-H, etc., from bonding to anti-bonding orbitals.
- Alkanes and other molecules with single bonds. These transitions are observed in non-conjugated molecules with saturated bonds.
- σ → σ* transitions require high energy and generally absorb in the far UV region (typically below 200 nm). These transitions are often too energetic to be observed in most biological or environmental samples, as they are outside the typical range of UV-Vis spectrometers.
- Example: Alkanes: The σ → σ* transition in alkanes occurs at wavelengths shorter than 180 nm.

(iv) n → σ * Transitions (Non-Bonding to Sigma-Star Transitions)

- This type of transition occurs when an electron from a non-bonding orbital (n) is excited to an anti-bonding σ orbital*. Non-bonding electrons are typically found in lone pairs on heteroatoms such as oxygen, nitrogen, or halogens with saturated bonds.
- Saturated molecules like's alcohols, amines, halides, ethers etc are capable of showing n to σ∗ transitions.
- These transitions require less energy than σ → σ* transitions and typically appear in the range of 150–250 nm. Compounds such as alcohols, amines, and alkyl halides exhibit this type of transition.
- Example: Methyl alcohol: n → σ* transition absorption maxima occur at 174 nm.

8.6.2 Key Factors Influencing Electronic Transitions

Several factors influence the occurrence and intensity of these electronic transitions in UV-Visible spectroscopy:

(i) Conjugation: The greater the conjugation of double bonds in a molecule (as in aromatic systems or polyenes), the more likely it is to undergo π → π transitions*, and these transitions will generally occur at longer wavelengths (shifting into the visible spectrum).

(ii) Substituents: The presence of electron-donating or electron-withdrawing groups can affect the energy gap between molecular orbitals. For example, electron-donating groups (like –OH, $–NH_2$) tend to shift absorption maxima to longer wavelengths (red shift), while electron-withdrawing groups (like $–NO_2$, –COOH) shift absorption maxima to shorter wavelengths (blue shift).

(ii) Solvent Effects: The solvent can influence the energy levels of the molecular orbitals, affecting the wavelengths at which transitions occur. Polar solvents can stabilize certain electronic states (such as n → π transitions*), which can alter the absorption spectrum.

8.7 CHROMOPHORE AND AUXOCHROME

In UV-Visible spectroscopy, the absorption of light by molecules occurs when electronic transitions take place, particularly those involving chromophores-specific groups or parts of molecules responsible for absorbing light. The nature and strength of the absorption can be influenced by the presence of auxochromes, which are groups that modify the absorption properties of the chromophore. Understanding the roles of chromophores and auxochromes is essential for interpreting UV-Vis spectra, as these components determine both the wavelengths of light absorbed and the intensity of absorption (Fig. 8.4).

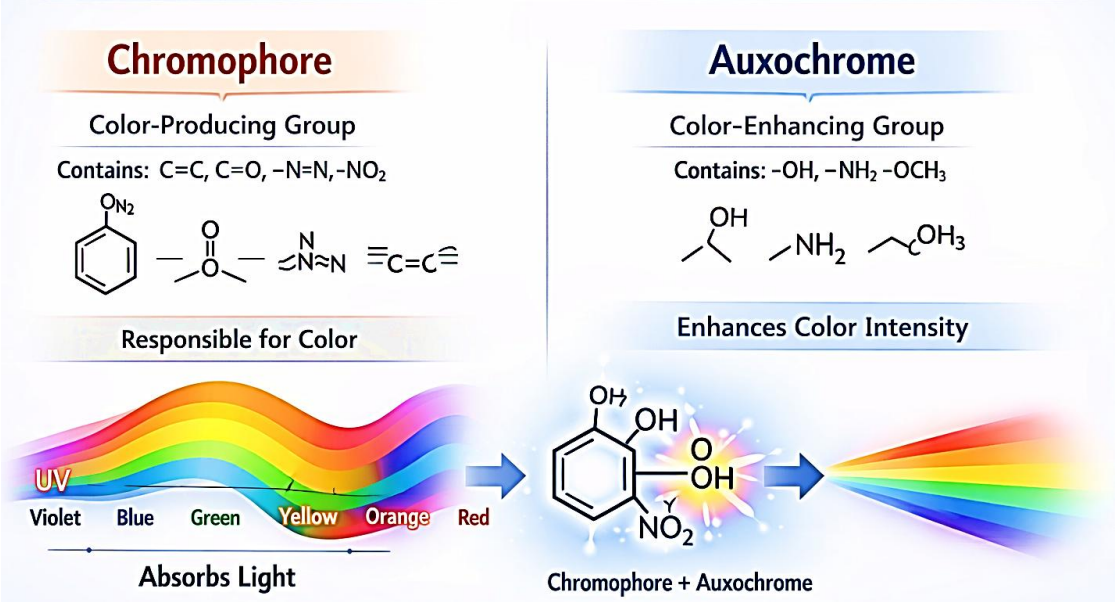


Fig. 8.4: Chromophores and auxochromes

8.7.1 Chromophores

A chromophore is a functional group or part of a molecule that absorbs light in the UV-Vis region (200–800 nm). The absorption occurs because the chromophore has electrons in specific molecular orbitals (like π and non-bonding orbitals) that can be excited by light energy. The specific wavelengths absorbed depend on the electronic structure of the chromophore, including factors like conjugation, polarity, and atomic composition.

Types of Chromophores: Chromophores are typically classified based on their molecular structure and the type of electronic transition they undergo in UV-Vis spectroscopy. Below are some of the common chromophores:

(i) Conjugated Systems (π → π* Transitions)

- Chromophores containing conjugated double bonds (alternating single and double bonds) or aromatic rings are among the most important in UV-Vis absorption. The conjugation allows for the delocalization of electrons over several atoms, which lowers the energy gap between the ground and excited states, making it easier for the molecule to absorb UV-Vis light.
- These chromophores absorb light typically in the UV region (200–400 nm), although conjugated systems can shift the absorption to longer wavelengths (near the visible range), resulting in vibrant colors (like in carotenoids).
- Examples: Aromatic compounds (e.g., benzene, toluene), Alkenes (e.g., butadiene), Polyene systems (e.g., carotenoids, lycopene).

(ii) Carbonyl Groups (n → π* Transitions)

- The carbonyl group (C=O) is another important chromophore in UV-Vis spectroscopy. The carbonyl group can undergo n → π* transitions, where the lone pair of electrons on the oxygen atom is excited to the anti-bonding π* orbital of the carbonyl group.
- The n → π* transition typically absorbs in the UV range, usually around 280–320 nm.
- Examples: Aldehydes, ketones, carboxylic acids, and esters.

(iii) Nitro Groups (n → π* and π → π* Transitions)

- The nitro group (NO_2) is another common chromophore, especially in aromatic compounds. Nitro groups can participate in both n → π* and π → π* transitions, contributing to their UV absorption.
- The nitro group absorbs strongly in the UV region, usually around 200–300 nm.
- Examples: Nitrobenzene, dinitrobenzenes, and other nitro-substituted aromatic compounds.

(iv) Azo Groups (π → π* Transitions)

- Azo groups (–N=N–) are a class of chromophores containing a nitrogen-nitrogen double bond. Azo compounds often have multiple conjugated systems, which extend the π-electron system and make them highly effective at absorbing UV and visible light.
- Azo compounds can absorb light in both the UV and visible regions (400–600 nm), which is why they often exhibit bright colors.
- Examples: Azo dyes, diazo compounds.

(v) Carbon-Carbon Double Bonds (π → π* Transitions)

- Simple carbon-carbon double bonds (C=C) can also act as chromophores. In molecules such as alkenes or dienes, these double bonds can undergo π → π* transitions, where an electron in the π-bonding orbital is excited to the anti-bonding π* orbital.
- These chromophores typically absorb in the UV range, often around 170–210 nm, depending on the degree of conjugation.
- Examples: Alkenes (e.g., ethylene, butene), dienes (e.g., butadiene).

8.7.2 Auxochromes

An auxochrome is a group that, when attached to a chromophore, modifies the absorption characteristics of the chromophore without itself being responsible for absorption. Auxochromes typically influence the intensity and wavelength of absorption by either donating or withdrawing electron density from the chromophore. This effect results in changes in the position (shift) and strength (intensity) of the absorption bands.

Types of Auxochromes: Auxochromes do not absorb light directly but alter the electronic structure of the chromophore, thereby influencing its UV-Vis absorption properties. The effect of an auxochrome can be electron-donating or electron-withdrawing, and both types can lead to changes in the absorption spectrum.

(i) Electron-Donating Auxochromes

- Electron-donating groups increase the electron density of the chromophore, making it easier to excite electrons to higher energy states. As a result, the absorption wavelength typically shifts to longer wavelengths (a phenomenon known as a red shift).
- Examples: –OH (hydroxyl), $–NH_2$ (amine), $–OCH_3$ (methoxy), $–CH_3$ (methyl).
- Effect on Absorption: Electron-donating auxochromes tend to shift the absorption maxima to longer wavelengths (red shift) and can increase the intensity of the absorption.

(ii) Electron-Withdrawing Auxochromes

- Electron-withdrawing groups reduce the electron density of the chromophore, making it harder to excite electrons to higher energy states. As a result, the absorption wavelength typically shifts to shorter wavelengths (a phenomenon known as a blue shift).
- Examples: $–NO_2$ (nitro), –CN (cyano), –COOH (carboxyl), –CO (carbonyl), $–CF_3$ (trifluoromethyl).
- Effect on Absorption: Electron-withdrawing auxochromes tend to shift the absorption maxima to shorter wavelengths (blue shift) and decrease the intensity of the absorption.

8.8 TYPES OF SHIFTS

In UV-Visible spectroscopy, the absorption spectrum of a molecule can change due to alterations in its molecular environment or structure. These changes are often observed as

shifts in the absorption peaks. These shifts provide valuable information about the molecule's electronic structure, the presence of substituents, or changes in the chemical environment. Four important types of shifts observed in UV-Vis spectra are:

(i) Bathochromic Shift (Red Shift)
(ii) Hypsochromic Shift (Blue Shift)
(iii) Hyperchromic Effect
(iv) Hypochromic Effect

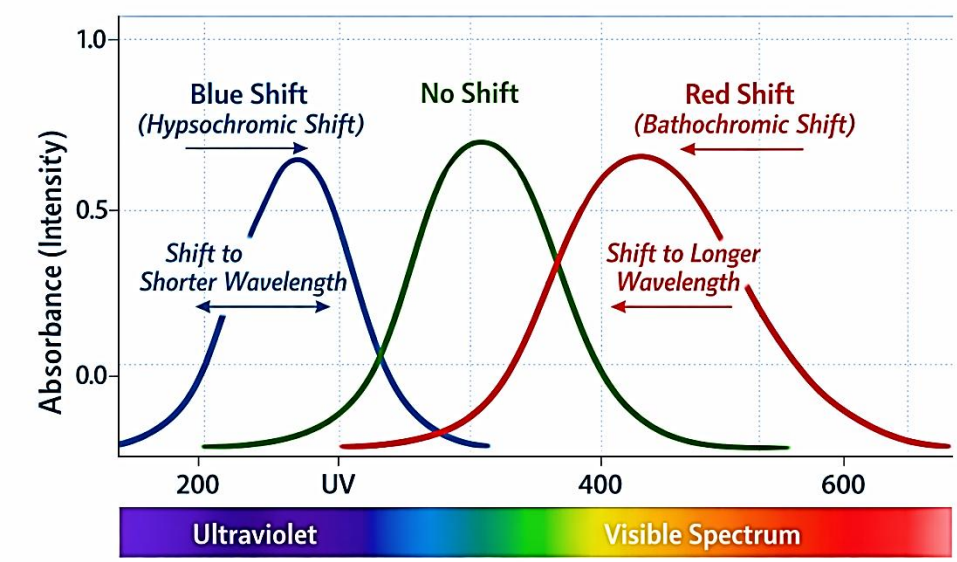
Each of these shifts corresponds to a specific change in the wavelength or intensity of the absorption peaks, and they are typically influenced by the presence of different functional groups or changes in molecular interactions (Fig. 8.5).

(i) Bathochromic Shift (Red Shift)

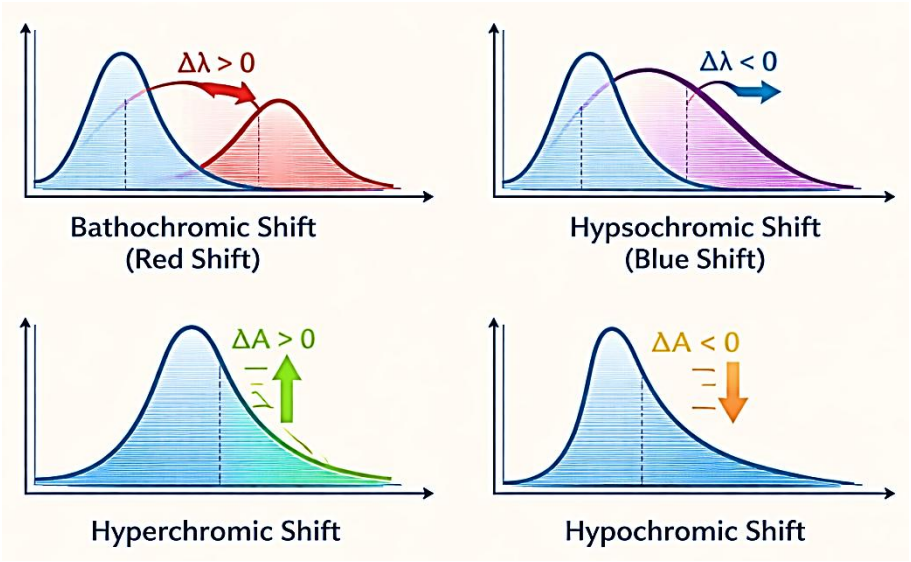
- A bathochromic shift refers to a shift of the absorption maxima to longer wavelengths (i.e., the red end of the spectrum). This shift is commonly known as a red shift.
- A bathochromic shift occurs when the energy gap between the ground state and the excited state of a molecule is reduced, which lowers the energy required to promote an electron to the excited state. As a result, the molecule absorbs light at longer wavelengths (lower energy). This shift is typically associated with increased conjugation or electron-donating groups.
- A bathochromic shift typically occurs when the absorption maximum moves to wavelengths > 400 nm, which corresponds to the red end of the visible spectrum or the near-infrared region.
- Cause:
  (a) Increased conjugation: The more conjugated the system (e.g., in aromatic compounds or polyenes), the more electron delocalization occurs, and the energy required for the electronic transition decreases. This leads to absorption at longer wavelengths.
  (b) Electron-donating substituents: Groups that donate electron density to the chromophore (such as –OH, $–NH_2$, $–OCH_3$) often induce a bathochromic shift by increasing electron density, which lowers the energy gap for electronic transitions.
- Example: Carotenoids (which are polyene compounds) exhibit a bathochromic shift, absorbing light in the visible spectrum and appearing yellow, orange, or red due to the extended conjugation.

(ii) Hypsochromic Shift (Blue Shift)

- A hypsochromic shift refers to a shift of the absorption maxima to shorter wavelengths (i.e., the blue end of the spectrum). This shift is commonly called a blue shift.
- A hypsochromic shift occurs when the energy gap between the ground and an excited state of a molecule increases, requiring more energy to excite an electron. As a result, the molecule absorbs light at shorter wavelengths (higher energy).
- A hypsochromic shift typically moves the absorption maximum to wavelengths < 400 nm, which corresponds to the violet or ultraviolet end of the spectrum.
- Cause:
  - (a) Decreased conjugation: A decrease in conjugation (e.g., breaking up conjugated double bonds or shortening conjugated systems) can result in a hypsochromic shift because the electronic transitions require higher energy.
  - (b) Electron-withdrawing substituents: Groups that withdraw electron density from the chromophore (such as $–NO_2$, –COOH, –CN) increase the energy gap between the ground and excited states, causing a shift to shorter wavelengths.
  - (c) Steric effects: In some cases, steric hindrance can affect the electronic structure and lead to a hypsochromic shift by altering the spatial arrangement of the molecule, increasing the excitation energy.
- Example: Azo compounds: When an electron-withdrawing group like $–NO_2$ is added to an azo compound, a hypsochromic shift is often observed because the added group increases the energy required for the electronic transition.



(a)



(b)

Fig. 8.5: Types of shifts in UV-Visible spectra

(iii) Hyperchromic Effect

- A hyperchromic effect refers to an increase in the intensity (absorbance) of the absorption bands, meaning the molecule absorbs more light at a given wavelength.
- This effect occurs when the absorption of light by a molecule becomes more efficient, usually due to changes in the molecular environment or electronic structure. The energy available for the electronic transition is enhanced, leading to a stronger absorption.
- A hyperchromic effect increases the absorption intensity but does not necessarily affect the wavelength of absorption. It is often observed in systems with increased conjugation or electron-donating groups.
- Cause:
  - (a) Increase in conjugation: Extended conjugation or delocalization of electrons often increases the transition dipole moment, leading to a stronger absorption.
  - (b) Electron-donating groups: Groups like $–NH_2$, –OH, or $–OCH_3$ can donate electron density to the chromophore, increasing the probability of electronic transitions and leading to a stronger absorption.
  - (c) Solvent effects: The solvent can affect the electronic structure of the molecule, enhancing the intensity of absorption. For example, polar solvents can stabilize charged states, increasing absorption.

- Example: In extended conjugated systems (like polycyclic aromatic hydrocarbons), a hyperchromic effect occurs as the system becomes more conjugated, leading to increased light absorption at specific wavelengths.

(iv) Hypochromic Effect

- A hypochromic effect refers to a decrease in the intensity (absorbance) of the absorption bands, meaning the molecule absorbs less light at a given wavelength.
- The hypochromic effect occurs when the molecule's ability to absorb light is reduced. This can happen if the molecule's electronic structure is altered in a way that makes the electronic transitions less likely or less efficient.
- A hypochromic effect results in a decrease in the absorption intensity without necessarily affecting the absorption wavelength.
- Cause:
  (a) Decrease in conjugation: Shortening the conjugated system or breaking up conjugated bonds can reduce the transition dipole moment and weaken the absorption.
  (b) Electron-withdrawing groups: Groups like $–NO_2$, –COOH, or –CN withdraw electron density from the chromophore, reducing the strength of the absorption.
  (c) Solvent effects: In some cases, the solvent can interact with the solute, reducing the efficiency of electronic transitions and causing a decrease in absorbance.
- Example: Benzene derivatives: When a nitro group (NO_2) is added to a benzene ring, the electron-withdrawing effect of the nitro group can result in a hypochromic effect by reducing the intensity of the absorption band of the benzene ring.

8.9 UV-VISIBLE SPECTROPHOTOMETER

UV-Vis spectroscopy requires specialized equipment that can generate, direct, and measure light in the appropriate wavelength range. The typical UV-Visible spectrometer (Fig. 8.6) consists of several key components:

(i) Light Source: The light source provides a continuous spectrum of light that spans the UV and visible regions. Common light sources used in UV-Vis spectroscopy include:

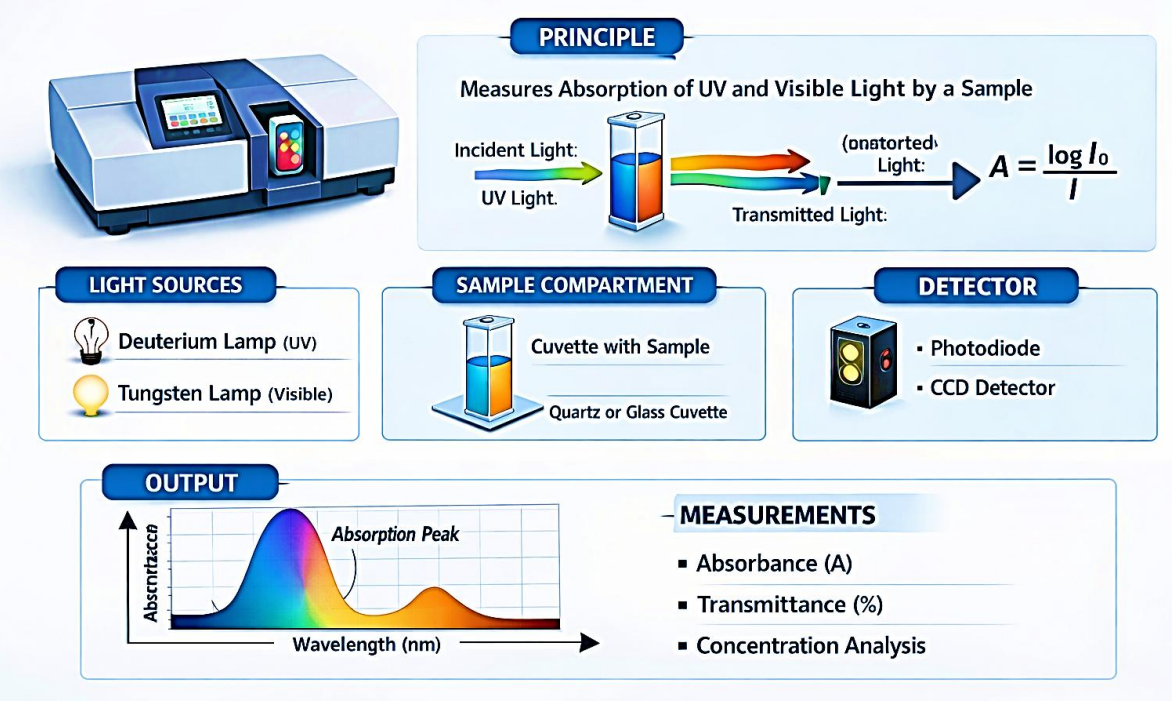


Fig. 8.6: UV-Visible spectrophotometer

(i) Light Source: The light source provides a continuous spectrum of light that spans the UV and visible regions. Common light sources used in UV-Vis spectroscopy include:

- Deuterium Lamp: Used for UV wavelengths (typically 190-400 nm).
- Tungsten Lamp: Used for visible wavelengths (typically 320-800 nm). Often combined with a deuterium lamp to cover the full UV-Vis range.

(ii) Monochromator: A monochromator is an optical device that selects a specific wavelength of light from the light source. It typically consists of a prism or diffraction grating that disperses the light into its component wavelengths, with a rotating slit that selects the desired wavelength.

(iii) Sample Holder (Cuvette): The sample is placed in a cuvette, which is typically a small rectangular container made from transparent material such as quartz or glass. The cuvette is placed in the path of the light beam, and the absorbance of the sample is measured. Cuvettes come in various sizes, with standard path lengths of 1 cm being the most common.

(iv) Detector: The detector measures the intensity of light that passes through the sample. Common detectors include:

- Photodiodes: Detect light intensity in the UV region.
- Photomultiplier Tubes (PMT): Highly sensitive detectors used for low light intensities.

- Charge-Coupled Devices (CCD): Detect light across a range of wavelengths and are commonly used in newer UV-Vis spectrometers.

(v) Data Processing Unit: The data processing unit (usually a computer or microprocessor) records the intensity of the transmitted light at each wavelength and generates the UV-Vis absorption spectrum. Modern instruments often include software for spectral analysis, including baseline correction, peak identification, and quantitative analysis.

8.9.1 Types of UV-Visible Spectrophotometer:

UV-Visible spectrophotometers are analytical instruments used to measure the absorption of ultraviolet (200–400 nm) and visible (400–800 nm) radiation by chemical substances. Based on optical design and mode of measurement, UV–Visible spectrophotometers are broadly classified into the following types.

(i) Single-Beam Spectrophotometer: In a single-beam instrument, light from the source passes through the monochromator and then through the sample cuvette before reaching the detector. The intensity of incident light (I_o) is first measured using a blank, followed by measurement of transmitted light (I) for the sample. These instruments are simple, economical, and suitable for routine analysis, but they are less accurate due to fluctuations in source intensity.

(ii) Double-Beam Spectrophotometer: In this type, the light beam is split into two paths- one passing through the reference (blank) and the other through the sample. The detector compares both signals simultaneously or alternately. This design compensates for variations in lamp intensity and provides higher accuracy and stability, making it ideal for precise quantitative analysis.

Fig. 8.7: Double-Beam UV-Visible Spectrophotometer

8.10 ANALYSIS OF UV-VISIBLE SPECTRA

The presentation and analysis of ultraviolet UV-visible spectra (Fig. 8.8) are essential steps in extracting meaningful information about the electronic structure of molecules. UV-Visible spectra are commonly presented as plots of absorbance (A) or molar absorptivity (ε) on the y-axis versus wavelength (λ), usually in the range of 200–800 nm on the x-axis. The spectrum typically shows one or more absorption bands corresponding to electronic transitions in a molecule. Key features presented include the wavelength of maximum absorption (λmax), intensity of absorption, band shape, and bandwidth. For quantitative studies, absorbance values are recorded at λ_{max} to ensure maximum sensitivity and adherence to Beer–Lambert's law. Proper presentation also includes experimental conditions such as solvent, concentration, path length, and temperature, as these factors influence spectral characteristics.

Analysis of UV-Visible spectra focuses on interpreting the origin and significance of absorption bands. The position of λ_{max} provides information about the type of electronic transition ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, or $\sigma \rightarrow \sigma^*$) and the extent of conjugation in a molecule. Conjugated systems typically show absorption at longer wavelengths (bathochromic shift) due to delocalization of π electrons, while non-conjugated systems absorb at shorter wavelengths. The intensity of absorption, expressed as molar absorptivity, helps distinguish between allowed and forbidden transitions; allowed transitions show high ε values, whereas forbidden transitions have low intensities.

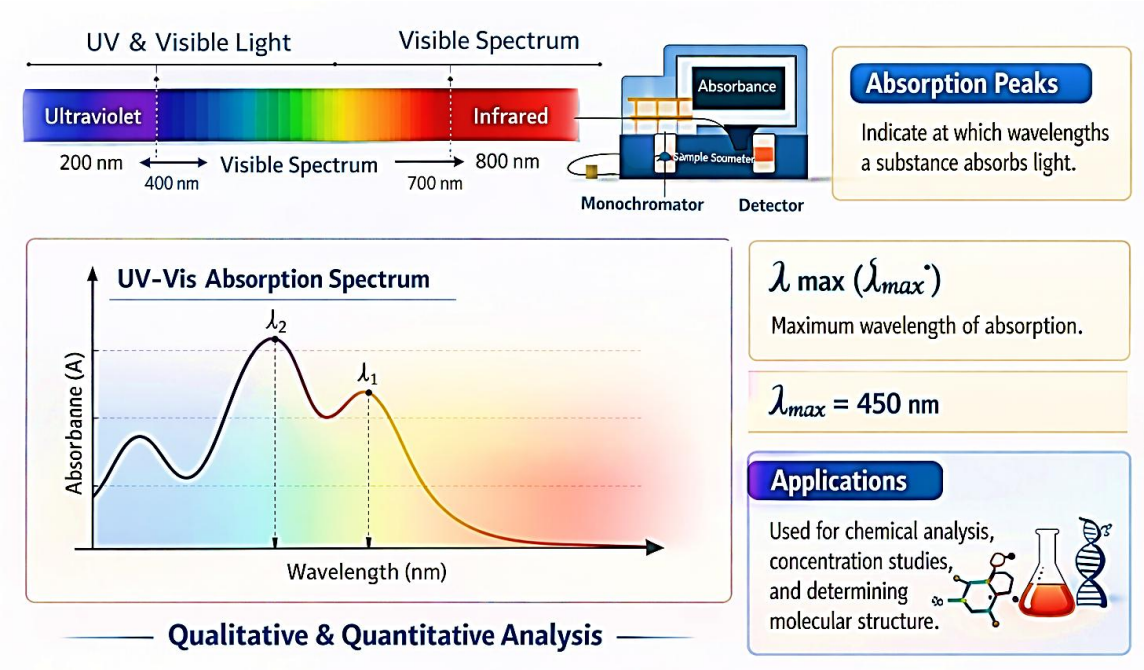


Fig. 8.8: Presentation and analysis of UV-Visible Spectra

Band shape and fine structure also aid in spectral interpretation. Broad bands are characteristic of solution-phase spectra due to vibrational and solvent effects, while sharper bands may be observed in gaseous samples. Solvent polarity, pH, and substituent effects can cause shifts in λ_{max} and changes in intensity, known as solvatochromic and substituent effects. By systematically analyzing these spectral parameters, UV-Visible spectroscopy becomes a powerful tool for qualitative identification, structural elucidation, and quantitative analysis of organic and inorganic compounds.

8.11 UV-VISIBLE SPECTRA OF CONJUGATED ENES AND ENONES

UV-Visible spectra of conjugated enes (alkenes) and enones (α,β-unsaturated carbonyl compounds) display distinct absorption characteristics due to their conjugated π-electron systems. The conjugation of double bonds in these molecules allows for more efficient absorption of UV light, with the absorption bands typically shifting to longer wavelengths as the degree of conjugation increases. Understanding the UV-Visible spectra of conjugated enes and enones is key to analyzing their electronic structure, and it plays a crucial role in various chemical and biological applications, including the study of organic compounds, reaction mechanisms, and the identification of functional groups.

8.11.1 Conjugated Enes (Conjugated Alkenes)

(i) Structure and Electronic Transitions:

- A conjugated alkene consists of alternating single and double bonds, resulting in a delocalized π-electron system. This delocalization lowers the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), making it easier for electrons to be excited from the ground state to the excited state upon absorption of UV light.
- In conjugated systems, the π → π transitions* (transition from a bonding π-orbital to an anti-bonding π*-orbital) dominate the UV absorption spectrum.

(ii) Effect of Conjugation: As the extent of conjugation increases (e.g., in dienes or polyene systems), the absorption shifts to longer wavelengths (bathochromic shift), because the energy gap between the HOMO and LUMO decreases.

(iii) Absorption Bands: Conjugated alkenes usually absorb light in the UV region, typically between 180 nm and 210 nm for simple alkenes. However, more conjugated systems, such as dienes (compounds with two conjugated double bonds), absorb at longer wavelengths (around 200 nm to 300 nm).

(iv) Example and characteristics absorption band:

- Simple Conjugated Alkene (e.g., Ethylene): Absorption occurs typically around 170-190 nm.
- Dienes (Two conjugated double bonds, e.g., butadiene): Absorption occurs in the 200–230 nm range. The increased conjugation lowers the energy gap, leading to a shift in the absorption maxima to longer wavelengths. Two absorption bands are often observed: one at about 217 nm and another, weaker band at about 280 nm due to the overlap of the conjugated π-electrons.
- Polyene Systems (Multiple conjugated double bonds, e.g., carotenoids): These compounds absorb light in the visible range (400–500 nm), giving them vivid colors (yellow, orange, red). The strong conjugation in polyenes reduces the energy gap significantly, causing the absorption to shift into the visible region.

(v) Effect of Substituents on Spectrum:

- Electron-Dongating Groups: Substituents such as –OH or $–NH_2$ (hydroxyl or amino groups) will increase the electron density of the conjugated system, lowering the energy required for the electronic transition and causing a bathochromic shift (shift to longer wavelengths).
- Electron-Withdrawing Groups: Substituents like $–NO_2$ or –CN (nitro or cyano groups) will withdraw electron density from the conjugated system, increasing the energy gap and leading to a hypsochromic shift (shift to shorter wavelengths).

8.11.2 Conjugated Enones (α,β-Unsaturated Carbonyl Compounds)

(i) Structure and Electronic Transitions:

- An enone refers to a compound that contains both a conjugated alkene and a carbonyl group (C=O), specifically in the α,β-position (the two carbons adjacent to the carbonyl group). In α,β-unsaturated carbonyl compounds, the $\pi \rightarrow \pi^*$ transition of the carbonyl group (C=O) can overlap with the $\pi \rightarrow \pi^*$ transition of the conjugated alkene (C=C), resulting in a complex absorption pattern.

- Effect of Conjugation: The conjugation between the carbonyl group and the alkene lowers the energy required for electronic transitions, causing the absorption to shift to longer wavelengths. This makes enones absorb light in the UV-visible region.

(ii) Absorption Characteristics of Enones:

- $\pi \rightarrow \pi^*$ Transition (C=C): The conjugated double bond of the alkene absorbs UV light in the 200–250 nm range due to $\pi \rightarrow \pi$ transitions.
- $n \rightarrow \pi^*$ Transition (C=O): The carbonyl group (C=O) also exhibits an $n \rightarrow \pi^*$ transition, which absorbs light at slightly longer wavelengths, typically between 270–320 nm. This transition involves the excitation of a non-bonding electron from the lone pair on oxygen to the anti-bonding π^* orbital of the C=O group.
- Effect of Conjugation: The stronger the conjugation, the more the absorption band shifts towards longer wavelengths (bathochromic shift). Conjugation between the carbonyl group and the double bond in enones enhances the absorption in the lower UV region (typically 250–350 nm).

(iii) Example:

- Methyl vinyl ketone: This molecule, an α,β-unsaturated ketone, absorbs in the 250–300 nm range due to both the $\pi \rightarrow \pi^*$ transition of the alkene and the $n \rightarrow \pi^*$ transition of the carbonyl group.
- Cyclohexenone: Similar to other enones, cyclohexenone absorbs light in the 240–280 nm range, with the contribution from both the alkene and the carbonyl group.

(iv) Effect of Substituents on UV Spectrum of Enones

- Electron-Dongating Groups: Substituents like –OH or $–NH_2$ can lower the energy of the electronic transitions, causing a bathochromic shift (shift to longer wavelengths) and enhancing the absorption intensity.
- Electron-Withdrawing Groups: Substituents such as $–NO_2$ or –COOH will tend to increase the energy gap between the ground and excited states, leading to a hypsochromic shift (shift to shorter wavelengths).

8.12 SUMMARY

In this unit you have learnt that:

- Spectroscopy is the study of interaction of electromagnetic radiations with the matter and is used to identify a substance, which may include UV, IR, NMR and Raman etc.
- The basic principles of UV-Visible spectroscopy, including the interaction of ultraviolet and visible radiation with matter and its role in studying electronic transitions in atoms and molecules.
- The components and working of a UV-Visible spectrophotometer, such as radiation sources, monochromators, sample cells, detectors, and recorders, and their importance in accurate spectral measurement.
- Beer-Lambert's law, explaining the relationship between absorbance, concentration, and path length, and its application in quantitative analysis.
- Different types of electronic transitions ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) and how molecular structure and conjugation influence absorption characteristics.
- Interpret UV–Visible spectra using parameters like λmax, absorbance, band intensity, and shifts (bathochromic, hypsochromic, hyperchromic, hypochromic).
- The use of UV-Visible spectroscopy in qualitative structure elucidation, quantitative determination of compounds, reaction monitoring, and pharmaceutical and chemical analysi

8.13 TERMINAL QUESTIONS

1. Explain the principle and scope of UV–Visible spectroscopy.
2. Describe in detail the construction and working of a UV-Visible spectrophotometer.
3. Explain the role of radiation sources, monochromators, sample cells, detectors, and signal processors.
4. State the Beer-Lambert law.
5. Describe various types of electronic transitions observed in UV–Visible spectroscopy with suitable molecular examples and energy order.

8.14 BIBLIOGRAPHY/REFERENCES

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UNIT 9: IR-SPECTROSCOPY

CONTENTS:

9.1 INTRODUCTION

In the previous unit we learn about UV-Visible spectroscopy, principle, electronic transition, instrumentation and interpretation of spectra. In this unit we learn about the Infra-Red (IR) absorption spectroscopy. Infrared (IR) spectroscopy studies the interaction of infrared radiation with molecules, causing vibrational transitions. It helps identify functional groups and chemical bonds based on characteristic absorption frequencies, making it a powerful tool for qualitative analysis and structural elucidation of organic and inorganic compounds.

9.2 OBJECTIVES

After studying this unit, you will be able to

- Understand the basic concept of Infra-red absorption spectroscopy
- Known fundamental modes of vibration of a molecule
- Known about the selection rule
- Learn about finger fingerprint region
- Identify the characteristics IR absorption functional group of molecules

9.3 INFRA-RED (IR) SPECTROSCOPY

Infrared (IR) spectroscopy is an important analytical technique used to identify functional groups and study molecular structure based on the interaction of infrared radiation with matter. The basic principle of IR spectroscopy involves the absorption of infrared radiation by molecules, leading to changes in their vibrational energy levels.

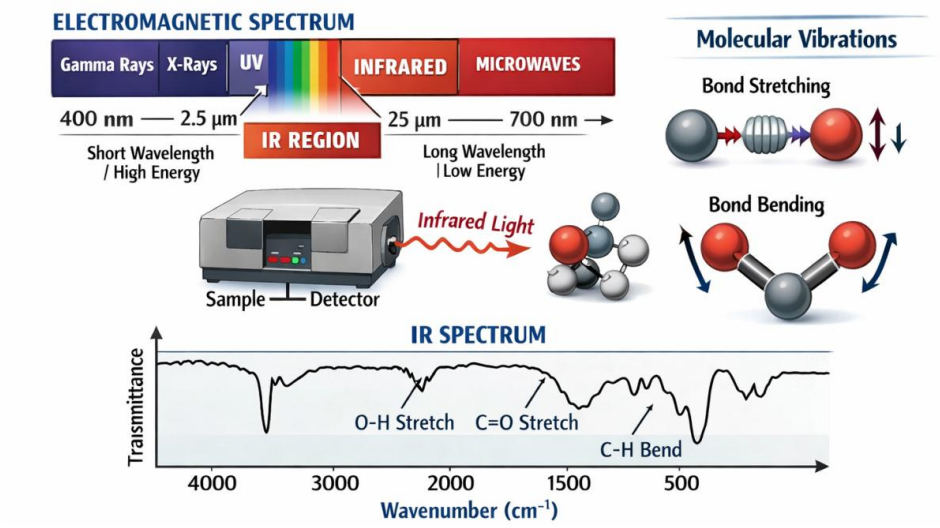

Fig. 9.1: Basics of IR Spectroscopy

Molecules consist of atoms connected by chemical bonds that behave like springs. When IR radiation of appropriate frequency passes through a sample, it is absorbed if the frequency of the radiation matches the natural vibrational frequency of a particular bond. This absorption causes transitions between vibrational energy levels, resulting in stretching or bending vibrations of the bonds. Each type of chemical bond and functional group absorbs IR radiation at characteristic frequencies, producing a unique absorption pattern known as an IR spectrum (Fig. 9.1).

For a molecular vibration to be IR active, it must involve a change in the dipole moment of the molecule. Thus, polar bonds such as O–H, N–H, and C=O show strong IR absorptions, whereas nonpolar molecules like N_2 or O_2 are generally IR inactive. The infrared region is commonly divided into near-IR (14,000–4,000 cm^{-1}), mid-IR (4,000–400 cm^{-1}), and far-IR (400–10 cm^{-1}), with the mid-IR region being most widely used for chemical analysis.

An IR spectrum is typically plotted as percentage transmittance or absorbance versus wavenumber (cm^{-1}). The region above 1,500 cm^{-1} is known as the functional group region, while the region below 1,500 cm^{-1} is called the fingerprint region, which is unique for each compound. The position, intensity, and shape of absorption bands provide valuable information about the presence of functional groups, molecular bonding, and intermolecular interactions. Thus, IR spectroscopy is widely used in organic, inorganic, pharmaceutical, and biochemical analysis for qualitative identification and structural characterisation of compounds.

9.4 MOLECULAR VIBRATIONS

Molecular vibrations refer to the periodic motions of atoms within a molecule about their equilibrium positions. These vibrations arise because chemical bonds behave like elastic springs: when atoms are displaced from their mean positions, restoring forces act to bring them back. Molecular vibrations are of fundamental importance in chemistry because they form the basis of infrared (IR) spectroscopy and Raman spectroscopy, which are widely used for molecular identification and structural analysis.

(a) Nature of Molecular Vibrations

In a molecule, atoms are not stationary; even at absolute zero, they possess zero-point energy and continue to vibrate. At ordinary temperatures, these vibrations become more pronounced. Each molecule has a specific set of vibrational modes determined by its number of atoms and geometry. For a molecule containing N atoms, the total number of vibrational degrees of freedom is 3N – 6 for non-linear molecules and 3N – 5 for linear molecules.

(b) Types of Molecular Vibrations

Molecular vibrations can be classified into two main categories: stretching and bending vibrations. These vibrations occur at different frequencies depending on the nature of the bonds and the masses of the atoms involved (Fig. 9.2).

(1) Stretching Vibrations: Stretching involves changes in the length of a bond. Stretching vibrations can be further divided into two types:

(i) Symmetrical stretching: Both atoms in a diatomic molecule or both bonds in a polyatomic molecule stretch simultaneously.
(ii) Asymmetrical stretching: One bond stretches while the other remains in place, leading to a fluctuation in the bond length.

(2) Bending Vibrations: Bending involves changes in the angle between two bonds. These are typically lower in energy compared to stretching vibrations. Bending vibrations can also be divided into different types:

(i) In-Plane Bending:

- Scissoring: The two atoms move toward and away from each other in a motion similar to a scissor (i.e., the bond angle opens and closes).
- Rocking: The atoms move in opposite directions, with the bond angle changing slightly in the same plane.

(ii) Out-of-Plane Bending:

- Wagging: The atoms move in and out of the plane, typically with a motion resembling a "wagging" motion.
- Twisting: The atoms move in a twisting motion around the bond axis, causing the bond angles to distort.

(c) Example, in a carbon dioxide (H_2O) molecule, the stretching vibrations occur as follows:

- Symmetrical stretch: Both O-H bonds elongate and shorten together.
- Asymmetrical stretch: One O-H bond elongates while the other shortens.

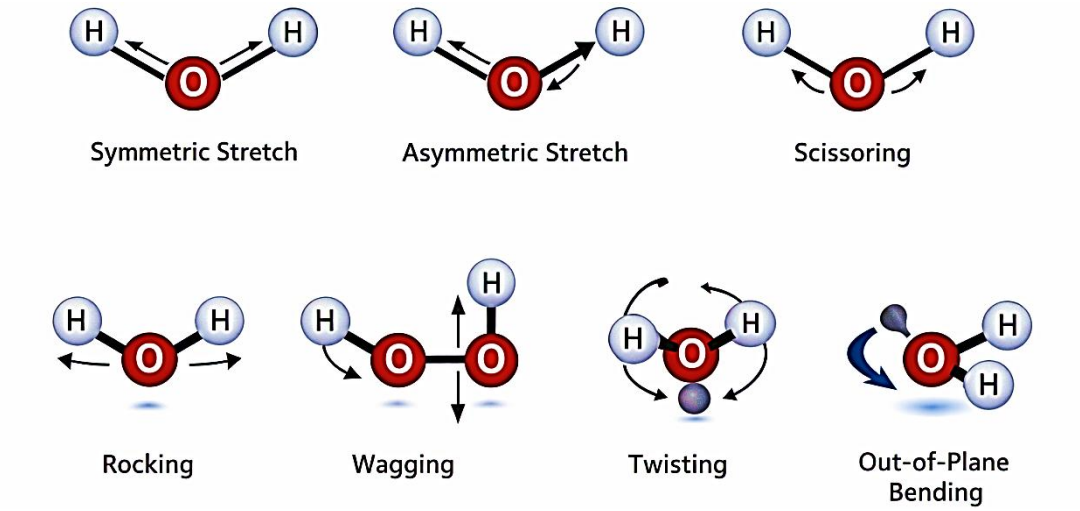

Fig.9.2: Types of molecular vibration

9.5 HOOKE'S LAW

Hooke's law plays a fundamental role in understanding molecular vibrations observed in infrared (IR) spectroscopy. In classical physics, Hooke's law states that the force required to stretch or compress a spring is directly proportional to the displacement from its equilibrium position. This concept can be applied to molecular bonds, which behave like tiny springs connecting atoms.

In IR spectroscopy, a chemical bond between two atoms is treated as a harmonic oscillator. When infrared radiation interacts with a molecule, it can cause stretching or bending vibrations of these bonds. According to Hooke's law, the vibrational frequency of a bond depends on two main factors: the bond strength (force constant, k) and the masses of the bonded atoms.

Mathematically, the vibrational frequency (ν) of a diatomic molecule is given by:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Where,

k = force constant of the bond (measure of bond strength),

μ = reduced mass of the two atoms.

From this relationship, it is clear that stronger bond (higher force constant), such as triple bonds, vibrate at higher frequencies, while weaker bonds vibrate at lower frequencies. Similarly, bonds involving lighter atoms absorb IR radiation at higher frequencies compared to those involving heavier atoms.

Hooke's law thus explains why different functional groups absorb IR radiation at characteristic frequencies. For example, O–H and N–H bonds absorb at higher wavenumbers due to their low reduced mass and relatively strong bond strength, whereas C–C and C–S bonds appear at lower frequencies.

Although real molecular vibrations are not perfectly harmonic and deviations occur at higher energy levels, Hooke's law provides a useful approximation for interpreting IR spectra. Therefore, it forms the theoretical basis for correlating IR absorption frequencies with molecular structure, making it essential for functional group identification in organic and inorganic chemistry.

9.6 SELECTION RULES

In IR spectroscopy, the selection rules are principles that determine whether a specific vibrational mode of a molecule will absorb infrared radiation. These rules are essential for understanding which vibrational modes in a molecule are IR-active (i.e., can absorb infrared light) and which are IR-inactive (i.e., do not absorb infrared light) Fig. 9.3.

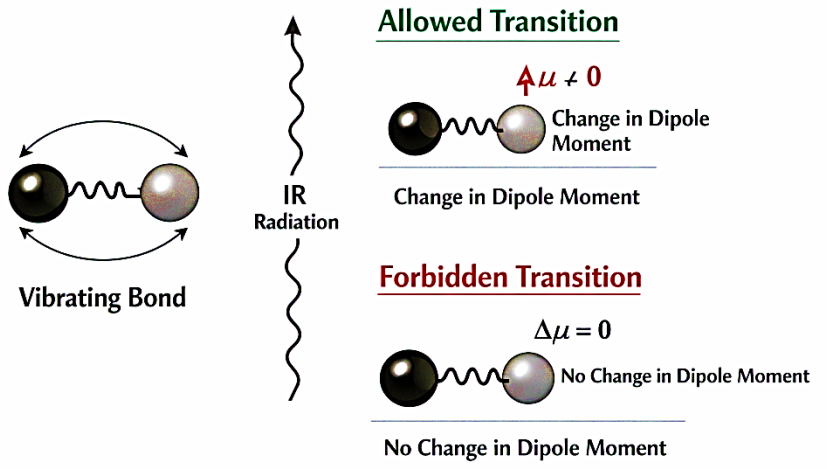

Fig. 9.3: IR active vibration mode

The selection rules in IR spectroscopy are based on the interaction between infrared radiation and the molecular vibrations. Specifically, they depend on the change in dipole moment of the molecule during vibration and the symmetry of the molecule.

(i) IR-active vibrations are those that cause a fluctuation in the dipole moment as the atoms in the molecule move during vibration. These vibrations interact with infrared light and are capable of absorbing energy at specific wavelengths.

(ii) IR-inactive vibrations, on the other hand, do not result in a change in dipole moment, and therefore cannot absorb infrared light. These vibrations are not detected in the IR spectrum.

There are two main selection rules in IR spectroscopy:

(1) Dipole Moment Change: A vibration will only be IR-active if it results in a change in the dipole moment of the molecule during the vibration.

Example: In a water (H_2O) molecule, the bending and asymmetric stretching modes cause a fluctuating dipole moment, making them IR-active.

Example: In a carbon dioxide (CO_2) molecule, the symmetric stretching mode does not induce a dipole moment change, so it is IR-inactive. However, the asymmetric stretching mode is IR-active because it creates a fluctuating dipole moment.

(2) Molecular Symmetry: The symmetry of the molecule influences whether a particular vibrational mode is IR-active. This is determined by the symmetry of the molecular structure and how the atoms or groups within the molecule move relative to each other.

(a) Symmetrical molecules: In highly symmetrical molecules (such as CO_2 or N_2), some vibrational modes may not induce a change in dipole moment because of the symmetry of the molecule. Symmetry rules dictate that these vibrations will be IR-inactive.

Example: In CO_2, the symmetric stretch (where both C=O bonds stretch and compress simultaneously) does not cause a dipole moment change and thus is IR-inactive. The molecule's overall symmetry cancels out any potential dipole moment fluctuation during the vibration.

(b) Asymmetric molecules: In molecules that lack symmetry (such as H_2O, NH_3, or HCl), most of the vibrational modes lead to a fluctuating dipole moment and thus are IR-active.

Example: In a water (H_2O) molecule, the bending and asymmetric stretching modes result in a change in the dipole moment as the atoms move, making these modes IR-active. Water's bent shape leads to non-symmetrical vibrations that induce dipole moment changes.

9.7 FINGER PRINT REGION

The fingerprint region is a crucial part of an infrared (IR) spectrum, typically lying in the range of 1500–400 cm^{-1}. This region is called the "fingerprint" region (Fig. 9.4) because the absorption pattern observed here is unique for every compound, much like a human fingerprint.

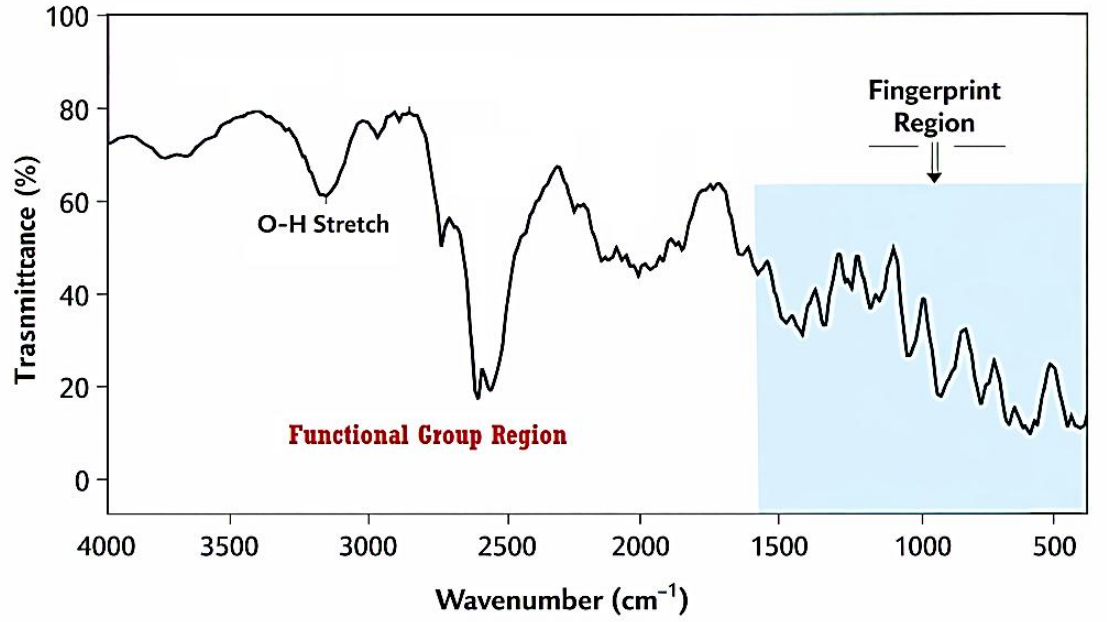

Fig. 9.4: IR spectrun showing fingerprint region

In the fingerprint region, absorption bands arise mainly due to complex vibrational modes, such as bending vibrations, skeletal vibrations, and coupled stretching–bending motions of bonds within a molecule. Unlike the functional group region (4000–1500 cm^{-1}), where peaks can be directly assigned to specific functional groups, the bands in the fingerprint region are numerous, closely spaced, and often overlapping, making individual peak assignment difficult.

Despite this complexity, the fingerprint region is extremely valuable for compound identification. Even molecules with the same functional groups and similar structures show noticeable differences in this region due to variations in atomic masses, bond strengths, and

molecular geometry. Therefore, comparison of an unknown compound's fingerprint region with that of a reference or standard spectrum allows confident identification.

The fingerprint region is especially important in quality control, pharmaceutical analysis, forensic chemistry, and polymer characterization. Any slight change in molecular structure-such as isomerism or substitution-produces a distinct change in this region of the spectrum.

The absorption bands in the fingerprint region are typically caused by various low-frequency vibrational modes of the molecule. These include:

- C-H Bending vibrations often appear in the 1300–1000 cm^{-1} range.
- C-C Stretching and bending vibrationsboften appear between 500–1000 cm^{-1}.
- O-H Bending vibrations can appear in the 1300–1000 cm^{-1} range.
- N-H bending vibrations are seen in the fingerprint region around 1600–1500 cm^{-1}.
- C-N stretching may appear in the 1200–1000 cm^{-1} region.

9.8 INTENSITY AND POSITION OF IR BANDS

Infrared (IR) spectroscopy is a powerful analytical technique used to identify functional groups in molecules based on their vibrational transitions. Two important characteristics of an IR absorption band are its position (wavenumber) and intensity, both of which provide valuable structural information.

(a) Position of IR Bands: The position of an IR band is expressed in terms of wavenumber (cm^{-1}) and corresponds to the energy required for a particular molecular vibration. The position of an absorption band depends mainly on the strength of the bond and the masses of the atoms involved, as described by Hooke's law. Factors affecting band position include:

(i) Bond strength (force constant): Stronger bonds vibrate at higher frequencies. For example, triple bonds absorb at higher wavenumbers than double or single bonds (C≡C > C=C > C–C).

(ii) Atomic masses: Lighter atoms vibrate at higher frequencies. Hence, O–H and N–H stretches appear at higher wavenumbers than C–H stretches.

(iii) Hybridization: Greater s-character increases bond strength and frequency ($sp > sp^2 > sp^3$).

(iv) Hydrogen bonding: Hydrogen bonding lowers the stretching frequency and broadens the band, as seen in O–H stretching vibrations.

(v) Electronic effects: Conjugation and inductive effects can shift absorption bands to lower or higher wavenumbers.

(b) Intensity of IR Bands: The intensity of an IR absorption band reflects how strongly a molecule absorbs IR radiation during a vibration. It depends on the change in dipole moment that occurs during the vibrational transition. Key points influencing intensity are:

(i) Change in dipole moment: Vibrations that involve a large change in dipole moment produce strong absorption bands. For example, C=O stretching vibrations are very intense.

(ii) Bond polarity: More polar bonds give rise to stronger IR bands than non-polar bonds.

(iii) Symmetry of molecules: Symmetrical vibrations may show weak or no absorption if there is little or no dipole moment change.

9.9 IR SPECTROMETER

When infrared radiation passes through a sample, specific frequencies are absorbed if they match the vibrational energy levels of the molecule. These absorptions appear as peaks in an IR spectrum, typically plotted as percent transmittance or absorbance versus wavenumber (cm^{-1}). An IR spectrometer (Fig. 9.5) mainly consists of:

(i) IR Radiation Source – Common sources include Nernst glower or Globar, which emit a continuous range of IR radiation.

(ii) Monochromator or Interferometer – In dispersive instruments, a prism or grating separates frequencies. In modern FTIR (Fourier Transform Infrared) spectrometers, a Michelson interferometer modulates all wavelengths simultaneously.

(iii) Sample Holder – The sample may be analyzed as a solid, liquid, or gas using appropriate accessories.

(iv) Detector – Thermal detectors (thermocouples, bolometers) or photon detectors (DTGS, MCT) convert IR radiation into an electrical signal.

(v) Data Processor/Recorder – The signal is amplified, processed, and displayed as an IR spectrum.

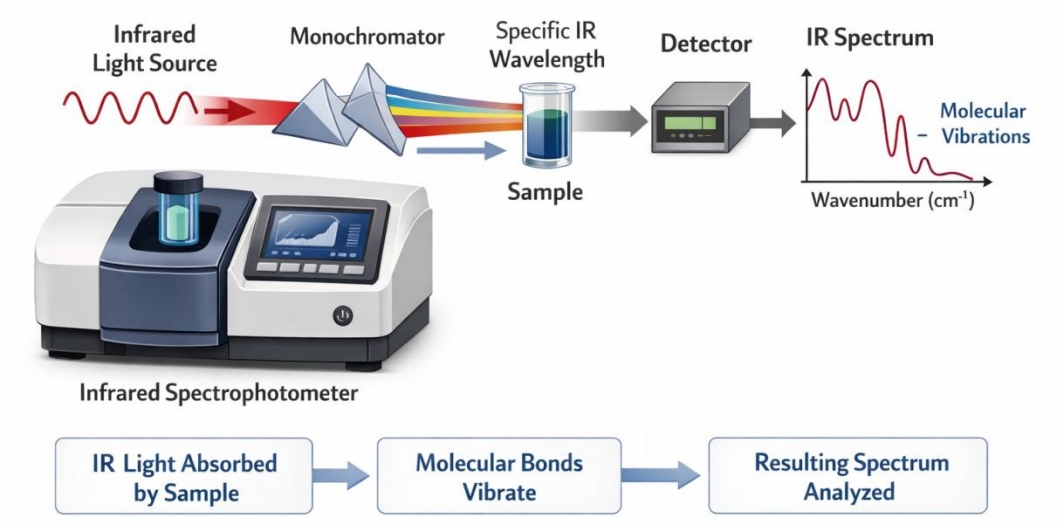

Fig. 9.5: Representation of IR spectrometer

Types of IR Spectrometers

Over time, two major types of IR spectrometers have evolved: Dispersive IR Spectrometers and Fourier Transform Infrared (FTIR) Spectrometers. Each type has distinct characteristics and advantages.

(i) Dispersive IR Spectrometers:

In a dispersive spectrometer, a monochromatic IR beam is generated by passing the radiation through a prism or diffraction grating. The grating separates the light into different wavelengths, which are then directed through the sample. After passing through the sample, the light is directed to a detector that measures the intensity of each wavelength.

While these instruments were widely used for many years, they are slower and less sensitive compared to FTIR spectrometers. They typically scan one wavelength at a time, which means they require more time to gather data.

(ii) Fourier Transform Infrared (FTIR) Spectrometers:

FTIR spectrometers have revolutionized IR spectroscopy. Unlike dispersive systems, FTIR instruments measure all wavelengths of infrared radiation simultaneously, using an interferometer. The interferometer splits the incoming infrared beam into two paths, with one being fixed and the other moving. The beams are recombined, producing an interference pattern that contains information about all the wavelengths in the sample. This pattern is then analyzed by a mathematical Fourier transform to generate the final spectrum.

FTIR spectrometers are faster, more sensitive, and capable of better resolution compared to traditional dispersive spectrometers. Moreover, FTIR instruments require less sample material, making them ideal for trace analysis and complex samples.

(b) Sample Preparation Techniques:

Sample preparation is a critical step in obtaining high-quality IR spectra. The method of preparation depends on the physical state of the sample—whether it is solid, liquid, or gas.

(i) Solid Samples:

For solid samples, one common technique involves grinding the sample with potassium bromide (KBr) to create a fine powder. This powder is then pressed into a transparent pellet, allowing the IR light to pass through the pellet. KBr is transparent in the IR region, making it an ideal medium for creating these pellets.

In some cases, particularly when dealing with very small quantities, the Attenuated Total Reflectance (ATR) technique is used. This technique requires no special sample preparation. Instead, a solid sample is placed in direct contact with a crystal (typically made from materials like diamond, zinc selenide, or germanium), and IR light is reflected within the crystal. The interaction between the sample and the light generates an absorption spectrum.

(ii) Liquid Samples:

Liquid samples are typically placed between two transparent windows made from materials like sodium chloride (NaCl) or potassium bromide (KBr), which are transparent to IR radiation. Thin liquid films can be used for transmission spectroscopy, or liquid samples can be placed in special cells, such as a Liquid transmission cell or microsampling cells for more concentrated analysis.

(iii) Gas Samples:

For gases, a gas cell with windows made of materials like NaCl or KBr is used. Gas-phase samples require a long path length to achieve adequate absorption, which is why gas cells typically have larger volumes than liquid or solid cells.

9.10 CHARACTERISTIC ABSORPTIONS OF VARIOUS FUNCTIONAL GROUPS

It is based on the absorption of infrared radiation by molecules, causing transitions between vibrational energy levels. Each functional group absorbs IR radiation at characteristic frequencies (expressed as wavenumbers, cm^{-1}), allowing qualitative structural identification.

Characteristic IR absorptions provide a fingerprint for functional groups in a molecule. By analysing the position, intensity, and shape of absorption bands, IR spectroscopy enables rapid identification of functional groups and plays a vital role in structural elucidation. The table below summarises the typical absorption Range (wavenumber ranges) for various types of molecular vibrations:

Vibrational Mode	Absorption Range (cm^{-1})	Description (Functional Group)
C–H Stretch	2800–3000 cm^{-1}	Alkane C–H bonds
C=O Stretch	1650–1750 cm^{-1}	Carbonyl groups (aldehydes, ketones, carboxylic acids)
C≡C Stretch	2100–2260 cm^{-1}	Alkynes (triple bonds)
O–H Stretch	3200–3550 cm^{-1}	Alcohols, phenols, carboxylic acids
N–H Stretch	3300–3500 cm^{-1}	Amines, amides
C–C Stretch	800–1300 cm^{-1}	Alkanes, alkenes
C=C Stretch	1600–1680 cm^{-1}	Alkenes
C–H Bending	1350–1450 cm^{-1}	Methyl (CH_3) and methylene (CH_2) groups
C–C Bending	500–1000 cm^{-1}	Alkanes, alkenes, cyclic compounds

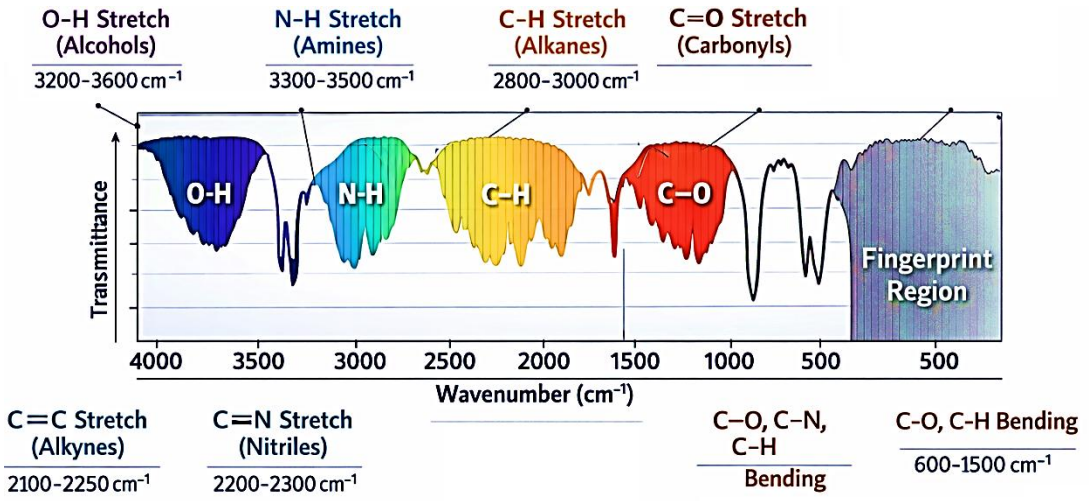

Fig.9.6 IR spectrum showing the absorption band of the functional group

9.11 INTERPRETATION OF IR SPECTRA

To interpret an IR spectrum of a simple organic compound, one must understand how to identify the functional groups, bond types, and molecular vibrations that produce characteristic absorption bands. Below are the key steps and considerations for interpreting IR spectra:

1. General Process of Interpreting an IR Spectrum: The basic steps in interpreting an IR spectrum include:

(i) Examine the entire spectrum: Identify the major absorption bands and the general regions where they occur.

(ii) Assign functional groups: Use the known wavenumber ranges to assign specific functional groups and bonds to the corresponding absorption peaks.

(iii) Consider molecular structure: Use the information gathered to infer the molecular structure and confirm the identity of the compound.

2. Key Regions of the IR Spectrum: The IR spectrum is divided into two main regions:

(i) The Functional Group Region (Above 1500 cm^{-1})

This region contains the stronger, more distinct absorption bands that correspond to the stretching vibrations of functional groups like C–H, O–H, C=O, N–H, and more. It is particularly useful for identifying functional groups.

(ii) The Fingerprint Region (Below 1500 cm^{-1})

The fingerprint region contains complex absorptions due to bending vibrations, twisting, and other low-frequency motions of the molecule. These bands are unique to the compound and are useful for confirming the molecular identity rather than functional group identification.

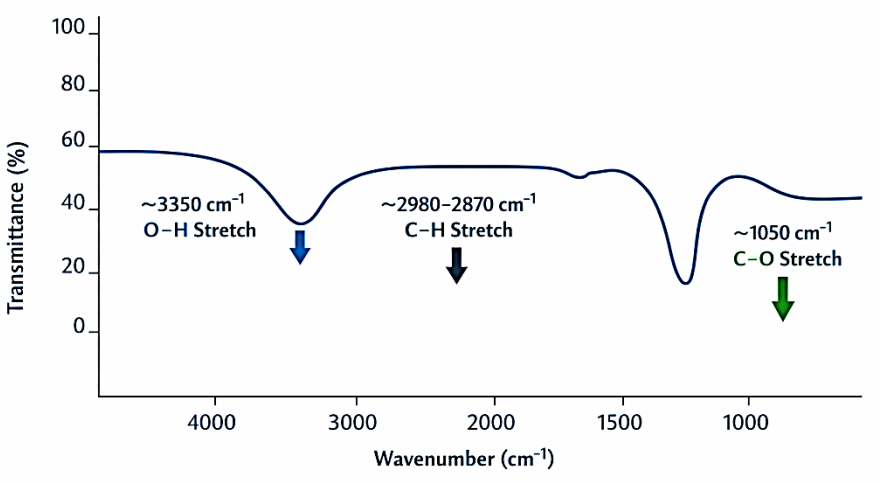

Fig. 9.7 IR spectrum of ethanol molecule

3. Example:

(i) Interpretation of IR spectra

- Look for the O-H: The broad peak in the 3200-3550 cm^{-1} regions is the most defining feature, indicating an alcohol.
- Check C-H Stretches: Verify the presence of alkyl C-H bonds near 2900-3000 cm^{-1}.
- Find the C-O Stretch: Confirm the C-O bond with the peak around 1050-1150 cm^{-1}.
- Absence of C=O: The absence of a strong peak around 1700 cm^{-1} (typical for carbonyls like in ethanal) helps confirm it's alcohol and not an aldehyde/ketone.

(ii) Significant bands in ethanol IR spectrum:

- O-H Stretch (Alcoholic): A very broad and strong absorption band, often centered around 3350 cm^{-1}, due to intermolecular hydrogen bonding.
- C-H Stretch (Alkyl): Peaks typically found between 2870-2980 cm^{-1}, corresponding to CH_3 and CH_2 groups (e.g., ~2981 cm^{-1} for CH_2).
- C-O Stretch: A strong, characteristic peak for primary alcohols, usually around 1050-1075 cm^{-1} (e.g., ~1050 cm^{-1} in ethanol).
- Thus the given spectra represent the molecular structure of ethanol.

9.12 SUMMARY

1. IR spectroscopy is based on the absorption of infrared radiation by molecules, causing vibrational transitions of chemical bonds.
2. Only vibrations that produce a change in dipole moment are IR-active and give rise to absorption bands.
3. The IR spectrum is divided into functional group region (4000–1500 cm^{-1}) and fingerprint region (1500–400 cm^{-1}), useful for identification.
4. Different functional groups absorb at characteristic frequencies, enabling qualitative analysis of organic compounds.
5. An IR spectrometer consists of a radiation source, monochromator or interferometer, sample holder, detector, and recorder to obtain an IR spectrum.
6. Fourier Transform Infrared (FTIR) spectroscopy uses an interferometer and mathematical Fourier transformation to obtain spectra with higher speed, sensitivity, and resolution.
7. The IR-spectrum can be obtained in all the three states, solid, liquid and gas.

9.13 TERMINAL QUESTIONS

1. Discuss the different types of molecular vibrations and the conditions required for a vibration to be IR active.
2. Explain group frequency and fingerprint regions in IR spectra. How are these regions useful in the structural identification of organic compounds?
3. Write a detailed note on sample preparation techniques in IR spectroscopy. Compare solid, liquid, and gaseous sample handling methods.

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UNIT 10: NMR SPECTROSCOPY

CONTENTS:

10.1 INTRODUCTION

The concept of NMR was represented at first in 1946 by two groups of eminent physicists; Black Hensen and Packard at Stanford University detected a signal from the Protons of water, and Parcell, Torrey and Pound at Harvard University observed a signal from the protons in Paraffin wax. Black and Parcell were jointly awarded a Nobel Prize for Physics in 1952 for this discovery.

NMR spectroscopy involves the transition of a nucleus from one spin state to other with the resultant absorption of electromagnetic radiation by spin-active nuclei (having nuclear spin not equal to zero) when they are placed in magnetic field. Nuclear magnetic resonance spectroscopy related to the nuclei and only one type of nucleus at a particular time.

^{1}H or C^{13}, F^{19} when the frequency of the rotating magnetic field and that of the processing nucleus(Lamar Frequency) become equal, they are said to be in resonance absorption or emission of energy by the nucleus can be obtained. Plot of the peak intensities versus the frequencies of objection (represented by δ or τ) establish an NMR spectrum.

The ^{1}H nucleus is most commonly studied by NMR spectroscopy because of its high natural abundance (99.98%) and the fact that it is present in the majority of organic compounds, the PMR or ^{1}H NMR spectrum provides information about the number of different types of protons and also the chemical environment of each of them.

A simple representation of NMR spectrum can be given as:

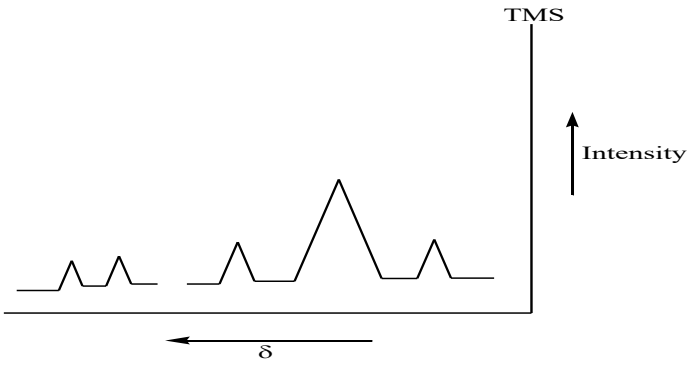


Figure: 1.1 *A simple representation of NMR spectrum*

10.2 OBJECTIVES

- Give a brief description of NMR, including what peaks represent, and what you can learn about a compound.
- Know how nuclear spins are affected by a magnetic field
- What happens when radiofrequency radiation is absorbed
- Use a list of common chemical shift ranges to predict the range of H's in various functional groups.
- Be able to predict the number of proton NMR signals expected from a compound given its structure.
- Be able to predict the splitting pattern in the proton NMR spectrum of a compound given its structure.
- Be able to use NMR spectra to determine the structures of compounds, given other information such as a molecular formula.
- Be able to calculate coupling constants from 1H NMR spectra, and utilize the coupling constants for determining compound structure.
- Be able to determine the compound structure based on information generated from mass spectrometry, IR, NMR, and elemental analysis.

10.3 PROTON MAGNETIC RESONANCE (^1H NMR) SPECTROSCOPY

^{1}HNMR or PMR spectroscopy is the most widely applicable Nuclear Magnetic Resonance spectroscopy for the structural determination of various organic compounds but the other NMR spectroscopic methods like C^{13} and P^{31} NMR spectroscopy, F^{19} spectroscopy, can also be helpful in the structural determination of the compounds.

Spin active nuclei: All those nuclei that have the full integer or half-integer nuclear spin value are known as spin active nuclei. With the help of the number of electrons/protons and neutrons in the various nuclei, the spin active or inactive nature for them can be defined as:

e^-/p	Neutron (n)	Nuclear spin (I)	Nuclei	Examples
Even	Even	0	Inactive	$_8O^{16}$
Odd	Odd	Full integer	Active	$_7N^{14}$, $_6C^{12}$
Even	Odd	Full integer	Active	$_6C^{13}$
Odd	Even	Half integer	Active	$_{15}P^{31}$, $_1H^1$

10.4 PHENOMENA OF ENERGY ABSORPTION (RESONANCE & RELAXATION PHENOMENA)

In the absence of external magnetic field H_0 the nuclear spin are randomly oriented, However when the sample is placed in an external magnetic field then the nuclei (proton) with the spin +half (1/2) are aligned with the applied field in that lower energy α- spin stagehand the nuclei with the spin -1/2 are aligned against to the external magnetic field in the higher energy β- spin state that can be represented as:

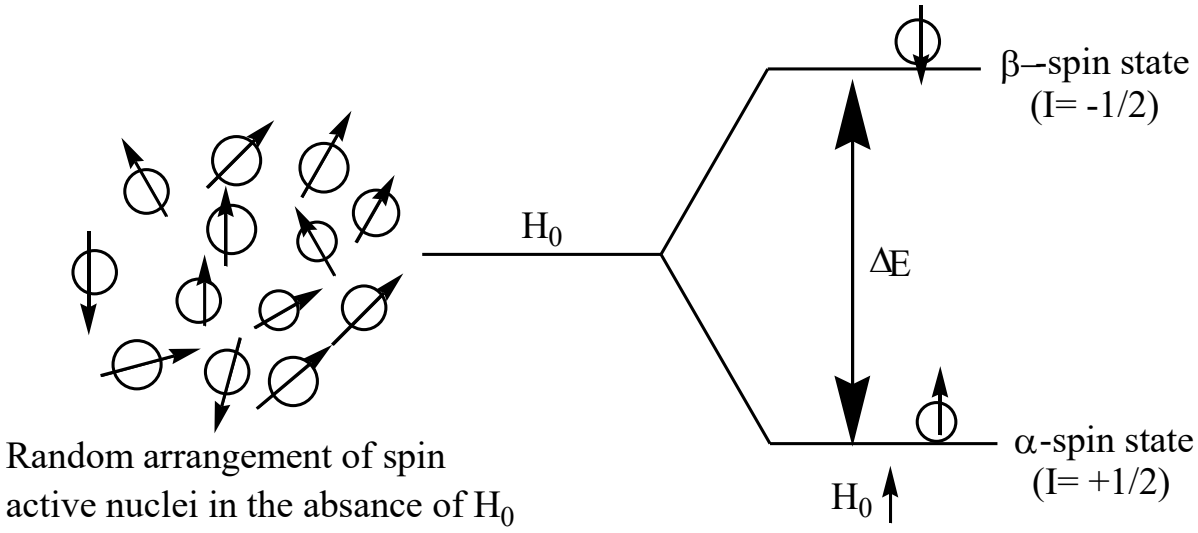


Figure 1.2. *Orientation of spinning nuclei in absence and presence of external magnetic field*

The value of energy difference b/w α and β spin state depends on the strength of external magnetic field H_0 according to the equation $\Delta E = 2\mu\, h0$ during the PMR spectroscopy, and then it can be represented as:

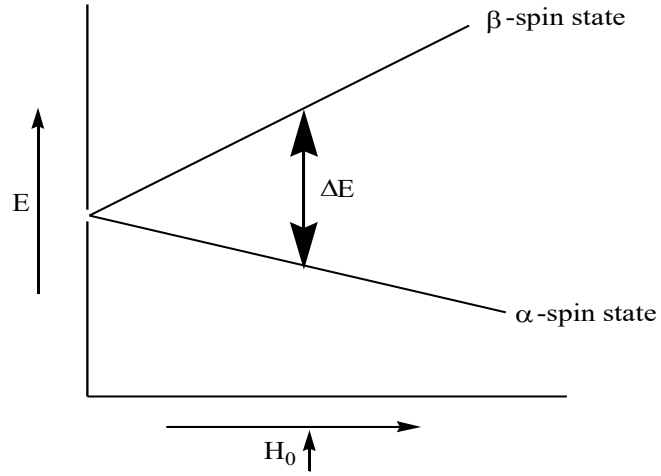


Figure 1.3. *Energy states of nuclear spin*

Thus according to above spin states **resonance phenomena** may be defined as the transition of spin active nuclei from α *spin* state to the β − *spin* state by the absorption of Rf radiation while the phenomena of returning the spin active nuclei from high energy β- spin state to the low energy α-spin state is known as **relaxation phenomena.** Both the resonance and relaxation phenomena can be represented as:

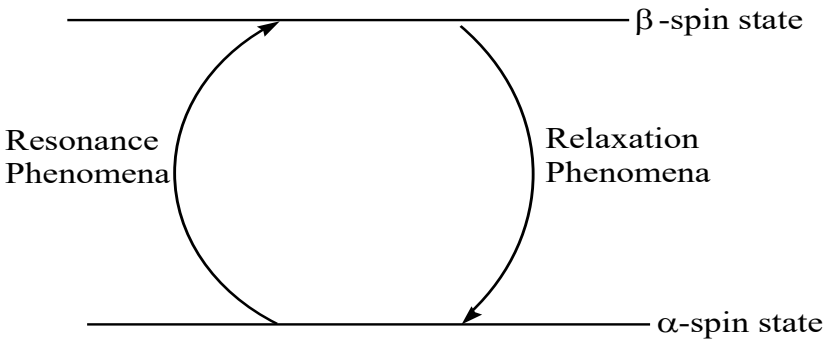


Figure 1.4. *Resonance and Relaxation*

10.4.1 NUCLEAR SHIELDING AND DESHIELDING

Electron surrounding the spin active nuclei can also generate their own magnetic field which is called as induced magnetic field, that oppose the applied magnetic field in the region of the nucleus and these e^- which generate their induced magnetic field are known as diamagnetic e^- and this effect on the nucleus by these e^- is known as diamagnetic shielding.

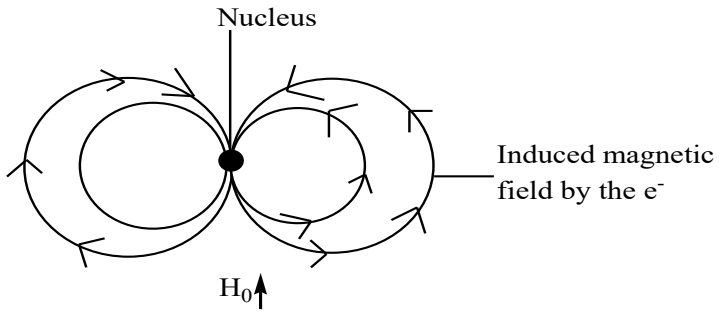


Figure 1.5. *Shielding and deshielding of a nucleus*

The external magnetic field is uniform over the entire molecule and therefore cannot differentiate to the different types of protons. However, the induced magnetic field generated by the e- around the nucleus is not uniform; this situation makes the different spin active nuclei 9proton) to be non-equivalent. Thus, each proton in the different electronic environment shows a slightly different magnetic field due to the circulation of e- in the neighbouring bond.

Thus the effective magnetic field for the different spin active nuclei can be calculated through the following equations:

$$\mathbf{H}_{\text{effect}} = \mathbf{H}_0 - \mathbf{H}_{\text{induced}}$$

Form the above equation the shielded and deshielded proton concept can be given as:

(i) For shielding:

Proton in the electron rich Environment → High $H_{induced}$ → Low H_{effect} → Low friquency absorption in PMR spectra → Low δ value

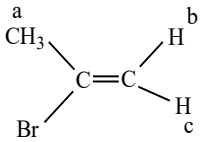
(ii) For deshielding:

Proton in the electron deficient Environment → Law $H_{induced}$ → High H_{effect} → High friquency absorption in PMR spectra → High δ value

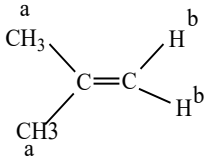
10.5 CHEMICALLY EQUIVALENT & NON- EQUIVALENT PROTONS

Those protons present in the sample of spin active nuclei which having same chemical environment are known as chemically equivalent protons. The entire chemically equivalent protons appear as a single signal in the PMR spectrum.

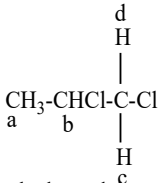
On the other hand those protons present in the sample of spin active nuclei which having different chemical environment are known as chemically non-equivalent proton. Chemically non-equivalent proton represents the different signal in the PMR spectrum.

1. 

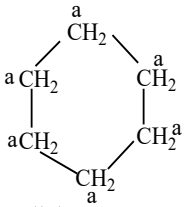
In a molecule reveals that thrre different types of protons, indicated by the letters a,b,c.

2. 

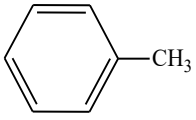
There are two types of protons. Six methyl protons on the LHS are equivalent. The protons on RHS are again equivalent

3. 

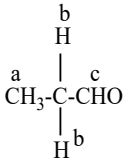
Protons marked c and d appear to be equivalent, but they are no actualy so.Thus it has four types of protons.

4. 

In this case all the protons are equivalent giving rise to only one PMR signals

5. 

There are two types of protons, benzene ring protons and the methyl protons. Two signals will be observed.

6. 

There are three kind of protonsgiving rise tothree signals.

10.6 CHEMICAL SHIFT

Chemical shift it expresses the difference in the resonance frequency of a given proton compared to that of the methyl protons of TMS, under the experimental conditions. In practice, this difference is divided by the operating radio-frequency of the instrument and the chemical shift (δ) is expressed, downfield from TMS, as per the given equation.

$$chemical\ shift \delta = \frac{V_s - V_{TMS}(H_z)}{V_0(MH_z)} \times 10^6$$

For example, if the observed shift from TMS is 200 Hz and the operating frequency of the instrument id 100 MHz, then the chemical shift δ is given by the following expression:

$$\delta \frac{200Hz}{100 \times 106^6\ \text{Hz}} = 2.0 \times 10^{-6}$$

This frequency ratio (2.0 x 10^{-6}) is multiplied by 10^{-6} in order to obtain an easily handled number (2.0 x 10^{-6} x 10^6 ppm) and consequently the chemical shift δ is expressed as part per million (10^6) of the operating frequency.

Thus,

$$\text{Chemical shift} = \frac{\nu s - \nu \text{TMS (Hz)}}{\text{Operating friquency}} \times 10^6$$

10.6.1 Chemical shift parameters:

The usual scale, for PMR studies, is about 10 ppm while for ^{13}C, the ful range range is over 200 ppm. The positions of various signals in an NMR spectrum are measured on δ and τ scale, relative to the resonance position of twelve equivalent protons of TMS, an arbitrary reference standard.

(i) Chemical shift measurement on δ scale:

The protons in the vast majority of organic compounds resonate at a low field than the protons of TMS. Therefore, by arbitrarily assigning TMS=o it is possible to device a scale, called δ scale, in which the chemical shift values for most protons will have the same sign (+ve convenience).

(ii) Chemical shift measurement on τ scale:

τ Scale is an alternative chemical shift scale, in which TMS is given an arbitrary value of 10 ppm.

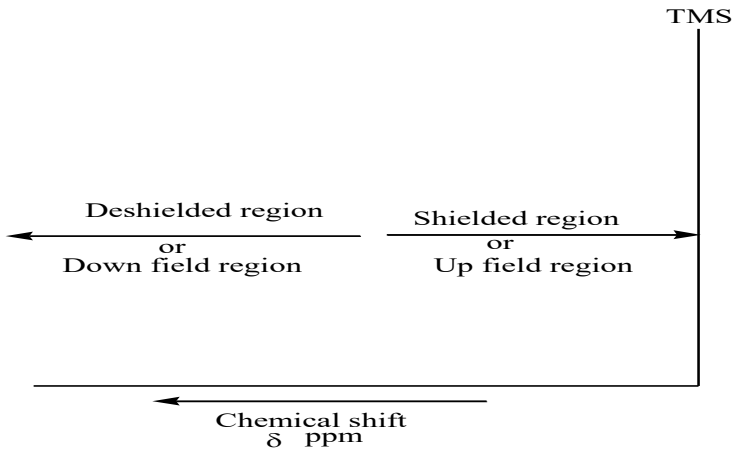


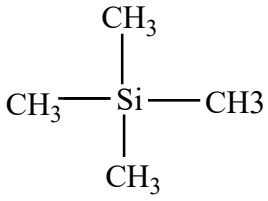
Figure 1.6. *Chemical shift region*

10.6.2 Internal standard for NMR spectroscopy:

That compound which is used as a reference standard to represent the NMR/PMR signal of the compounds, is known as an internal standard for the NMR or PMR spectroscopy.

In case of PMR spectroscopy, Tetramethylsilane (TMS) is used as an internal standard due to the following reasons:

(i) Due to the more shielded nature of the proton of TMS in compare to the protons of most of the organic compound.
(ii) It is chemically inert and miscible with large range of solvent.
(iii) It does not take part in intermolecular association with the sample.
(iv) Due to the volatile nature of TMS.



TMS

The internal standard for some other type of the NMR spectroscopic methods can be given as:

F^{19} NMR – $CFCl_3$

N^{15} NMR – NH_4NO_3

C^{13} NMR – TMS

10.7 SPIN-SPIN SPLITTING AND COUPLING CONSTANTS

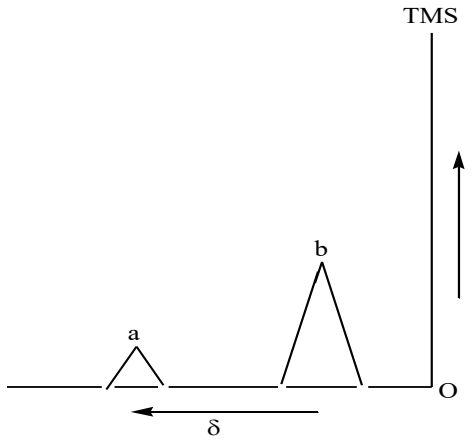
The coupling interaction between two or more protons, most often through the bond, results in splitting of the spectral lines. This is called spin-spin coupling. It is related to the possible combinations of the spin orientations of the neighboring protons.

The phenomena of splitting the signal of any particular type of proton by the spin orientation of the non-equivalent proton present adjacent to it is known as spin-spin coupling phenomena.

Example:

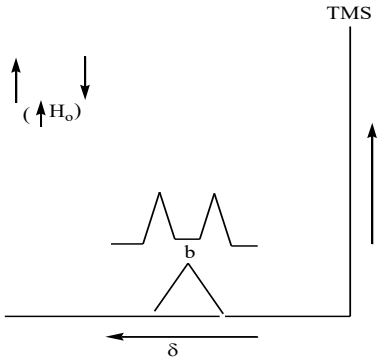
$$\overset{b}{CH_3}\overset{a}{CHCl_2}$$

According to the NMR spectroscopy the signal of two different type of the proton present in this compound can be give as:

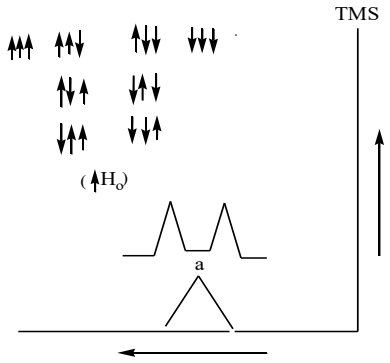


According to the spin-spin coupling phenomena the splitting of the signal of H^b proton & H_a proton according to the spin orientation of non-equivalent adjacent proton can be given as:

(i) Spin orientation of H_a for the splitting of the signal of H_b :



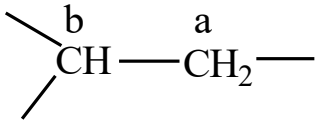
(ii) Spin orientation of H_b for the splitting of the signal of H_a



Coupling constant (J):

The ddistance between the centers of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant. The value of coupling constant is independent of the external field. It is measured Hertz (Hz) or in cps (cycle per second). It is denote by the letter J. In other words, we can say the value of J remains the same whatever the applied field. The value of J generally lies between 0 and 20 Hertz (Hz). Always the value of coupling constant being same for the protons which causing the splitting each other signal.

Now, let us consider a compound:



In this compound two signals are expected in the NMR spectrum. Under the influence of two equivalent proton a, the signal for proton b will appear as a triplet. The distance between any two adjacent peaks in a multiplet will be exactly the same. The spin-spin coupling is given below:

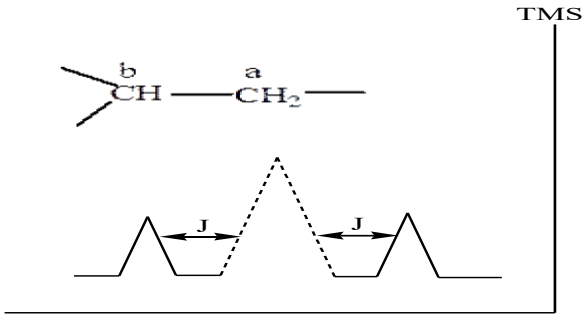
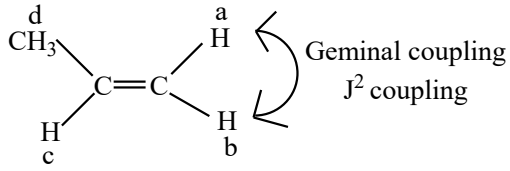


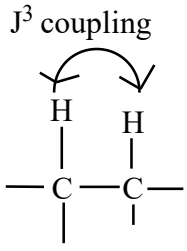
Figure 1.7: *spin-spin coupling*

It may be clearly noted that the value of coupling constant depends on the number of covalent bonds through which protons may interact and also upon the structural relationship between the coupled protons. Various types of the coupling may be given as:

(i) Geminal coupling: Such type of the spin-spin coupling phenomena in which two chemically non-equivalent protons present at the same c atom causing the splitting of each other signal will be called as Germinal coupling or J^2coupling.

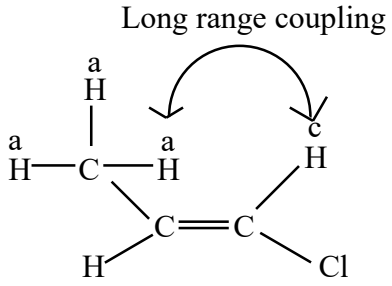


(ii) Vicinal coupling-Such type of the coupling phenomena in which two chemically non-equivalent protons present at the adjacent carleon atom causing the splitting of each other signal are known as vicinal coupling or J^3 coupling.



(iii) Long range coupling: such type of the coupling phenomena in which two chemically non-equivalent protons causing the splitting of each other signal being separated by more than three

covalent bonds are known as multi range/long range coupling. The probability of this type of the coupling phenomena in the organic compounds being very low.



10.8 AREA OF SIGNALS

In an NMR spectrum, various peaks represent equivalent sets of protons. The size or the area of each peak tells the number of protons in each set present in the compound under investigation. The area under an NMR signal is directly proportional to the number of protons giving rise to signal. For flipping over a proton, a quantum of energy is absorbed in the same effective magnetic field. Greater the number of protons that flip over at a particular frequency, greater will be the energy absorbed and greater is the area under the absorption peak. Squares under each peak are simply counted and from this, the ration between various kinds of protons is found out. These ratios are then converted into whole numbers. The whole numbers (or some multiple of them) tell the number of protons represented by the various NMR signals.

Let us consider the spectrum of toluene. It shows two types of protons as is clear from the two signals. If the number of squares under each signal are counted. It will be found that the areas under the two peaks have the ration 5:3. Thus, in toluene, five protons are of one kind and three protons are of another kind. Hence, we say that the NMR spectrum of toluene represents two kinds of protons which are in the ration 5:3.

(i) Five proton signal (downfield due to deshieliding) and
(ii) Three protons signal (up field)

10.9 APPLICATIONS OF NMR SPECTROSCOPY

The NMR spectroscopy is very widely used for the identification of an unknown compound.

1. Identification of structural isomers. The distinction between the following isomers can be easily made from their NMR spectra:

1. a. $CH_3—CH_2—CH_2—Cl$

b. $CH_3—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_3$

In the isomer 'a', three signals are observed, whereas we see only two signals in the spectrum for 'b', which is a clear distinction between the above isomers. The three signals for isomer 'a' in order of decreasing tau values are:

(i) A three-proton triplet

(ii) A two-proton sextet and

(iii) A two-proton triplet

For isomer (b), two signals have their multiplicities as:

(i) Doublet (6H)-up field and

(ii) Septet (1H)-downfield

2. Detection of hydrogen bonding: Intermolecular hydrogen bonding shifts the absorption for a concerned proton downfield. The extent of hydrogen bonding varies with the nature of the solvent, concentration of the solution and the temperature. The intramolecular hydrogen bonding also shifts the absorption downfield. The two types of hydrogen bonding can be distinguished as the intramolecular hydrogen bonding is not concentration-dependent.

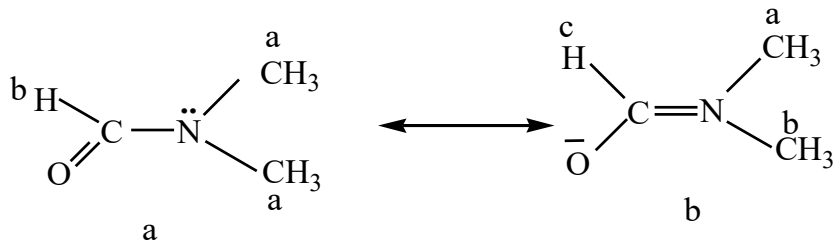
3. Detection of aromaticity. Protons attached to the benzoly, polynuclear and heterocyclic compounds whose π electrons follow Huckel's rule [i.e. (4n+2) π electrons where n=1,2,3…..(whole numbers)] are extremely deshielded due to the circulating sextet (ring current) of π electrons. As a result of this, the signal for the aromatic protons appears at a much lower field than that observed even for benzene. From this, the aromatic character of the compound under investigation can be predicted.

4. Distinction between Cis-Trans Isomers and Conformers. The is and trans isomers of a compound can be easily distinguished as the concerned protons have different values of the chemical shift as well as the coupling constants. Similarly, the various conformations of a

compound, the axial and equatorial positions of the proton or group carrying a proton can be distinguished from their different values of the coupling.

5. Detection of electronegative atom or group: It is known that the presence of an electronegative atom or group in the neighborhood of the proton cause deshielding and the signal is shifted downfield. Greater the electro negativity of the adjacent atom, smaller is the tau value of absorption for the concerned proton. Fluorine causes more downward shift as compared to oxygen and oxygen in turn causes more downward shift as compared to nitrogen and so on.

6. Detection of some double bond character due to resonance: In some compounds, the molecule acquires a little double bond character due to resonance. Due to this, two signals can be expected for apparently equivalent protons, It is due to the hindered rotation which changes the geometry of the molecules. Consider N, N- dimethyl formamide. It can be written in the following resonating structures:



For structure (a), two signals (singlets) should be expected with peak areas 6:1 as the two methyls are exactly equivalent.

In structure (b), the presence of double bond restricts rotation and now the two methyl groups remain no longer equivalent (Geometrical isomers). For this structure, two signals, appear for two methyl groups.

7. Importance in quantitative analysis: NMR spectroscopy is gaining importance for the quantitative analysis of the compounds. Equilibrium mixtures can be analyzed when the proton signals of the components are well separated. In the NMR spectrum of pure ethanol (CH_3CH_2OH), a triplet is formed for the OH proton but when water is added in alcohol, then due to proton exchange, the triplet collapses to a singlet. The position of this singlet depends upon the water content in alcohol. From the values of the chemical shift, the ration of water and alcohol can be estimated by comparing with the known results.

10.10 INTERPRETATION OF PMR SPECTRA OF SIMPLE ORGANIC MOLECULES

NMR interpretation plays a important role in molecular identifications. As interpreting NMR spectra, the structure of an unknown compound, as well as known structures, can be assigned by several factors such as chemical shift, spin multiplicity, coupling constants, and integration. For the interpreting of the NMR spectra, the following points may be noted:

1. Molecular formula is determined by chemical analysis such as elementary analysis.

2. **Double-bond equivalent or Degree of Unsaturation**: It is calculated by a simple equation to estimate the number of the multiple bonds and rings. It assumes that oxygen (O) and sulfur (S) are ignored and halogen (Cl, Br) and nitrogen is replaced by CH. The resulting empirical formula is C_xH_y

$$\textbf{Double Bond Equivalent (DBE)} = \frac{(2x + 2) - y}{2}$$

3. Structure fragmentation is determined by chemical shift, spin multiplicity, integral (peak area), and coupling constant (1J, 2J)
4. Molecular skeleton is built up using 2-dimensional NMR spectroscopy.
5. Relative configuration is predicted by coupling constant (^{3}J).

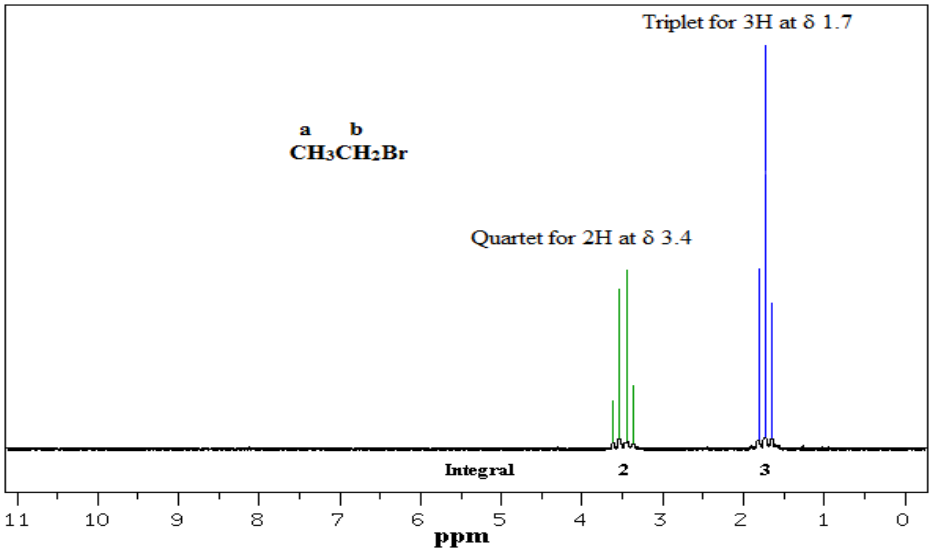


Figure 1.8: *NMR Spectra of ethyl bromide*

1. Ethyl bromide (CH_3CH_2Br):

In this compound (Ethyl bromide) containing two set of equivalent protons 'a' and 'b' types. The signal due to equivalent protons a will be under the influence of neighboring proton b. Similarly, the signal for proton b will be under the influence of three equivalent proton a whose spin possibilities with respect to the applied field can be given as-

The following peaks can be identified in the spectrum

(a) Triplet, δ 1.7, 3H (b) Quartet, δ 3.4, 2H

The proton at δ 1.7 is given by the three methyl protons which are magnetically equivalent and are coupled with the two methylene protons to give a shielding. While the quartet at δ 3.4 is from the two equivalent methylene protons which are coupled with the three methylene protons to produce a downfield quartet as a result of deshielding influence of bromine.

2. Interpretation of PMR spectra of ethanol:

The ^1H NMR spectrum of ethanol (Figure 1.9) shows the methyl peak has been split into three peaks (triplet) and the methylene peak has been split into four peaks (quartet). This occurs because there is a small interaction between the two groups of protons. The space between the peaks of the methyl triplet is equal to the space between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the coupling constant, J.

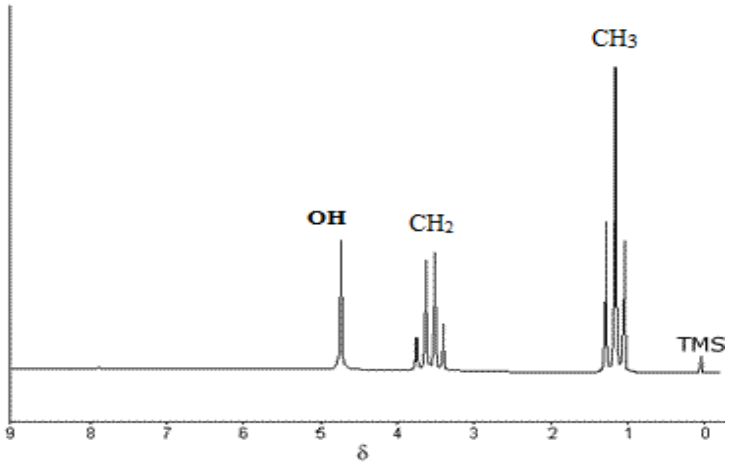


Figure 1.9: *PMR Spectrum of Ethyl alcohol*

In the above PMR spectrum of ethyl alcohol the following observation takes place:

1. A triplet centered at 1.18 δ, equivalent to 3H, represents the CH_3 (a) proton.

2. A singlet at 4.51 δ, equivalent to 1H, exhibit the OH (c) proton.
3. A quartet centered at 3.63 δ, equivalent to 2H indicates the CH_2 (b) proton.

3. Interpretation of PMR spectra of Acetaldehyde:

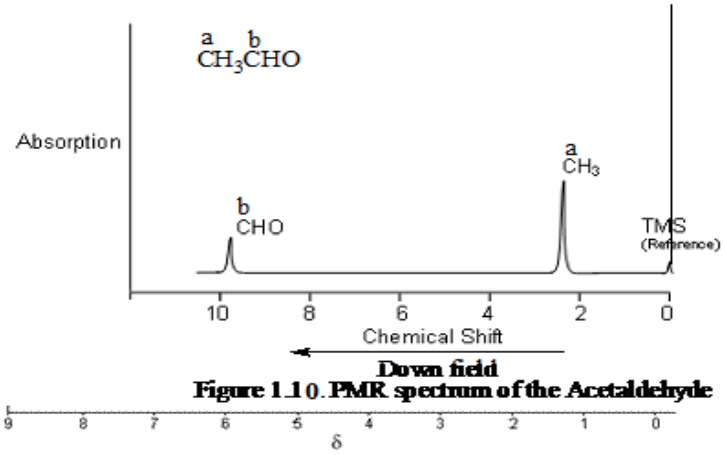


Figure 1.10. PMR spectrum of the Acetaldehyde

1. A doublet centred at 2.14 δ, equivalent to 3H, represents the methyl proton (a).
2. A quartet, centred at 9.78, equivalent to 1H, indicates the aldehydic proton (b).

4. Interpretation of PMR spectra of Ethyl acetate:

The PMR spectrum of ethyl acetate is given in Figure 1.11. There are three different peaks in the spectrum. Two of the peaks are split or have multiplicities greater than one.

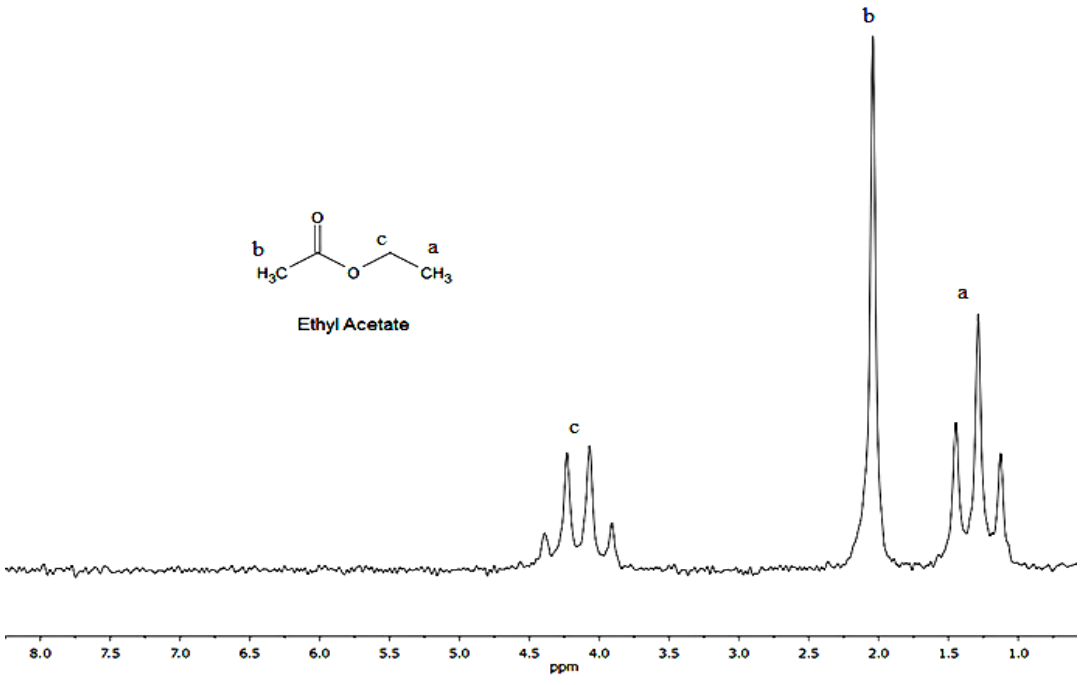


Figure 1.11: *PMR Spectrum of Ethyl acetate*

The following peaks are observed in the NMR spectrum of Ethyl acetate.

1. A triplet at 1.23 δ equivalent to 3H, indicate the methyl protons (a).
2. A singlet at 1.97 δ, equivalent to 3H indicates the methyl protons (b).
3. A quartet at 4.06 δ, equivalent to 2H, indicates the methylene protons (c).

5. Interpretation of PMR spectra of Toluene:

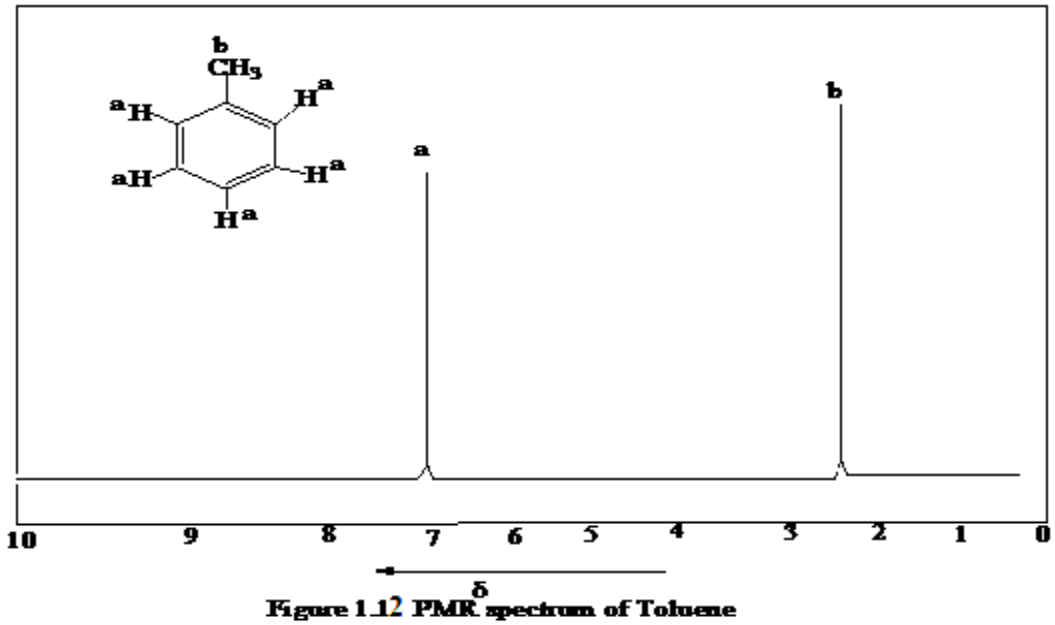


Figure 1.12 PMR spectrum of Toluene

The following peaks are observed in the NMR spectrum of toluene:

1. Singlet, δ 2.34, 3H
2. Singlet, δ 7.17, 5H

The compound toluene has eight protons, five of which are aromatic and remaining three from the methyl group. The signals for three protons of methyl, which are attached to an aromatic ring appear as a singlet at δ 2.34. All the five protons are chemically equivalent because they are unaffected by methyl protons. Hence these protons do not couple with each other and give rise to only one signal at δ 7.17.

10.11. PROBLEMS PERTAINING TO THE STRUCTURE ELUCIDATION OF SIMPLE ORGANIC COMPOUNDS USING UV, IR AND PMR SPECTROSCOPIC TECHNIQUES

1.11.1. Determination of the number of double bonds and ring Equivalent (DBE) from the molecular formula of Organic compounds:

The number of double bonds and rind equivalent (DBE) can be calculated if the molecular formula of the compound is known and thus the structure of the compounds may be calculated with the help of given spectroscopic data.

The DBE of the various organic compounds can be determined from the molecular formula as per given formula:

a. Compounds containing carbon and Hydrogen only:

If the compound is a hydrocarbon and the general formula is C_xH_y then:

$$DBE = x + 1 - \frac{y}{2}$$

For example: If the molecular formula of the compound is C_2H_6, then the DBE is given by-

$$DBE = 2 + 1 - \frac{6}{2} = 0$$

b. If the compound containing carbon, hydrogen and divalent atoms:

If the compound containing carbon, hydrogen and divalent atoms like Oxygen and Sulphour etc; then DBE may be calculated by given as:

$$DBE = x + 1 - \frac{y}{2}$$

For example: If the molecular formula of the compounds is $C_3H_8O_3$, then the DBE will be given as:

$$DBE = 3 + 1 - \frac{8}{2} = 0$$

c. If compound containing carbon, hydrogen and monovalent atoms:

If an Organic compound containing some monovalent atoms like (X= Cl, Br, I etc.),

Then the DBE can be calculated by given formula:

$$DBE = x + 1 - \frac{y + z}{2}$$

For example: If the molecular formula of the compound is $C_{10}H_7Br$, then the DBE is given by the following equation:

$$DBE = 10 + 1 - \frac{7 + 1}{2} = 11 - 4 = 7$$

1.11.2. Problems pertaining to the structure elucidation of simple organic compounds:

Problem 1:

An organic compound contains 66.6% carbon, 11.1% hydrogen. In UV, it gave a characteristics band at 275 275mμ $E_{max.}$ 17. In infra-red, bands are formed at 2941-2857(m), 1715 (s) and 1460 cm-1(m). In NMR, three signals appear at (i) 7.52 τ quartet, (2H), 7.88τ singlet, (3H) and 8.93 τ Triplet, (3H). Determine the structural formula of the compound.

Solution:

The compound contains

C = 66.6%

H = 11.1%

O = 100 - (66.6 + 11.1) = 22.3%

From the above data, the empirical formula of the compound is found to be C_4H_8O. This must be the molecular formula since eight hydrogen atoms are shown by NMR spectrum.

(i) The absorption at 275mμ $E_{max.}$ 17 is characteristic of a carbonyl group.

(ii) The absorption at 2941-2857 cm^{-1} (m) in the IR spectrum is due to C-H stretching, at 1715 cm^{-1} (s) is characteristic of saturated ketonic group and that at 1460 cm^{-1} (s) is characteristic of saturated ketonic group and that at 1460 cm^{-1} (m) may be due to bonding.

(iii) The NMR spectrum reveals three kinds of protons.

The presence of a triplet at 8.93 τ and a quartet at 7.25τ is characteristic of CH_3-CH_2- group group in the compound. The singlet at 7.88 τ is due to methyl group adjacent to a carbonyl group.

Thus the molecular formula of the compounds is **CH_3-CH_2-CO-CH_3**.

Problem 2.

A compound with molecular weight 116 gave the following data.

(I) UV: 283 22.

(II) IR: 3000-2500(b), 1715(s), 1342 cm^{-1}(w).

(III) NMR: 7.88τ singlet (3H), 7.40τ Triplet (2H), 7.75 τ Triplet (2H) and -1.1 τ singlet (1H). Find the structural formula of the compound.

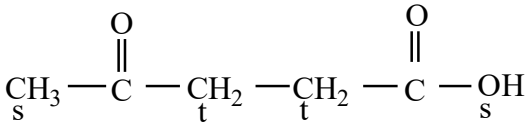
Solution: In the ultraviolet spectrum, the absorption at 283 mμ indicates the presence of carbonyl group.

The presence of an acid group is also shown by NMR which gives a signal (singlet) at the negative tau value. Thus, the compound under investigation contains

(i) –CO- Group and

(ii) –COOH- Group

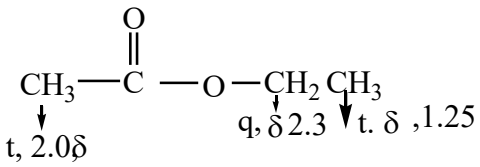
Further two triplets result at 7.4 τ and 7.75 τ having the same integral area. It must be due to clearly, two methylene groups must be under different environments and thus, couple to give rise to two triplets. The three protons singlet at 7.88 τ must be a methyl group attached with the carbonyl group. Thus the structure of the compound is-



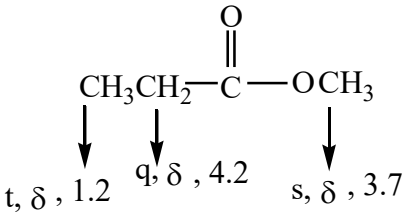
Problem 3.

Ethyl acetate and methyl propionate both have the molecular formula $C_4H_8O_2$. How do they differ in their PMR spectra?

Solution: (Ethyl acetate) shows a downfield singlet at δ 2.0 due to the methyl group of the acetate part, methylene quartet at δ 2.3 and methyl triplet at δ 1.25 due to the ethyl group attached to oxygen. While (methyl propionate) shows a methylene quartet at δ 4.2 and a methyl triplet at δ 1.2 due to the group of propionate part; downfield methyl singlet at δ 3.7due to the methyl group attached to oxygen.



Ethyl acetate



Methyl propionate

Problem 4:

Carbonyl compound containing carbon, hydrogen and oxygen and having a molecular mass of 72 gives a PMR spectrum which shows a triplet, a singlet and a quartet (at increasing values of δ). What is the structure of the compound?

Solution: The possible structure of the given data is:

$CH_3COCH_2CH_3$

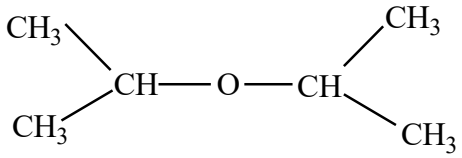
A compound **Problem 5:**

having the percentage composition C = 70.6%, H=13.7% and O =15.7% exhibits the following PMR spectrum:

Multiplet at δ, 3.56 (2H); Doublet at δ, 1.05 (12H).

Determine its molecular formula and assign a suitable structure to it.

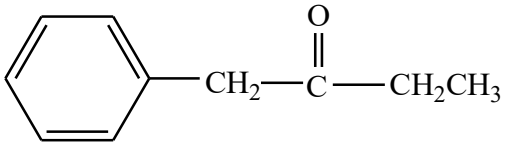
Solution: The molecular formula of the compound with the above percentage composition comes out to be $C_6H_{14}O$. The structure of the compound is given below:



Problem 5:

PMR spectrum of a compound shows the following peaks: δ 7.22 (s, 5H); δ 2.77 (q, 2H); δ 0.97 (t, 3H). Give the structure with the above data:

Solution: On the basis of the above spectral data, the structure of the compound is:

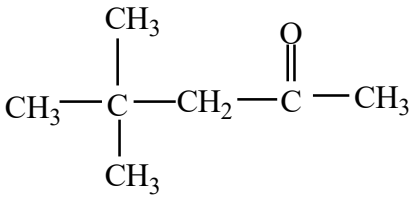


Problem 6:

A carbonyl compound having the molecular formula gives the following PMR spectrum. Identify the compound. δ 1.01 (Singlet, 9H); δ 2.32 (Singlet, 2H): δ 2.11 (Singlet, 3H).

Solution:

The structure of the compound with the formula is:



Problem 7:

How can you explain the following difference in the chemical shifts of aromatic protons in the following compounds?

Benzene δ7.37, Toluene δ 7.14, p-xylene 7.05

Solution. The chemical shifts of aromatic protons in toluene and p-xylene are slightly upfield due to electron-releasing and shielding effect of methyl groups.

10.12. SUMMARY

Nuclear magnetic resonance spectroscopy, commonly known as **NMR** spectroscopy, it is an analytical technique that exploits the magnetic properties of certain atomic nuclei. This type of spectroscopy determines the physical and chemical properties of atoms or molecules. It relies on the phenomenon of nuclear magnetic resonance and can provide information about the structure, chemical environment of molecules and details of the electronic structure of a molecule and its functional groups present in the sample.

NMR spectra are unique analytical tool and often highly predictable for small molecules. Thus, in organic chemistry practice, NMR analysis is used to confirm the identity of a substance.

10.13 REVIEW QUESTIONS

A. Short Answer Type Questions:

1. Describe briefly the theory of NMR spectrometry.

2. What do you understand by the positions of the signals in an nmr spectrum? How many signals are expected in each of the following compounds? (a) propane (b) isobutance (c) Ethanol (d) Cyclobutance (e) Ethylmethly ether
3. What do you mean by the term chemical shift?
4. Write with suitable examples, the shielding and the deshielding.
5. Describe with suitable examples the various effect the magnitude of the chemical shift.
6. Define the term chemical shift and describe the factors which affect it.
7. Explain the term 'spin-spin' coupling. Why does a peak for a particular set of protons spilt into a multiplet? Give with examples.
8. Write a short note on the use of standard solvents in the NMR spectrometry.
9. An Organic compound has a molecular formula at $C_{10}H_{13}Cl$ assign its structure with the help of the following data:

   Singlet δ 1.57, 6H

   Singlet 3.07 δ 2H

   Singlet 7.27 δ 5H

Describe briefly the various applications the NMR spectroscopy.

10. Write a detailed note on coupling constant.
11. An Organic compound with molecular formula formula$C_6H_5NO_3$ is found to show two signals in the PMR spectrum.
12. (i) Unsymmetrical patter-multiplet =1.8-2.9τ(4H)
13. (ii) Singlet = 0.1 τ (1H)
14. What is meant by the term chemical shift? Give the various factors which affect the value of chemical shift.
15. Name some important solvents used in NMR spectroscopy. What are the important characteristics of the solvents used in the technique?
16. Write brief notes on the following:

    (i) Chemical shift

    (ii) Spin-spin coupling

    (iii) Coupling constant

    (iv) Resonance Phenomenon

18. Write short notes on:

(i) Spin-Spin coupling

(ii) Areas of the various signals

(iii)Deshielding due to hydrogen bonding

19. Explain the term PMR spectrum of ethyl bromide.
20. Explain the term PMR spectrum of acetaldehyde.
21. Tetramethylsilane is chosen as reference compounds in PMR studies. Why?
22. Write a brief account of equivalent and non equivalent protons.
23. Write a detailed not on spin-spin coupling?
24. Distinguish the following pair on the basis of PMR data.
    a. CH_3OCH_3 and CH_3CH_2OH
    b. $CH_3COOC_2H_5$ and $C_2H_5COOCH_3$

25. A compound having the molecular formula $C_9H_{11}Br$ showed the following set of NMR data:

a. δ 2.25, 2H, Multiplet b. δ 2.72, 2H, Triplet

c. δ 3.38, 2H, Triplet d. δ, 7.22, 5H, Singlet

B. Multiple choice questions

1. How many signals are obtained for ethyl alcohol in its PMR spectrum?

a. Four b. three c. Five d. One

2. How many singles are obtained for 1, 1, 2 tribromoethane in its pmr spectrum.

a. Four b. three c. five d. two

3. How may NMR signals is formed for 2-chloro propene.

(a) 2 (b) 3 (c) 1 (d) none

4. Tell the number of NMR signals in case of 1,2 dichloropropane.

(a) 2 (b) 3 (c) 4 (d) 5

5. Write the multiplicity of the signlas in $CH_3CH_2OCH_2CH_3$ in NMR spectrum.

(a) Two triplets (b) a triplet and a quartet (c) Three signal (d) Two singlets and two triplets.

6. Write the multiplicity of signals in CH_3CH_2OH in NMR spectroscopy.

(a) singlet, triplet and quartet (b) Two triplets and a quinlet. (c) Three sing lets

(d) None of these

7. In an organic compound, the proton linked to Sp^2 hybridized carbonation is more deshielded than that linked to.

(a) Sp hybridized carbon (b) hybridized carbon (c) Both of these (d) None of these.

8. Which of the following solvents cannot be used in NMR spectroscopy?

(a) CCl_4 (b) CS_2 (c) $CHCl_3$ (d) (CCl_3) CO

9. The spin is an integer 1, 2, 3 ……n for a nucleus having

(a) even number of protons and neturons

(b) odd mass number

(c) even mass number and odd number of protons

10. NMR spectra are observed in the region.

(a) Radio frequency (b) Microwave (c) UV/Vis (d)X-ray.

Answer: 1. b, 2. d, 3. B, 4. C, 5. b, 6. a, 7. c, 8. C, 9. C, 10. a

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Unit- 11: RAMAN SPECTROSCOPY

CONTENTS:

11.1 INTRODUCTION

We know that within molecule, there are certain energy levels which are associated with rotation, vibration or electronic level. When radiation of a particular wavelength falls on a molecule, there is absorption of radiation which results in transition between these energy levels. This technique is known as spectroscopy. Nowadays, spectroscopy is a very vast topic in chemistry and constitutes one of the subjects in chemistry. It involves several spectra depending on the type of radiation absorbed. For example, if a molecule absorbs radiations falling in microwave region, there is a transition between rotational energy levels. This spectroscopy is known as pure rotational spectroscopy or microwave spectroscopy. Likewise, when a molecule absorbs radiations falling in infrared region, the spectroscopy is known as vibrational spectroscopy in which there is transition between the vibrational energy levels of a molecule.

The present unit deals with Raman spectroscopy which was observed by C. V. Raman (Physicist) and for this, he was awarded the Nobel Prize. This spectroscopy includes the concept of polarizability that changes on exposure to the radiations. Polarizability is defined as the ability of a non-polar molecule to acquire dipole moment in presence of an electric field. We will discuss about the selection rule based on which we decide whether the transition between energy levels are allowed or forbidden. In order to understand the unit more clearly, we will consider Raman spectra of a diatomic molecule which includes pure rotational and pure vibrational Raman spectra.

Raman spectra are different from all other types of spectra, as all other spectra involve absorption of radiation while in Raman spectra, there is scattering of radiation instead of absorption. This makes this spectroscopy quite different from the other and this is the reason for taking interest in having complete knowledge of Raman spectroscopy.

11.2 OBJECTIVES

After reading this unit, you will be able to:

- Define Raman spectroscopy.
- To know the region of radiation in which molecule shows Raman spectroscopy.
- Explain the selection rule involved during the transition between different energy levels.
- Define polarizability of a molecule.
- Explain pure rotational Raman spectra of a diatomic molecule.
- Explain pure vibrational Raman spectra of a diatomic molecule
- Have knowledge of Raman shift.

11.3 CONCEPT OF POLARIZABILITY

As we have discussed earlier that there is scattering of radiation in Raman spectroscopy instead of absorption. We can obtain Raman spectra for solid, liquid and gaseous sample. Homo diatomic molecules or molecules without permanent dipole moment like N_2, O_2, H_2 etc also show Raman spectra whereas for a molecule to be infrared active, molecule must possess permanent dipole moment. In Raman spectroscopy, an intense beam of monochromatic light of visible region is allowed to pass through the molecule and the scattered light which is observed at right angle to the incident beam is observed. It has been seen that some of the scattered light have same frequency as that of the incident light while some scattered light have frequencies different (less or more) from the incident light. This is known as Raman Effect or Raman shift. The scattering in which the scattered light and the incident light possess same frequency is called Rayleigh scattering and the line produced is called Rayleigh line. When the scattered light has more frequency than the incident light, anti-stokes lines are produced whereas when the scattered light has less frequency than the incident light, the lines produced are called stokes lines. In this way, scattering results in the formation of three types of lines: Rayleigh lines, stokes lines and anti-stokes lines.

Raman shift ($\Delta\upsilon$) is the difference in the frequency of the incident light and the scattered light. Therefore:

$$\Delta\upsilon = \upsilon_i - \upsilon_s$$

Where υ_i is the frequency of the incident light, υ_s is the frequency of the scattered light and $\Delta\upsilon$ is Raman shift or Raman Effect. Raman shift lies in the region of near and far infrared radiation.

We know that in case of stokes lines, the frequency of the scattered light is less than the frequency of the incident light i.e. $\upsilon_i > \upsilon_s$. Hence Raman shift is positive whereas, in the case of anti-stoke lines, the frequency of the scattered light is more than the frequency of the incident light i.e. $\upsilon_i < \upsilon_s$. Hence Raman shift is negative. It is important to remember that Raman shift ($\Delta\upsilon$) is independent of the frequency of the incident radiation but it depends on the characteristic of the molecule showing Raman effect. This has been explained on the basis of classical theory of Raman effect.

11.3.1 Classical theory of Raman scattering

This theory is also known as theory of polarizability. According to this theory, in the presence of an electric field, the electrons of a molecule (neutral) are attracted to the positive pole while nuclei of a molecule are attracted towards the negative pole. As a result, a dipole moment is induced or produced in the molecule. In this state, a molecule is said to be polarised. In this way, electron cloud gets distorted in the presence of an electric field. This ability of a molecule to gain dipole moment is called polarizability. The induced dipole moment (μ) is related to electric field (E) by an expression:

$$\mu = P\,E$$

Where, P is the polarizability of the molecule.

$$E = E_o \operatorname{Sin} 2\Pi\upsilon t$$

Where υ is the frequency of the incident light, $E_o$is the vibrating electric field's amplitude

$$\mu = PE_o \operatorname{Sin} 2\Pi\upsilon t$$

This equation shows that an oscillating dipole scatters light having same frequency. If the vibration in the molecule does not change the polarizability of the molecule then we will observe Rayleigh lines. There must be a change in polarizability of the molecule to be Raman active (Stokes and anti-stokes lines). Homo-nuclear diatomic molecule such as O_2, N_2, show Raman spectra as there is change in polarizability of the molecule due to vibration.

11.3.2 Quantum theory of Raman scattering

According to the quantum theory, there is a collision between the incident photon and the molecule. Let a photon of frequency (υ) collides with a molecule in an elastic manner then there is conservation of energy i.e. the energy of the incident photon is equal to the energy of the scattered photon whereas if the collision is inelastic, there is no conservation of energy. Therefore the scattered radiations have energy different from the incident radiation. The energy will be higher or lower than the energy of the incident radiation. Form the law of conservation of energy:

$$E + h\upsilon_i = E^l + h\upsilon_s$$

Where $h\upsilon_i$ is the energy of the incident photon, $h\upsilon_s$ is the energy of the scattered photon, E^l is the energy of the molecule after collision and E is the energy of the molecule before collision. Three conditions arise:

Case 1: If $\upsilon_i = \upsilon_s$: $E = E^l$: Rayleigh lines are produced

Case 2: If $\upsilon_i > \upsilon_s$: $E^l > E$: Stokes lines are produced

Case 3: If $\upsilon_i < \upsilon_s$: $E^l < E$: Anti-stokes lines are produced

11.4 PURE ROTATIONAL RAMAN SPECTRA OF A DIATOMIC MOLECULE

The diatomic molecule as we know, consist of two atoms. When two atoms are same, the molecule is called a homo-nuclear diatomic molecule like H_2, N_2, whereas when two atoms are different, the molecule is called a hetero-diatomic molecule like HCl, HCN. When a homo-nuclear diatomic molecule undergoes rotation, there is a change in the orientation of the molecule with respect to the electric field of rotation. If a molecule possess different polarizabilities in different directions or we can say that if the molecule is optically anisotropic, then there is variation in the polarization with time. If α is the change in polarizability of a molecule then:

$$P = P_o + \beta \sin 2\Pi (2\upsilon_r) t \qquad (1)$$

Where, υ_r is the rotational frequency. The induced dipole moment (μ) is related to electric field (E) by an expression:

$$\mu = P\ E$$

Where, P is polarizability of the molecule.

$$E = E_o \text{ Sin } 2\Pi\upsilon t$$

Where υ is the frequency of the incident light, $E_o$is the vibrating electric field's amplitude

$$\mu = PE_o \text{ Sin } 2\Pi\upsilon t$$

On putting the value of P from equation 1 in the above equation, we obtain:

$$\mu = P_o + \beta \sin 2\Pi (2\upsilon_r)\ t\ (E_o \text{ Sin } 2\Pi\upsilon t)$$

$$\mu = P_oE_o \text{ Sin } 2\Pi\upsilon t + \beta\ E_o \text{ Sin } 2\Pi\upsilon t \sin 4\Pi\ \upsilon_r\ t$$

$$\mu = P_oE_o \text{ Sin } 2\Pi\upsilon t + \tfrac{1}{2}\ \beta\ E_o\ [\text{Cos } 2\Pi\ (\upsilon - 2\upsilon_r)\ t - \text{Cos } 2\Pi\ (\upsilon + 2\upsilon_r)\ t]$$

It is clear from the above equation that Raman lines have frequencies ($\upsilon - 2\upsilon_r$) and ($\upsilon + 2\upsilon_r$). Raman shift ($\Delta\upsilon$) is therefore equal to twice the frequency of rotation of a molecule.

$$\Delta\upsilon = (\upsilon + 2\upsilon_r) - \upsilon = 2\upsilon_r$$

The pure rotational Raman spectra contain a series of equidistant lines on both side of a Rayleigh line as shown in Figure 1. On the right of the Rayleigh line, anti-stokes lines are present. The separation between Rayleigh line and first anti-stokes line is 6B followed with the separation of 4B between two successive anti-stokes lines. Here B is rotational constant. On the left of the Rayleigh line, stokes lines are present. The separation between Rayleigh line and first stokes line is 6B followed with the separation of 4B between two successive stokes lines. It has been observed that greater is the anisotropy of the molecule, more will be the intensity of the rotational Raman lines.

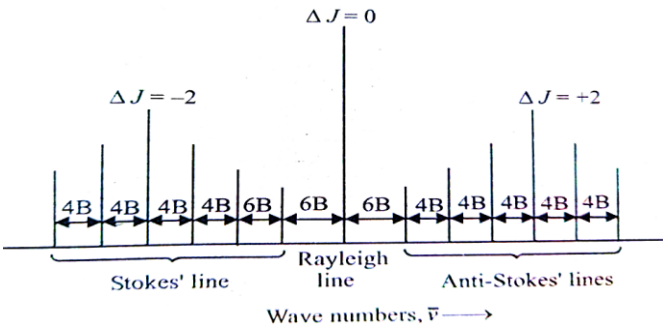

Figure11.1 Pure rotational Raman spectra

11.4.1 Selection rule

There are certain rules on the basis of which we decide whether the transition between energy level is allowed or forbidden. For rotational Raman spectra, the selection rule is:

$$\Delta J = 0, \pm 2$$

Where, J is rotational quantum number.

Case 1: If $\Delta J = 0$

This shows that there is no change in the rotational quantum number. In this case, the frequency of the incident and scattered radiation is same i.e. the scattering is Rayleigh scattering.

Case 2: $\Delta J = -2$

This corresponds to anti-stokes Raman lines. Here the scattered radiations have more frequency than the incident radiation.

Case 3: $\Delta J = +2$

This corresponds to stokes Raman lines. Here the scattered radiations have less frequency than the incident radiation.

11.5 PURE VIBRATIONAL RAMAN SPECTRA OF A DIATOMIC MOLECULE

This type of Raman spectra results from the change in polarizability of a molecule that results when a photon strikes a molecule. As we have studied that in case of rotational Raman spectra, more is the anisotropy, more is the intensity of Raman line. Similarly, in case of pure vibrational Raman spectra, more is the change in polarizability of the molecule; more is the intensity of vibrational Raman line produced. Examples of molecules that show pure vibrational Raman spectra are CO_2, NO_2. Let us consider a diatomic molecule, when light falls on a molecule, there is vibration in the molecule that results in the change in polarizability of the molecule. If d represents the change in the displacement due to vibration, the change in polarizability of a molecule (P) is given by expression:

$$P = P^o + \beta\, d/A$$

Where P^o represents the polarizability when there is no vibration or P^o represent equilibrium polarizability, A is the amplitude while β is the rate of vibration of the polarizability with displacement. Assuming that molecule undergoes simple harmonic motion, then the displacement (d) is written as:

$$d = A \text{ Sin } 2\Pi\upsilon_v t$$

Where, υ_v is the frequency of vibration of a molecule. We know that:

$$\mu = PE_o \text{ Sin } 2\Pi\upsilon t$$

$$\mu = (P^o + \beta\, d/A)\, E_o \text{ Sin } 2\Pi\upsilon t$$

$$\mu = P^oE_o \text{ Sin } 2\Pi\upsilon t + \beta\, E_o \text{ Sin } 2\Pi\upsilon t \text{ Sin } 2\Pi\upsilon_v t$$

$$\mu = P^oE_o \text{ Sin } 2\Pi\upsilon t + 1/2\beta\, E_o[\text{Cos } 2\Pi\, (\upsilon - \upsilon_v)t - \text{Cos } 2\Pi\, (\upsilon + \upsilon_v)t]$$

In the above equation, $(\upsilon - \upsilon_v)$ and $(\upsilon + \upsilon_v)$ terms are present, which indicates that there are certain lines in the vibrational Raman spectra that have frequency more than that of the frequency of the incident radiation while other have frequency less than that of the frequency of the incident radiation. Thus Raman shift ($\Delta\upsilon$) is given by expression:

$$\Delta\upsilon = (\upsilon - \upsilon_v) - \upsilon = \upsilon_v$$

It is therefore concluded that Raman shift in case of pure vibrational Raman spectra of a diatomic molecule is equal to the frequency of vibration.

5.5.1 Selection rule

Whether the transition is allowed or not, there is selection rule. For pure vibrational Raman spectra, selection rules are:

$$\Delta v = \pm 1$$

Where, v is vibrational quantum number. Two cases arise:

Case 1: $\Delta v = +1$

This corresponds to stokes Raman lines when there is transition from v to v + 1.

Case 2: $\Delta v = -1$

This corresponds to anti-stokes Raman lines when there is transition from v + 1 to v.

11.6 ROTATIONAL-VIBRATIONALRAMAN SPECTRA OF A DIATOMIC MOLECULE

This type of Raman spectra involves both rotation and vibration of a diatomic molecule when a monochromatic light falls on the molecule. Therefore there is change both in the vibrational and rotational quantum number. The selection rule for rotational-vibrational Raman spectra is:

$$\Delta J = 0, \pm 2; \Delta v = \pm 1$$

For rotational-vibrational Raman spectra, three branches are observed named as O branch, Q branch and S branch. The O branch refers to $\Delta J = -2$; Q branch refers to $\Delta J = 0$ while S branch refers to $\Delta J = +2$.

11.7 EXPERIMENTAL SETUP FOR RAMAN SPECTROSCOPY

The experimental setup consists of a cell into which a sample is taken. One end of a cell is horn like while the other end is provided with optically glass plate. A beam of monochromatic radiation is allowed to fall on the cell containing the sample. Sample must be colorless, pure and clean solid, liquid or gas molecule. Concentrated samples are taken so that the Raman lines produced possess high intensity. The source of monochromatic radiation is helium tube which was used in previous time but nowadays mercury arc is used. This mercury arc is placed close to the cell so that the cell receives radiations of high intensity. The scattered radiations emerge through the optically plane glass plate. There is a lens that directs the scattered radiations on the spectrograph. Spectrograph possesses short focus camera, prism having high resolving power and large light gathering power. The complete experimental setup for Raman spectra is shown in Figure 11.2.

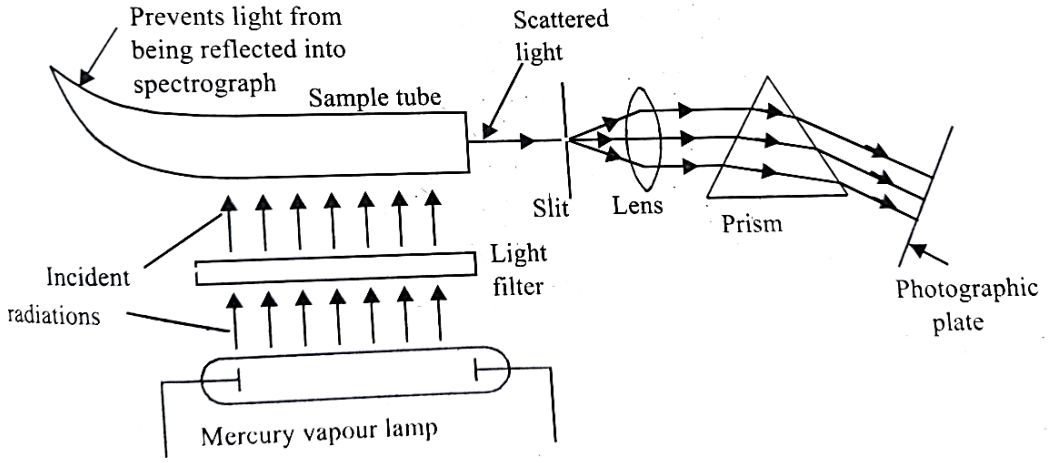

Figure 11.2: Experimental setup for Raman spectroscopy (Raman Spectrophotometer)

11.8 INTENSITY OF RAMAN LINES

It is to be noted here that the intensity of Raman lines depends on the frequency of the incident radiation and concentration of the sample used. Intensity is directly proportional to the frequency of the incident light raise to the power four. Rayleigh line possess more intensity than stokes lines whereas stokes lines possess more intensity than the anti-stokes lines.

11.9 MUTUAL EXCLUSION PRINCIPLES

According to mutual exclusion principle, those molecules which possess center of symmetry i.e. they are centrosymmetric, the vibrations that are active in infrared spectroscopy are inactive in Raman spectroscopy. For example, CO_2 symmetric stretching vibrations are inactive in infrared but are active in Raman spectra. Similarly, H_2, O_2 (homonuclear diatomic molecule) are infrared inactive but are Raman active. This principle provides information about the structure of a molecule whether it contains center of symmetry or not.

11.10 APPLICATION OF RAMAN SPECTROSCOPY

There are several applications of Raman spectroscopy. These are:

1. Identification of unknown compound: It is one of the most important applications of Raman spectroscopy. This can be done by comparing the spectra of unknown compound with the spectra of the known compound. Each compound possesses a unique spectrum as there is a fingerprint region which is the characteristic of a particular molecule or a compound.

2. By using Raman spectra, we can determine whether a substance possess crystalline form or an amorphous form. Raman spectra of the crystalline form of a substance consist of fine lines whereas Raman spectra of an amorphous form of a substance consist of broad and closely packed lines.

3. Using Raman spectra, we can determine whether the dissociation of an electrolyte is partial, incomplete or complete. We can obtain Raman spectra of pure substance (electrolyte) as well as Raman spectra of ions into which an electrolyte dissociates. By comparing the intensity and position of Raman lines, we can detect the number of ions produced.

4. Raman spectra are also used in order to produce whether the compound is covalent or ionic. It has been found that Raman lines in case of covalent compounds possess high intensity whereas ionic compounds which are also known as electrovalent compounds possess low intensity Raman lines. For example, NaCl does not show Raman lines as it is ionic whereas on the other hand $HgCl_2$ which is a covalent in nature show sharp Raman lines.

5. By using Raman spectra, we can determine whether a given organic compound is aliphatic or aromatic.

11.11 SUMMARY

In this unit, we have discussed Raman spectroscopy which includes polarizability concept, theories of Raman scattering, selection rules, pure rotational Raman spectra of diatomic molecules, pure vibrational Raman spectra of diatomic molecules and mutual exclusion principle. By using mutual exclusion principle, one can predict whether a molecule contains center of symmetry or not. In addition to this, we have also discussed about the intensity of Raman line along with the application of Raman spectroscopy as applied for the identification of the unknown compounds

11.12 TERMINAL QUESTIONS AND ANSWERS

Q.1. Long Questions :

Q.1 Explain Raman scattering in detail with respect to pure vibrational and pure rotational Raman spectra of a diatomic molecule.

Q.2 Explain the applications of Raman spectroscopy.

Q.3 Explain the classical and quantum theory of Raman scattering.

Q.4 Describe the concept of polarizability in Raman scattering.

Q.5 Discuss the experimental setup of Raman spectra along with the diagram.

Q.6 What is the most important use of studying pure rotational Raman spectrum?

Q.7What are the selection rules for rotation- vibration Raman spectra of diatomic molecules?Applying these rule explain what type of rotation –vibration spectrum is obtained for a diatomic molecules?

Q.2 Fill in the blanks:

1. Raman spectra involve ……. of radiations.
2. In Raman spectra, there is ……. in polarizability.
3. In Raman spectra, when the scattered radiation has frequency same as the incident radiation, ……. line is produced.
4. In Raman spectroscopy, when the scattered radiation has frequency less than the frequency of the incident radiation, the line produced is called ……. line.
5. In Raman spectroscopy, when the scattered radiation has frequency more than the frequency of the incident radiation, the line produced is called ……. line.
6. The sample taken for Raman spectra may be ……., ……. and ……..
7. Homo-nuclear diatomic molecule can even undergo ……. effect.
8. Ionic compounds possess Raman spectra that are ……. in intensity.
9. The selection rule for pure vibrational Raman effect of a diatomic molecule is …….
10. The selection rule for pure rotational Raman effect of a diatomic molecule is given by …….
11. Law of mutual exclusion principle is applied to those molecules that possess ……
12. The radiation used for studying Raman effect is …….
13. The selection rule for rotational- vibrational Raman spectra of a diatomic molecule is ……

14. The sample used for Raman scattering should be ……. and …….

Q.3 True and False

1. We can observe Raman effect only for solid samples.

2. According to mutual exclusion principle, Raman active vibrations are infra-red inactive while infra-red active vibrations are Raman inactive in case of molecules that contains center of symmetry.

3. We can determine the structure of a molecule by using Raman spectroscopy.

4. Covalent compounds possess Raman lines of higher intensity than the ionic compounds.

5. The selection rule for pure rotational Raman spectra is $\Delta v = \pm 1$.

6. Selection rule predicts whether the transition within the energy level is allowed or not.

7. Molecules must possess center of symmetry in order to obey law of mutual exclusion principle.

8. Intensity of Raman line is directly proportional to the fourth power of the frequency of the incident radiation.

9. The frequency of Raman lines or Raman shift depends on the frequency of the incident radiation.

10. The polarizability of a molecule remains unchanged in Raman spectroscopy.

Q.4 Multiple Choice Questions:

1. Raman spectroscopy occurs in

a)Infrared region b) Microwave region

c)Visible region d) Ultraviolet region

2. In Raman spectroscopy, which condition of frequency is satisfied for anti-stokes lines provided that $\upsilon_i$is the frequency of the incident light, $\upsilon_s$is the frequency of the scattered light.

a) $\upsilon_i=\upsilon_s$ b) $\upsilon_i>\upsilon_s$

c) $\upsilon_i<\upsilon_s$ d) No relation between $\upsilon_i$and υ_s

3. In Raman spectroscopy, which condition is satisfied for stokes lines provided that $\upsilon_i$is the frequency of the incident light, $\upsilon_s$is the frequency of the scattered light.

a) $\upsilon_i=\upsilon_s$ b) $\upsilon_i>\upsilon_s$

c) $\upsilon_i<\upsilon_s$ d) No relation between υ_i and υ_s

4. For pure vibrational Raman spectra of diatomic molecule, selection rule is

a)$\Delta v = 0$ b) $\Delta v = \pm 1$

c)$\Delta v = \pm 2$ d) $\Delta v = \pm 3$

5. For pure rotational Raman spectra of diatomic molecule, selection rule is

a) $\Delta J = 0, +1$ b) $\Delta J = 0, \pm 1$

c) $\Delta J = 0, \pm 2$ d) $\Delta J = \pm 1$

6. Raman shift ($\Delta\upsilon$) is zero for which of the following scattered line:

a)Stokes line b)Anti-stokes line

c) Rayleigh line d)None of the above

7. By using Raman spectroscopy, we can determine whether a substance possess crystalline form or amorphous form. Which of the following statement is correct?

a) Crystalline form shows Raman spectra with fine lines.

b) Amorphous form shows Raman spectra with fine lines.

c) Crystalline form and amorphous form do not show Raman spectra.

d) All of the above statements are false.

8. Raman spectra can be obtained for

a)Solids only b) Liquids only

c)Gases only d) All of the above

9. Which is the correct statement?

a. Covalent compounds possess less intensity than the ionic compounds.
b. Covalent compounds possess more intensity than the ionic compounds.
c. Both covalent compounds, as well as ionic compounds, possess same intensity.
d. Covalent compounds do not show Raman spectra.

10. Raman shift ($\Delta\upsilon$) is positive for

a) Stokes lines b)Rayleigh lines

c)Anti-stokes lines d)None of the above

11. For rotational- vibrational Raman spectra of diatomic molecule, selection rule is

a) $\Delta J = 0, \pm 2$ b) $\Delta v = \pm 1$

c) Both a and b d) None of the above

12. In Raman spectroscopy, the spectrograph must possess

a) High light gathering power b)High resolving power

c) Short focus camera d)All of the above

ANSWERS:

Q.2 Fill in the blanks:

1. Scattering; 2. Change; 3. Rayleigh; 4. Stokes; 5. Anti- stokes; 6. Solid, liquid and gas; 7. Raman effect; 8. Low; 9. $\Delta v = \pm 1$; 10. $\Delta J = 0, \pm 2$; 11. Centre of symmetry; 12. Visible radiation; 13. $\Delta J = 0, \pm 2$; $\Delta v = \pm 1$; 14. Pure and colorless

Q.3 True and False

1. False; 2. True; 3. True; 4. True; 5. False; 6. True; 7. True; 8. True; 9. False; 10. False

Q.4 Multiple choice Questions:

1. (c)	**2.** (c)	**3**.(b)	**4**. (b)	**5**.(c)	6. (c)
7.(a)	**8**.(d)	**9**. (b)	**10**. (a)	**11.** (c)	**12.** (d)

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11.14 GLOSSARY

- **Polarizability**: Ability of a non-polar molecule or atom to acquire dipole moment in presence of an electric field.
- **Selection rule**: Rules that decides whether the transition between energy levels are allowed or not.
- **Homo-nuclear diatomic molecule:** Molecule in which both atoms possess same nuclei like O_2, N_2.
- **Hetero-nuclear diatomic molecule**: Molecule in which atom possess different nuclei like HCl, NO_2.
- **Stokes lines**: Raman lines that possess frequency less than the frequency of the incident radiations.
- **Anti-stokes lines**: Raman lines that possess frequency more than the frequency of the incident radiations.

UNIT 12: BASIC CONCEPTS OF CHROMATOGRAPHY

CONTENTS:

12.1 INTRODUCTION

In this unit, we will cover the general aspects of chromatography. The unit will begin with a discussion on the general principles and classification of chromatographic methods. We will also explain the theory of chromatography as well as the efficiency of the chromatographic technique. The mechanism of separation will also be discussed and the development of the chromatograms will be explained. We will also discuss the characteristics of the stationary, mobile phases and other terminology used in chromatography.

12.2 OBJECTIVES/LEARNING OUTCOMES

After studying this unit, you should be able to

- Understand the fundamental concepts of separation technique-Chromatography
- General principles behind chromatographic separations
- Various types of chromatography
- Efficiency of chromatographic techniques
- Method involved in the development of a chromatogram

12.3 CHROMATOGRAPHY

Chromatography is one of the most widely used methods of separation in the analytical chemistry. It allows the components in a mixture to be separated based on their interaction properties with stationary phase and mobile phase. The name “chromatography” comes from two Greek words: chroma, which means color, and graphein, which means to write. It was originally used to separate and identify the pigments in plants, hence the name.

The basic principle of chromatography involves the distribution or partition of components between two phases: a stationary phase and a mobile phase. The stationary phase is typically a solid or a liquid supported on a solid, while the mobile phase is a liquid or gas. As the mixture is introduced into the system, the different components interact differently with the stationary and mobile phases, leading to their separation over time.

“Thus chromatography may be defined as a method of separating a mixture of components into individual components through equlibrium distribution between two paases”.

It is an analytical method used to separate and analyze complicated mixtures, identify individual molecules, and purify substances. It is used in many different fields of science, such as Chemistry, Biochemistry, Pharmacology, Environmental Science, and Food Science.

12.3.1 History of Chromatography:

The history of chromatography dates back to the early 20th century, and its development has been a result of contributions from various scientists. Chromatography is a technique used for separating and analysing mixtures of compounds based on their differential affinities for a stationary phase and a mobile phase. Here is a brief overview of the key milestones in the history of chromatography:

- **Michael Tswett (1903):** Russian scientist Michael Tswett is credited with the discovery of chromatography. In 1903, he separated plant pigments using a column of calcium carbonate, marking the first application of chromatography. He called the technique "chromatography" from the Greek words "chroma" (color) and "graphein" (to write), emphasizing its application to separate pigments.
- **Richard Synge and Archer Martin (1940s):** British biochemists Richard Synge and Archer Martin developed paper chromatography, for which they were awarded the Nobel Prize in Chemistry in 1952. Paper chromatography involved using a strip of paper as the stationary phase, and gas-liquid chromatography utilized a liquid stationary phase coated on a solid support.
- **Colin F. Poole and Paul J. W. Dearden (1950s-1960s):** Their work focused on the development of high-performance liquid chromatography (HPLC), which involves the use of a liquid mobile phase and a solid stationary phase. This method greatly improved the speed and efficiency of chromatographic separations.
- **Martin and James (1952):** Raymond D. Martin and A. T. James introduced a technique known as partition chromatography, which laid the foundation for liquid-liquid chromatography. This technique uses a liquid stationary phase coated on a solid support.
- **Gas Chromatography (1950s):** The development of gas chromatography, which uses a gaseous mobile phase and a liquid or solid stationary phase, was a significant advancement. This technique became widely used for the separation and analysis of volatile compounds.
- **Advancements in Instrumentation (1960s-1970s):** The development of more sophisticated instrumentation, including detectors and columns with improved resolution, greatly enhanced the capabilities of chromatography. This period saw the widespread adoption of gas chromatography and the continued refinement of HPLC.

- **Liquid Chromatography-Mass Spectrometry (LC-MS) (1970s):** The combination of liquid chromatography with mass spectrometry (LC-MS) became a powerful tool for identifying and quantifying compounds in complex mixtures. This hybrid technique is widely used in various scientific disciplines.
- **Advancements in Column Technology (1980s-1990s):** Continued improvements in column technology, including the development of new stationary phases and column geometries, further enhanced the efficiency and selectivity of chromatographic separations.
- **Ultra-Performance Liquid Chromatography (UPLC) (2000s):** UPLC represents a more recent advancement in liquid chromatography, offering higher resolution and faster analysis times compared to traditional HPLC.

12.3.2 General terms used in chromatography

- **Chromatography:** A physical separation method in which the components to be separated are distributed between two phases, one stationary (stationary phase) and the other (mobile phase) moving in a specific direction.
- **Chromatogram:** A chromatogram is a graphical representation of eluents, concentration of analytes or other quantity versus volume or time. It can be used to identify compounds and determine their relative concentrations in a mixture.
- **Stationary phase**: Stationary phase is the phase over which the mobile phase passes in the technique of chromatography. It may be solid (e.g., glass, silica, or alumina), liquid that is packed into a glass or metal tube or that constitutes the walls of an open-tube capillary.
- **Mobile phase:** A fluid which flows through or along the stationary phase, in a specific direction. It may be a liquid (liquid chromatography) or a gas (gas chromatography) or a supercritical fluid (supercritical-fluid chromatography)
- **Analyte:** Analyte is the substance that is to be separated from the mixture during chromatography
- **Eluent:** Eluent refers to the fluid that enters and passes through the chromatographic column.
- **Elute:** Elute is the fluid containing the sample that exits the chromatographic column

- **Elution:** Elution is the process of removal or extraction of a solid by washing out it with a suitable solvent in a chromatographic column.
- **Column:** The column is the part of the chromatographic system where the separation of components occurs. It contains the stationary phase.
- **Retention factor (R_f):** The Rf is a ratio that represents the distance travelled by a compound relative to the distance travelled by the solvent (mobile phase).
- **Retention time (t_R):** Retention time refers to the time it takes for a particular compound to travel through a chromatographic column and reach the detector.
- **Peak:** A peak is a distinct raised portion of a chromatogram that corresponds to a specific component of the sample.
- **Peak width:** Peak width refers to the width of a peak at its base and is an important parameter in evaluating the efficiency of a chromatographic separation.
- **Resolution**: Resolution is the ability of a chromatographic method to separate and distinguish between different components in a mixture. Resolution is typically assessed by considering the separation of adjacent peaks in a chromatogram. The higher the resolution, the better the separation of components.
- **Detector:** The detector is the instrument that measures the concentration of the separated components as they elute from the chromatographic column.

12.4 CLASSIFICATION OF CHROMATOGRAPHY

Chromatographic methods are analytical techniques widely employed in various scientific and industrial fields, including chemistry, biochemistry, pharmaceuticals, environmental science, and more. There are several types of chromatography, and they can be classified based on various criteria, listed as follows:

- Purpose of chromatography experiment
- Shape/ Geometry of stationary phase and support used
- Physical states of stationary phase and mobile phases.
- Mechanism of separation used
- Polarity of stationary phase and mobile phase used

Chromatographic methods classified on each basis are:

1. On the basis of purpose of chromatography experiment

(a) Preparative chromatography: This type of chromatography is meant to separate the components of a mixture for further use and is thus a form of purification. The separated compounds are often pure and may be used for quantification or other applications. Thus the preparative chromatography is used to purify and isolate larger quantities of individual components for further use. Example: High Performance liquid chromatography (HPLC) and Supercritical fluid chromatography (SFC)

(b) Analytical chromatography: This type of chromatography is used to separate, identify and quantify the analytes in the given sample. The sample size applied to the chromatographic system is very small. It is basically used for qualitative and quantitative analysis of chemical or biological compounds in industry and academia. Example: HPLC, Thin layer chromatography (TLC), Gas chromatography (GC)

2. based on shape of stationary phase and support

Depending upon the type of stationary support or more accurately the shape of the stationary support, chromatographic technique can be twodimensional or three-dimensional.

(a) Planar chromatography (Two-dimensional chromatography): In this type of chromatography, the stationary phase is a planar surface and the chromatogram development is a two dimensional. The stationary phase may be the paper or the adsorbent/solvent coated on a glass plate. It is form of liquid chromatography in which the mobile phase moves through the stationary phase by capillary action and/or by gravity. Example: Paper chromatography and Thin layer chromatography (TLC).

(b) Column chromatography (Three dimensional chromatography)- In this chromatographic techniques stationary phase is filled in a tube or column which is three dimensional in shape and the separation is achieved on the basis of different retention time or differential partition of analytes between mobile phase and stationary phase. The stationary phase may be packed inside the column completely (packed column) or may stick to the walls of the column allowing the passage for mobile phase (open tubular column). Column chromatography is used to purify compounds depending on their polarity or hydrophobicity. Examples: HPLC and GC.

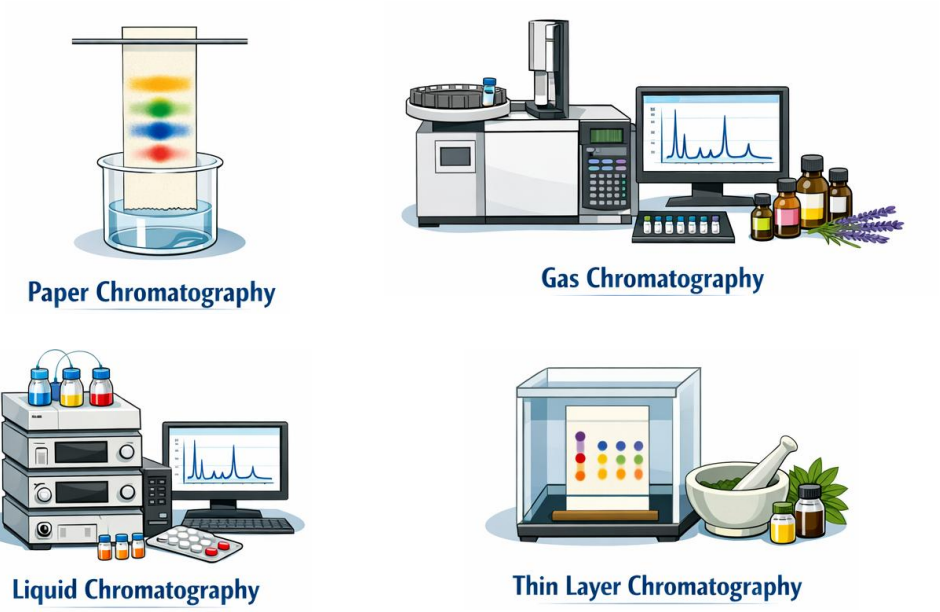


Fig. 12.1: Types of chromatography

3. On the basis of the physical state of the stationary phase and mobile phases

Depending upon the physical state of the stationary phase and mobile phases are solid, liqiud or supercritical fluid, and gas the chromatographic techniques can be classified as:

(a) Solid-Liquid Chromatography: In this chromatography, the stationary phase is an active solid (e.g. silica, alumina or a polymer) and mobile phase is liquid, and the separation is based on adsorption affinities between the sample molecules and the surface of the active solid. The sample/analyte is adsorbed on the solid stationary phase material and separation occurs on the basis of differential solubility of analytes in the mobile phase. Example: Ion exchange chromatography (IEC), Thin layer chromatography (TLC), High Performance liquid chromatography (HPLC), High Performance Thin layer chromatography (HPTLC).

(b) Liquid-Liquid Chromatography: In this chromatographic method, both the stationary and mobile phase is liquid but differs in their polarities/immiscible liquid. In which one phase being the mobile carrier and the other being the thin liquid layer supported on the inert stationary phase. The separation occurs on the basis of difference in partition coefficients of analytes in the two phases. Example: Partition chromatography, Paper chromatography

(c) Gas-Solid Chromatography (GSC): In this chromatographic technique the stationary phase is an active solid adsorbent and inert gas like helium is used as the

mobile phase or carrier gas. It is used for the seperation and identification of volatile component in a mixture, gases and small polar molecule. Example: Gas chromatography (GC)

(d) Gas-Liquid Chromatography (GLC): In this chromatographic technique the mobile phase is the gaseous state (inert gas) and stationary phase is in the liquid state (nonvolatile liquid) coated as a thin layer on an inactive solid support or on the inside walls of the capillary tube. The compounds are separated according to their partition-coefficients. GLC is used for the analysis of sterols, hydrocarbons, pesticides.

4. On the basis of principle of separation/mechamism of separation:

According to mechanism involved in the seperation or interaction of analyte with stationary and mobile phase the chromatographic techniques classified as:

(a) Adsorption Chromatography: In adsorption chromatography, the stationary phase is a solid and mobile phase is either a liquid or a gas. The seperation is based on the differential adsorption of solute/molecule onto the soild stationary phase (silica, alumina) and the solubility in mobile phase (polarity of mobile phase). The compounds are adsorbed on the solid stationary phase through various interactions like covalent bonding and electrostatic attraction. Example: Coulmn chromatography, HPLC, GC, TLC

(b) Partition Chromatography: In partition chromatography the mobile phase is either or gas while stationary phase is a liquid supported on an inert solid. The separation occurs as the components/compounds of the sample partition between the mobile and stationary phases based on their relative affinities for each phase. Example: Paper chromatograhy, GLC.

(c) Ion Exchange Chromatography: This chromatographic technique used for separating and purifying charged molecules based on their interactions with charged groups immobilized on a solid stationary phase. The separation is achieved through reversible exchange of ions between the stationary phase (resin or gel functionalized with cationic or ionic groups) and the mobile phase (buffer solution). The buffer serves to weaken the electrostatic interactions between the analyte and the resin and elutes it out at a particular pH.

(d) Molecular Exclusion Chromatography: It is also known as size exclusion chromatography or gel filtration chromatography and the separation ocuurs on the

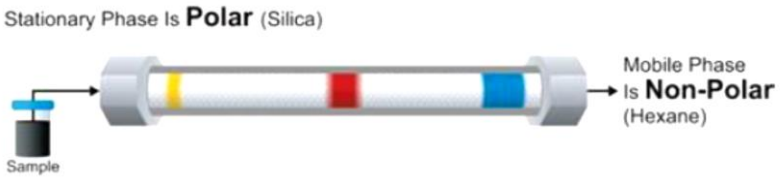
basis of molecular size of the molecule. The stationary phase is a porous matrix of beads or gel with specific pore size. As the mobile phase (buffer solution) passes through a porous gel, larger solute molecules pass through the pores while smaller molecules are entrapped in the pores of gel beads. Consequently larger molecules to pass through the column at a faster rate than the smaller ones, and thus the compounds are separated on the basis of their molecular size. It used for the molecule like proteins, nucleic acids, and polysaccharides.

(e) Affinity Chromatography: It is highly selective type of chromatography that is based upon the specific interaction between the analyte molecule and another compatible molecule immobilized on a stationary phase. For example, for separation of antigens, an antibody may be immobilized on a matrix that forms a stationary phase. When sample consisting of a mixture of proteins is passed through the column, only the specific antigen is bound to the antibody immobilized on the stationary phase. This antigen can be extracted either by changing the ionic strength / pH or through dialysis.

5. On the basis of polarity of stationary phase and mobile phase used

According to polarity of stationary and mobile phase the chromatographic techniques classified as:

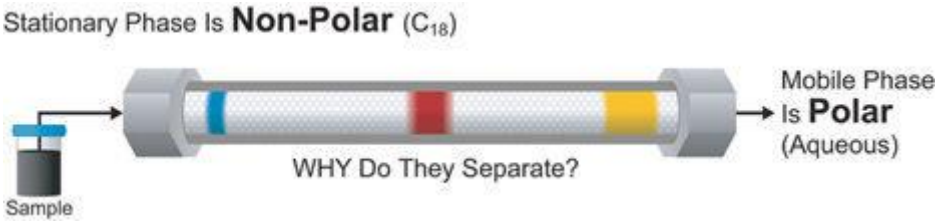
(a) Normal phase chromatography: In this chromatographic technique, mobile phase is in non-polar solvent (hexane, chloroform, diethyl ether) and the stationary phase is polar in nature (silica gel or alumina).The polar compounds have greater affinity (interact more strongly) to the polar stationary phase, thus their mobility is slow in the system, therefore they eluted later and non-polar compounds are eluted first. It is useful for separating polar compounds such as carbohydrates, amino acids, peptides, and some natural products.



(https://i.stack.imgur.com/GzU3n.jpg)

(b) Reverse phase chromatography: This chromatographic method is reverse to the normal phase chromatography. The stationary phase is non-polar such as hydrophobic

alkyl chains (e.g., C18) attached with soild surface and mobile phase is polar in nature like water and organic solvent like methanol and acetonitrile, therefore polar compounds are eluted first and non-polar are eluted later. This technique is used especially in the analysis and purification of organic compounds, pharmaceuticals, peptides, proteins, and nucleic acids.



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6. Based on the Technique Used for Detection:

In the recent advancement of technologies there is different detection techniques used for the analysis of analytes According to detection techniques the chromatographic techniques classified as:

(a) Gas Chromatography-Mass Spectrometry (GC-MS): The combination of gas chromatography and mass spectrometry provides a highly selective and sensitive method for the identification and quantification of a wide range of compounds in a sample. GC-MS is widely used in various fields such as environmental analysis, forensic science, pharmaceuticals, food and beverage testing, and many others. It allows researchers to identify unknown substances, determine the concentration of known substances, and study complex mixtures of compounds. Thus GC-MS combines two different analytical techniques to provide detailed information about the composition of a substance.

(b) Liquid Chromatography-Mass Spectrometry (LC-MS): LC-MS is a versatile and powerful technique that combines the separation capabilities of liquid chromatography with the sensitivity and specificity of mass spectrometry, making it an essential tool in modern analytical chemistry. This technique used in the fields of chemistry, biochemistry, biology, pharmaceuticals, environmental analysis, metabolomics, proteomics, and forensic science for the identification, quantification, and characterisation of chemical compounds, such as drugs, metabolites, and proteins.

12.5 COLUMN CHROMATOGRAPHY

The column chromatography involves the use of liquid mobile phase and a solid stationary phase; hence, it is a type of liquid-solid chromatography as mentioned above. Column chromatography is a technique used in chemistry to separate and purify individual components from a mixture. It was developed by the American petroeum chemist D.T. Day in 1900 after that M.S. Tswett the Polish botanist, in 1906 used adsorption columns for the investigations of plant pigments. Now days this method was extensively used by the chemists and other scientist, academician.

Fig. 12.2: Column chromatography

12.5.1 Principle of Column chromatography:

Column chromatography is a versatile technique widely used in analytical chemistry or laboratories for the purification of compounds. It allows for the separation of compounds based on differences in polarity, size, and other chemical properties, making it an essential tool for isolating pure substances from complex mixtures. The separation and purification of compounds based on their differential interactions with a stationary phase and a mobile phase. The principle behind column chromatography can be summarized as follows:

(i) **Stationary Phase:** A column is packed with a stationary phase, typically a solid support material such as silica gel or alumina. The availability of a large number of materials offer a wide range of flexibility in choosing the desired stationary phase in terms of the surface area, particle size and type of adsorbent. The stationary phase has specific properties that enable it to interact differently with different compounds. For example, polar stationary phases like silica gel tend to interact more strongly with polar

compounds, while non-polar stationary phases like alumina interact more strongly with non-polar compounds.

(ii) Mobile Phase: The mobile phase is a solvent or solvent mixture that flows through the column, carrying the sample mixture. The choice of mobile phase depends on the nature of the compounds being separated and their interactions with the stationary phase. Generally, the mobile phase should be less polar than the stationary phase to facilitate compound elution.

(iii) Adsorption and Elution: Column which is a long tube which is filled with the solid support (stationary phase). The mixture to be separated is first dissolved in a suitable solvent and its slurry is prepared which is then placed at the top of column. Different components of the mixture get adsorbed on the stationary phase to different extents. When the mobile phase is allowed to pass over stationary phase, compounds that interact more strongly (strongly adsorbed) with the stationary phase will move more slowly through the column, while those that interact less strongly (least adsorbed) will move more quickly along the mobile phase. This differential interaction causes the components to separate as they travel through the column. The various bands present in the coulmn become more define. The banded column of adsorbent is termed a *chromatogra*m, and the operation is spoken of as the *development of chromatogram*. The portion of a column which is occupied by a particularn substance (compound) is called *zone*.

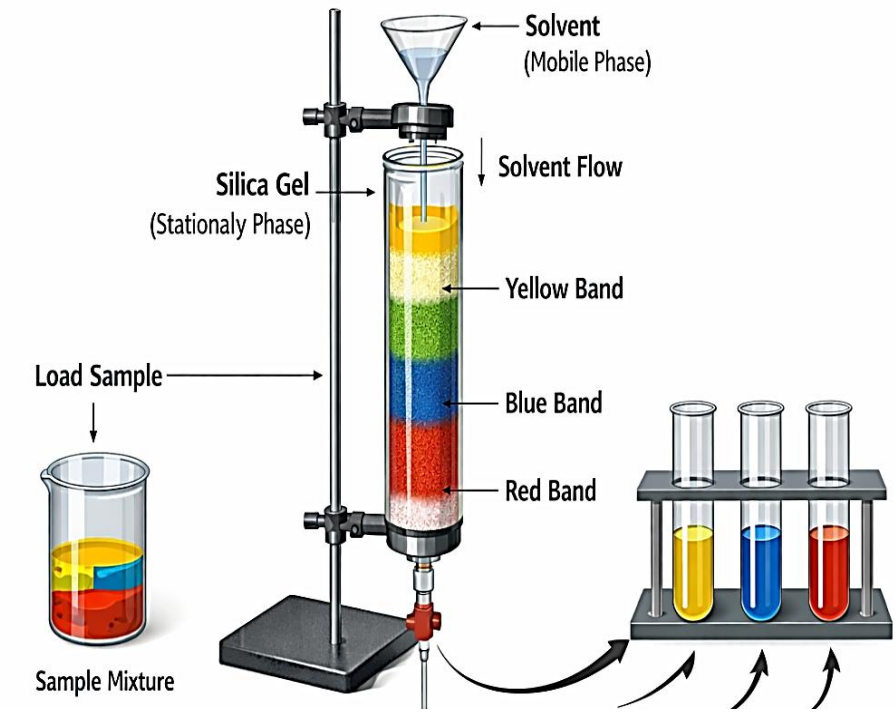

Fig. 12.3: Column chromatography with separated molecules

(iv) Fractionation: The mobile phase is continuously added from the top of the column and allowed to move out of the bottom column by opening the stop cock. The different components of the mixture keep moving downwards as bands in the column. These are then collected as different fractions in the flask placed at the bottom of the column. The different components are then obtained from the eluent by removal of the solvent.

(v) Detection: Compounds separated by column chromatography are typically detected using techniques such as UV-visible spectroscopy, refractive index detection, or fluorescence detection. This allows for the identification and quantification of separated compounds.

12.5.2 Efficiency of techniques:

Column chromatography is a very useful and convenient technique, both for the effective separation of components of a mixture and for the purification of an impure compound. Virtually, any type of mixture occurring naturally (in plants, animals or in any other source) or obtained synthetically from chemical reactions, can be separated into its components using column chromatography. Its efficiency can be evaluated based on several factors:

(i) Plate number and plate height:

(a). Number of Theoretical Plates (N):

- The efficiency of a chromatographic column is often quantified by the number of theoretical plates (N). The more theoretical plates a column has, the better its ability to separate components.
- The equation to calculate the number of theoretical plates is

$$N = \left(\frac{t_R}{\sigma}\right)^2 = 16\left(\frac{t_R}{w}\right)^2 = 5.54\left(\frac{t_R}{w_{1/2}}\right)^2$$

Where

t_R is the retention time of the peak;

σ is the standard deviation as a measure of peak width.

W is the peak width measured in time units as the distance between the intersections of the tangents to the peak inflexion points with the baseline and $W_{1/2}$ is the peak width at half height.

(b). Plate Height (H):

- Plate height (H), also known as the height equivalent to a theoretical plate (HETP), is a measure of the column's efficiency.

$$H = \frac{L}{N}$$

Where, L is the column length and N is the number of theoretical plates.

- The greater the number of theoretical plates (N) or the smaller the plate height, the more efficient the analyte exchange between two phases and the greater is the efficiency of the column, which means the better the separation. That is why column efficiency is measured by N. Thus A lower plate height indicates better efficiency.

(ii) Resolution: This refers to the ability of the column to separate different compounds from each other. Higher resolution means that closely related compounds are separated effectively. Factors such as the choice of stationary phase, mobile phase, and column dimensions can affect resolution.

- The number of theoretical plates is directly related to the resolution (Rs) between two peaks in a chromatogram.
- A higher number of theoretical plates contribute to better resolution.
- Resolution can be calculated by using this formula

$$Rs = \frac{2(tR2 - tR1)}{W1 + W2}$$

Where, Rs is peak resolution; t_{R1} and t_{R2} are the retention times, and W_1 and W_2 are the peak widths at their bases.

(iii) Nature of solvent/mobile phase: The solvent of low viscosities are generally used for the high efficiency separations. The reaseon for that this is that rate of flow is inversely proportional to viscosity and hence it becomes nesessary to select a solvent of lowest viscosity and proper elution strength.

(iv) Dimension of column: Longer columns generally provide better resolution but may require longer run times. The diameter of the column also influences efficiency, with smaller diameters offering higher resolution and efficiency due to reduce longitudinal diffusion. Thus the longer the column and smaller the diameter, the better will be the separation. The ideal length to width ratio for the column is 20:1 or 30:1.

(v) Particle size of the column packing: Smaller particle sizes and efficient packing of the stationary phase can improve efficiency by increasing surface area and reducing mass transfer limitations for interaction between the analyte and the stationary phase. Its

particles should be of uniform size. The finely divided nature of stationary phase leads to better separations. Particle size from74 to149μ is suggested with the mesh size of 100 to 200 mesh.

(vi) Sample Concentration: Overloading the column with a high concentration of sample can reduce efficiency due to band broadening effects. Optimal sample loading should be determined empirically for each application. Ideally, the sample to the adsorbent ratio is chosen as 1:20 to 1:50. Otherwise, more concentrated samples may not lead to clear separations.

(vii) Flow Rate: The flow rate of the mobile phase affects the efficiency of separation. Too high a flow rate may result in poor resolution and lead to band broadening; while too low a flow rate can lead to excessively long run times. Thus the flow rate of the solvent or the mobile phase should be uniform and not very fast. This will give better separation of bands of different components of the mixture without much tailing.

(viii) Retention Time: Efficient column chromatography should provide reasonable retention times for compounds of interest. Too short a retention time may lead to poor separation, while too long a retention time may result in extended run times and reduced throughput.

(ix) Detection Method: The detection method used to monitor elution from the column can impact efficiency. High-sensitivity detection methods can improve resolution and enable the detection of low-abundance compounds.

(x) Temperature: Difficult solution sample are generally separated at higher temparsature while other samplea are separated at room temperature.

12.5.3 Mechanism of Separation:

The separation of components of mixture using column chromatography (adsorption chromatography) involves their adsorption on the stationary support. The mobile phase then displaces the different components selectively one by one. The separation mechanism in column chromatography relies on the principles of adsorption, partitioning, and molecular size exclusion, depending on the nature of the stationary phase used. Common stationary phases include silica gel, alumina, or polymers, which interact differently with different compounds based on factors such as polarity, size, and functional groups. For example silica gel which is polar in nature; polar solvents may have better interactions with it as compared to the non-polar ones. The polarity of the mobile phase will also affect how effectively the separations can be carried out.

The following aspects, thus, need to be considered for the separation process:

- How strongly is the component adsorbed to the stationary phase?
- How much is the surface area of the stationary phase?
- What is the binding strength of the mobile phase is there to get adsorbed on the stationary phase, and how much it can displace the adsorbed components(s)?
- Which types of force of interactions are involved like hydrogen bonding, van der Waals forces and dipole-dipole interactions as the process of adsorption take place?

The mechanism of separation involves several key steps:

(i) Column Packing: The first step is to prepare the column. The stationary phase is typically a solid support material such as silica gel or alumina, packed into a glass column. The packing material should be chosen based on the polarity of the compounds to be separated.

(ii) Sample Loading: Once the column is prepared, the sample mixture is dissolved in a suitable solvent and loaded onto the top of the column. Care must be taken to ensure that the sample is evenly distributed on the top of the column to prevent channelling and uneven separation.

(iii) Mobile Phase Flow: A mobile phase, typically a solvent or a mixture of solvents, is continuously passed through the column. The mobile phase carries the sample mixture through the column.

(iv) Adsorption and partition: As the mobile phase travels through the column, the individual components of the sample mixture interact differently with the stationary phase. This interaction results in differential partitioning of the components between the mobile and stationary phases.

(v) Seperation and Development of Chromatogram: As the mobile phase flows through the column, individual components of the sample interact with the stationary phase to varying degrees. Compounds with stronger interactions with the stationary phase will move more slowly through the column, while those with weaker interactions will move more quickly. This results in separation of the components along the column.

(vi) Elution: Elution is the process of passing a mobile phase through the column. The choice of mobile phase (e.g., solvent or solvent mixture) depends on the nature of the sample and the stationary phase. The mobile phase carries the sample components

through the column at different rates based on their interactions with the stationary phase.

(vii) Collection of Fractions: As the separated components elute from the column, fractions are collected at specific time intervals or based on detection of individual components. Each fraction contains a purified compound or a mixture of compounds that can be further analyzed or used for downstream applications.

(viii) Detection: Detection of separated components can be done using various techniques depending on the nature of the compounds and the available equipment. Common detection methods include UV-Vis spectroscopy, fluorescence detection, refractive index detection, or simply visual inspection for colored compounds.

(ix) Analysis of Fractions: After collection, each fraction is typically analyzed to determine the purity and identity of the separated compounds. This can be done using spectroscopic techniques, such as nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), or by performing chemical tests.

12.5.4 Development of Chromatogram:

The most important aspect of column chromatography separations is the development of chromatograms. Three methods, frontal, elution and displacement analysis, have been used to develop chromatograms. Understanding the differences between them and which method will be most useful will be discussed in detail.

(i) Frontal analysis: Frontal analysis is a technique used in column chromatography to determine the adsorption isotherm of a solute onto the stationary phase. In this method, a fixed concentration of solute is continuously applied to the column, while the mobile phase flows through at a constant rate. As the solute passes through the column, it interacts with the stationary phase and begins to adsorb onto it.

The process begins with the solute being introduced into the column, and initially, all available adsorption sites on the stationary phase are vacant. As the solute moves through the column, it starts to occupy these sites, gradually increasing the concentration of the solute on the stationary phase until equilibrium is reached. At equilibrium, the rate of adsorption onto the stationary phase equals the rate of desorption back into the mobile phase. The least adsorbed solutes out from the column first than the strongly adsorbed solute.

The data obtained from frontal analysis can be used to calculate important parameters related to the chromatographic separation process, such as the distribution coefficient (Kd), the maximum adsorption capacity of the stationary phase (Cmax), and the affinity of the solute for the stationary phase.

Example: The eluent (solvent) contains three substances B, C and D with the strongly adsorbed ability order B < C < D, then the least adsorbed component (substance) B leaves the column first in the pure form and component C, D get adsorbed more strongly and consequently move slowly. The separation in the column and on the chromatogram can be represented schematically (Fig. 12.4).

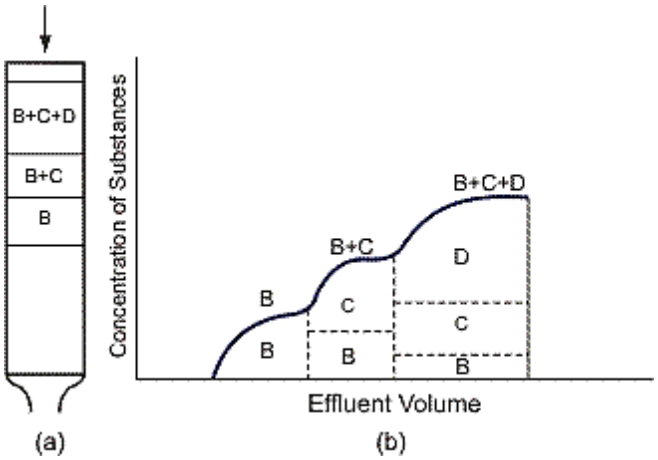

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Fig. 12.4: Chromatogram development in frontal analysis

(ii) Elution Analysis: This method is most widely used to develop chromatograme. In this method the chromatograph column is first washed by the eluent/ solvent (mobile phase), the eluent having lower adsorption power/afinity than any of the separated substances/components. Then the solution of analyzed mixture is added at regular intervals at the top of column into the solvent or eluent/mobile flow, the mixture in the column being separated into components with eluent zones between them depending on its partition coefficients.

Example: A mixture contains substances B, C and D with the adsorption ability/affinity for the stationary phase in order B < C < D and the solvent A is an eluent, its adsorption ability being lower than that of B, C, D, i.e., A < B < C < D. The components get eluted in the order of their affinities with the stationary phase but their migation is determined by the mobile phase. The component can be separated completely with a zone of the mobile phase (eluent A). The separation of substances in the column and on the chromatogram is shown in Fig. 12.5.

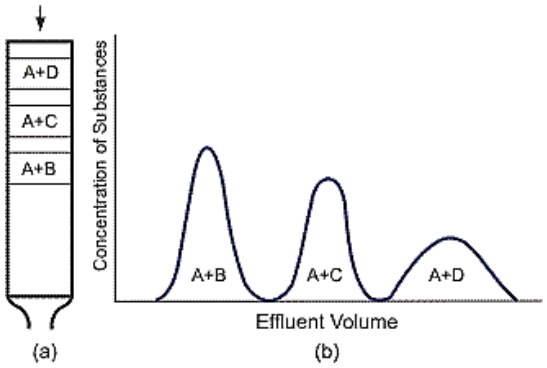

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Fig. 12.5: Chromatogram development in elution analysis

(iii) Displacement Analysis: In this method the small quantity of the sample solution added on the top of the column and the component of the mixture are separated by the continuously passed a solution of a substance (displacer) which is more strongly adsorbed than any of the components of the mixture. This results in the formation of adjoining zones of separated substances. During the process the components undergoes separation because of the differences in the partition or adsorption properties. The least adsorbed component will leave the column first followed by the others depending uopon their degree of adsorptivities.

(iv) Example: A nmixture containing B, C, D are the separated substance and E is the eluent (displacer or displacing agent) having a greater affinity for the stationary phase than the B, C, D i.e. B < C < D < E is the adsorption ability order. So that the speration order of the pure component is B > C > D. The separation of substances in the column and on the chromatogram is shown in Fig. 12.6.

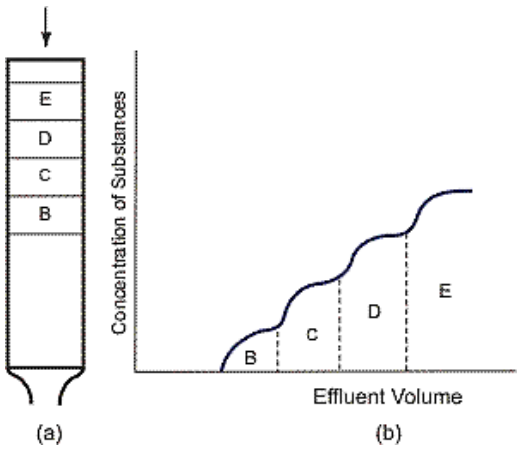

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Fig. 12.6: Chromatogram development in displacement analysis

12.6 PAPER CHROMATOGRAPHY

Paper chromatography is a simple, economical, and widely used planar chromatographic technique for the separation, identification, and analysis of mixtures. It is especially useful for qualitative analysis of organic and inorganic compounds present in small quantities. The method was developed by Consden, Gordon, and Martin (1944) and has found extensive application in biochemistry, pharmaceutical analysis, food chemistry, and forensic science.

12.6.1 Principle

Paper chromatography is a type of partition chromatography in which separation is based on the differential partitioning of solutes between a stationary phase and a mobile phase. The stationary phase consists of water molecules held by hydrogen bonding within the cellulose fibers of the paper, while the mobile phase is an organic solvent or a mixture of solvents. As the mobile phase moves through the paper by capillary action, components of the mixture distribute themselves between the stationary and mobile phases according to their partition coefficients, resulting in separation.

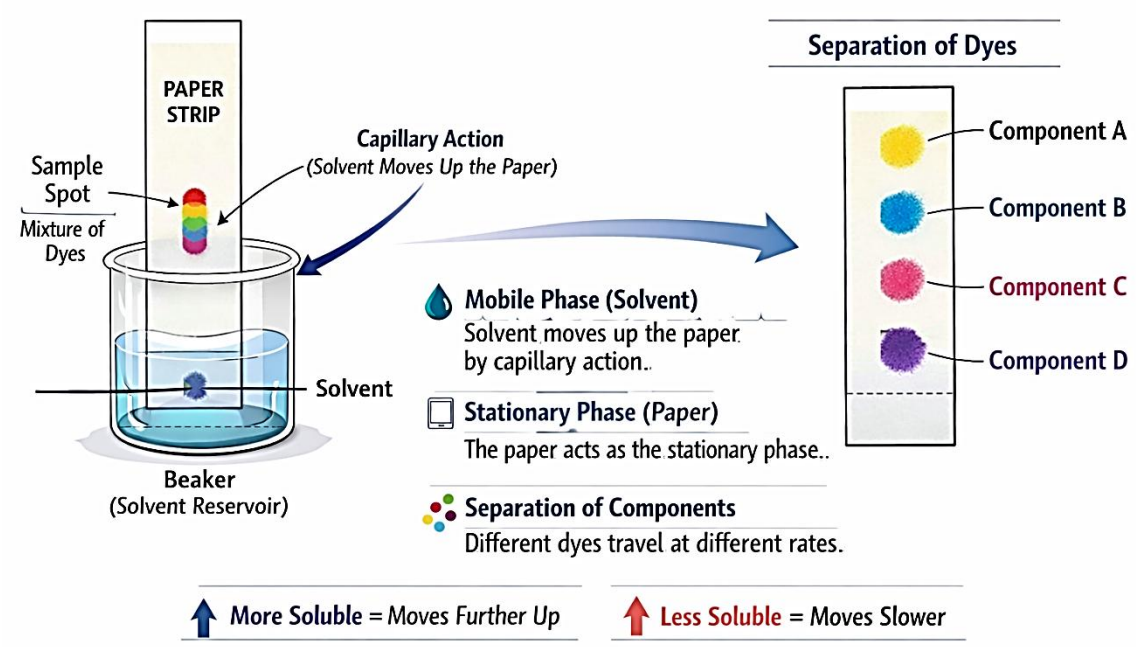

Fig.12.7: Paper Chromatography

The principle of paper chromatography (Fig. 12.7) depends on the difference in solubility and affinity of the components of a mixture between the stationary and mobile phases. Substances that have greater affinity for the mobile phase travel faster and move farther along the paper, whereas those with stronger attraction to the stationary phase move more slowly. This

differential movement results in the separation of components into distinct spots at different heights on the paper.

The movement of each component is characterized by its R_f value, which is a constant for a given compound under fixed experimental conditions. R_f values are useful for identifying compounds by comparing them with standard values.

$$R_f = \frac{\text{Distance travelled by solute}}{\text{Distance traveled by the solvent front}}$$

12.6.2 Types of Paper Chromatography

Paper chromatography is a simple, economical, and widely used planar chromatographic technique for the separation, identification, and analysis of mixtures such as amino acids, sugars, alkaloids, pigments, drugs, and inorganic ions. It is based on the partition of solutes between two phases: a stationary phase (water molecules held in cellulose fibers of the paper) and a mobile phase (solvent or solvent mixture). Depending on the direction of solvent movement, arrangement of the paper, and method of development, paper chromatography is classified into several types (Fig.12.8).

(i) Ascending chromatography: Solvent moves upward against gravity
(ii) Descending chromatography: Solvent flows downward due to gravity
(iii) Radial (circular) chromatography

(i) Ascending Paper Chromatography

Ascending paper chromatography is a simple and widely used chromatographic technique for separating and identifying components of a mixture, especially amino acids, sugars, dyes, and plant pigments. Ascending paper chromatography is valued for its simplicity, low cost, and effectiveness in qualitative analysis.

In this method, a strip of chromatography paper (usually Whatman No. 1) acts as the stationary phase, while a suitable solvent or solvent mixture serves as the mobile phase. A small spot of the sample solution is applied near the lower end of the paper, above the solvent level. The paper is then placed vertically in a closed chromatographic chamber containing the solvent at the bottom. Due to capillary action, the solvent rises upward through the paper. As the solvent ascends, different components of the sample move at different rates depending on their solubility in the mobile phase and adsorption on the stationary phase. After the solvent front reaches a certain height, the paper is removed, dried, and the separated components are

visualized using suitable detecting agents. The separation is expressed in terms of R_f (retardation factor) values.

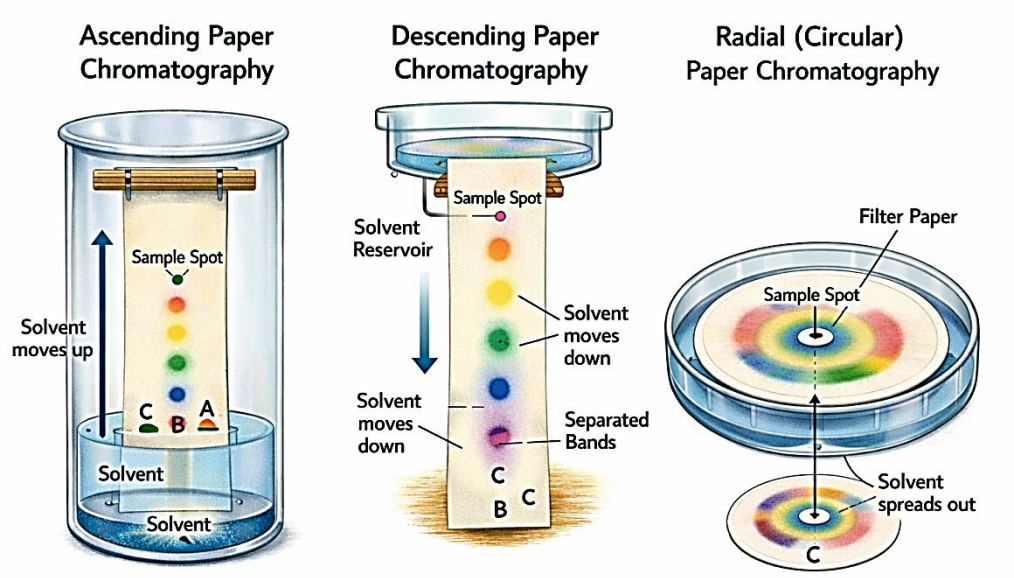

Fig.12.8 Types of paper chromatography

(ii) Descending Paper Chromatography is a type of paper chromatography in which the mobile phase (solvent) moves downward over the stationary phase due to the combined effect of capillary action and gravity. In descending paper chromatography, a sheet of chromatography paper (usually Whatman No. 1) acts as the stationary phase, retaining a thin layer of water within its fibers. The mobile phase is an organic solvent or solvent mixture. When the solvent flows downward, components of the sample separate based on their different partition coefficients between the stationary water layer and the moving solvent.

(iii) Radial (Circular) Paper Chromatography

Radial or circular paper chromatography is a modification of paper chromatography in which the separation of components occurs radially from a central point rather than along a straight line. It is mainly used for the qualitative analysis of mixtures, especially pigments, dyes, amino acids, and plant extracts. The technique is based on the differential distribution of solute components between the stationary phase (water held in the cellulose fibers of the paper) and the mobile phase (a suitable solvent). As the solvent moves outward in all directions from the centre by capillary action, different components travel at different rates depending on their solubility and affinity for the stationary phase.

12.7 SUMMARY

In this unit, we have learnt the following aspects of chromatography:

- The chromatographic techniques can be classified in various ways according to the shape of the stationary support, nature of the mobile phase and the mechanism of separation.
- The technique of column chromatography (liqiud-solid chromatography) is very efficient method for the separation of a wide range of mixtures.
- A variety of adsorbents and mobile phases are used in column chromatography for separating different mixtures.
- The force of interactions involved like hydrogen bonding, van der Waals forces and dipole-dipole interactions as the process of adsorption take place.
- The principle of paper chromatography and its types and separation of components in the mixture.

12.8 TERMINAL QUESTIONS

1. Define chromatography? State its basic principle.
2. What are the main types of chromatography? Mention any four with one example each.
3. Explain the column chromatography and its separation mechanism.
4. Define R_f value. Write its formula and significance in paper chromatography.
5. What is column chromatography? Discuss its types.

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BLOCK -V: LABORATORY WORK

UNIT 13: LABORATORY HAZARDS AND SAFETY PRECAUTIONS

CONTENTS:

13.1 INTRODUCTION

In the laboratory, it requires great care and attention in order to avoid safety hazards occurring due to delicate lab instruments, open flames, hazardous chemicals etc. Negligent handling of dangerous/harmful chemicals can result in both short-term (acute) and long-term (Chronic) health issues. Burns, eye injuries, lung diseases, asphyxiation, and suffocation are some of these potential issues. Chemicals cause adverse reactions in the body through ingestion, inhalation, skin contact, and percutaneous exposure. No matter how much is being used or how it is used, a substance, operation, or activity has intrinsic hazardous characteristics or properties. Various risks to human health and physical injury can be posed by the chemicals given below:

Health Hazards	Physical Hazards
Toxic	Combustible
Carcinogenic	Flammable
Mutagenic	Explosive
Reproductive toxins	Reactive or pyrophoric
Sensitizers	Oxidizers
Irritants and Corrosives	Corrosive
Asphyxiants	Compressed Gas and Liquid

The chemistry practical could involve a minor incident. Inform your teacher or the lab attendant right away, remain calm, do not panic, and use the first aid provided in the laboratory. However, if any of these symptoms occur, you should immediately stop working, take off your personal protective equipment, wash your hands, and contact your healthcare provider.

- Unusual taste or odor,
- Respiratory irritation, coughing, choking, or shortness of breath,
- Sudden headache, dizziness, blurred vision, or loss of consciousness,
- Burning or painful sensation,
- Swelling, reddening, or itching skin.

13.2 OBJECTIVE

After completing this unit, learners will be able:-

- To known ‘What is a laboratory hazard’? The physical hazards and the chemical hazards in the laboratory.

- How to prevent chemical hazards in the laboratory.
- To know the effect of laboratory incidents on learner's health, such as heat burns, glass cuts, and the inhalation of gas.
- To assess and reduce the risks associated with chemical hazards in the laboratory.

13.3 PURPOSE OF LABORATORY & CHEMICAL SAFETY

- To promote safety awareness and encourage safe working practices in the laboratory.
- Safety guidelines should serve as a reminder of things you can do to work more safely and apply to all users of the laboratory.
- All learners are expected to adhere to safety guidelines and maintain safety standard strictly.

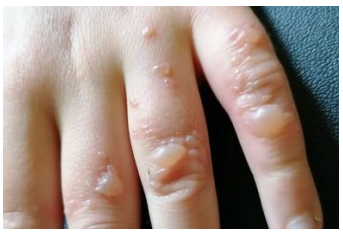
13.4 TYPES OF HAZARDS IN THE LABORATORY AND THEIR PREVENTION

Chemical and physical hazards in the laboratory fall into five major categories. Now discuss each category in details with their prevention in the laboratory.

- Chemical burns
- Heat burns
- Eyes injuries
- Injury from glassware
- Inhaling dangerous gases

13.4.1 Chemical burns

Acids, bases, etching solutions and solvents are commonly used in chemistry lab and classified as corrosive substance, and also present a serious health hazards such as chemical burns, tissue damage, organ damage, asphyxiation, corneal damage, which can lead to blindness and genetic damage if used improperly.



(Burns are a common type of hazard when dealing with harmful substances).

- Wear the gloves when working in lab.
- If the skin burns with acid, wash it with ammonium hydroxide, while in case of concentrated H_2SO_4, wash the affected part with Barium chloride solution and then with cold water and apply burnol.
- If the skin burns due to the concentrated/strong alkali (base), wash it with acetic acid and finally with cold water and apply burnol. If the injury is deep then immediately contact with the health consultant/doctor.

13.4.2 Heat burns

Burners and other heating devices are frequently used in laboratories to expedite chemical reactions and processes. As with any activity that involves fire, it is important to be aware of the potential risks associated with heat-related injuries. If exposed to temperatures higher than 70°C, a burn will likely occur, even if the skin is only exposed for a split second.

It is essential to maintain a safe distance away from open flames and heating devices in order to reduce the likelihood of heat-related burn injuries in the laboratory.

- Skin clothing and protective equipment should be kept away from any other combustible materials in the vicinity. Furthermore, it is imperative to ensure that burners are not left on after use.
- If a heat-related burn occurs while in the laboratory, it is recommended to immediately put the affected area in cold running water and hold it for a few minutes before allowing the burning sensation to subside. After that apply coconut oil or burnol on the burnt part.

(The heat generated by Bunsen burners can create a range of serious physical hazards for laboratory learner who are using the equipment)

13.4.3 Eye injuries

In the laboratory at the time of working, you need to be aware of the chemicals that can be harmful to your eyes. You can be exposed to chemicals if you accidentally release liquids or gases that can damage your eyes. The severity of your injury depends on hazardus properties of chemical are and how much you have been exposed to it. For instance, if you get a mild eye injury from exposure to a chemical, it could just cause redness and irritation. But if you get a really bad eye injury, it could lead to permanent blindness. To prevent eye injuries in the lab, you need to wear the right protective eyewear.

- If the eyes injuries occur due to the some pungent vapours in the eye first go away from the working place (lab) in the open place and wash your eye with cold water. If still eatvhing persists consult an eye doctor immediately.
- If chemical solution or dust particle enter into eye thenwash your eye with cold water untill you feel relief.
- If acid has been entered into eye then eye must be washed with a dilute solution of alkali sodium bicarbonate solution few timesand after that with cold water till you feel relief. an eye doctor
- If base/alkali has been entered into eye then eye must be washed with dilute boric acid solution and finally washed with cold water till irritation persists. If still problem exist immediately consult an eye doctor.

13.4.4 Injury from glassware

The use of laboratory glassware for the storage and mixing of hazardous chemicals is a common practice; however, there is a risk of laboratory glassware breaking. If the glass is broken, it can expose sharp edges, particularly if it is very thin, which can cause severe eye and skin damage. Therefore, it is important to take steps to reduce the risk of glass breaking in laboratories.

- In order to prevent cuts from glassware, it is important to handle the glassware with caution. It is recommended to hold the glassware in a secure grip and to avoid handling the glassware with wet or wet hands.

- It is important to ensure that when glassware is not in use, it is stored in a safe and secure place where there is no potential for it to fall and shatter. If glassware is not stored in an accessible cupboard with a well-maintained and even surface, it is likely to fall and break, potentially exposing to physical injury.
- If the is due to the breakage of some glassware, glass apparatus, wound washed with sprit and then aqueous alum solution because alum is antiseptic in nature and can also help in stop bleeding by coagulation.
- It is essential to take prompt action in the case of a glass cut in order to avoid the development of an infection. If a cut is sustained from glassware, the first aid officer/doctor should be contacted so that they will dress the wound.

13.4.5 Inhaling dangerous gases

A wide variety of hazardous chemicals emit toxic vapors and gases that pose a risk to human life. The health consequences associated with exposure to these hazardous vapors can be classified as acute, chronic, or both. Acute consequences are those that occur immediately after exposure to the vapors. Chronic consequences are those that do not occur immediately but occur months and even years after exposure. Heath effects of gas inhalation can include symptoms such as:

Irritation to mucous membranes in the nose, throat, respiratory tract; Headache; Vomiting; Coughing; Burning; Difficulty in breathing etc.

- If you feel any symptoms occurs due to the inhalation of gaes first go away from the working place (lab) in the open place. If still feel some problems consult with doctor immediately.

13.5 LABORATORY SAFETY

In the laboratory following safety will be taken while working in the lab.

(i) Laboratory hygiene
(ii) Fire safety
(iii)Chemical safety
(iv)Personal safety

(i) Laboratory hygiene

- Scrub hands thoroughly when finished.

- Avoid cross contamination
- Do not touch self, faucets, doorknobs, notebooks, pens etc. with gloves on.
- Keep a pen or two in your drawer for lab use only.
- Clean and disinfect your workspace

(ii) Fire safety

- Never leave flames unattended.
- Do not use flammables near ignition sources.
- Fire Extinguishers
- Fire Blanket
- Fire alarm pulls

(iii) Chemical Safety

- Wear gloves and glasses where appropriate.
- Follow instructor's directions.
- Dispose of waste properly-Do Not pour down the drain.

(iv) Personal Safety

- Lab coat to be worn all the time.
- Safety goggles must be worn all the time while working in the lab.
- Wear sensible clothing and Wear shoes.
- Appropriate gloves while handling chemicals.
- Working of alone student is not allowed

13.6 ASSESS AND MINIMIZE THE RISK OF THE HAZARDS

When you are working in a chemical lab, there is a risk associated with every chemical and glassware you use. Once you have evaluated the risks, your next step is to consider how you can reduce exposures. There are following step to assess and minimize the risk of hazards in the laboratory.

13.6.1 Before an experiment

This is likely the most significant steps you can take to reduce the risk in any laboratory environment. While incidents can occur even in the well-prepared environment, meticulous attention to detail can reduce the risk.

I. Know what you are working with. It is important to always recognize the substance that is being used and to consider how to reduce the exposure to that substance during

the experiment. For example, sodium hydroxide is commonly known as lye or caustic soda. If you are unsure, look for the Chemical.

II. Ensure that the proper concentrations are prepared. In laboratory should not routinely work with basic (NaOH) or acidic (HCl) solutions at concentrations greater than 1 M.

III. Ensure that all chemical bottles are properly labeled. For example sodium hydroxide, the bottle should have the chemical name ("sodium hydroxide") spelled out, not just the formula ("NaOH"), and the concentration of the solution should also be listed.

- The signal words "Danger", "Warning", and "Caution" are used to describe the level of the hazard.
- Words such as "Caustic", "Corrosive", and "Flammable" are used to describe specific hazards.

IV. Write down all the chemicals you are going to use and how much you will need for the experiment.

V. Consider the physical arrangement and the facilities available in your laboratory.

13.6.2 During an experiment

Learners must be monitored consistently in the laboratory. The teacher must be physically present in the duration of the experiment, focusing on the students.

I. Use the lowest concentrations and smallest volumes possible for all chemicals. Do not allow learners to handle solids that are classified as fatal or toxic if swallowed.

II. Wear appropriate eye protection that offers both impact and splash protection. This is not only for your safety but also as a precaution in the event that an accident is caused by someone else in the laboratory.

III. Wear appropriate protective clothing (laboratory apron, coat, and gloves).

IV. Long hair must be pulled back, and clothing must be tucked in.

V. After transferring a chemical (solid or liquid) from a reagent bottle into a secondary container, be certain that the reagent bottle and the container are properly closed.

VI. Students should take only the amount required of each reagent. If there is excess, it must be disposed of properly and not returned to the reagent container.

VII. No mixing of chemicals should be allowed, other than that specified in an experimental procedure.

13.6.3 What if an emergency occurs?

I. If the chemical is in the eye: Flush water using an eyewash station for at least 15 minutes. Medical attention must be summoned as soon as possible.

II. If the chemical is swallowed or ingested: Do not induce vomiting unless the SDS recommends vomiting. Medical attention must be summoned as soon as possible.

III. If the chemical comes into contact with skin: Rinse the affected area for 15 minutes with tap water. It may be necessary to use a safety shower. If the safety shower is used, all contaminated clothing should be removed while the person is under the safety shower, and medical attention must be summoned as soon as possible.

13.6.4 After an experiment

I. Return any chemicals (excess reagent, product, or waste) to the appropriate location, or dispose of them as instructed.

II. Clean any used glassware and return the items to the appropriate location.

III. Ensure that all chemicals are properly stored. Make sure that the caps on the reagent bottles are tightly secured.

IV. Ensure that benches are clean before the next class comes in. One of the major causes of accidents is carelessness on the part of someone else.

V. All gas outlets are closed; especially burners were used during the experiment.

13.7 SUMMARY

- Keep tabletops clean. Return all equipment to its original location before leaving the lab.
- Report all accidents, no matter how minor, to the instructor. If you break something made of glass, be sure to use dustpan and hand broom to sweep it up and dispose of it in the glass waste receptacle.
- In case of an emergency where we have to evacuate, proceed out the nearest exit.
- Both the door should remain open all the time while working in the lab.
- Never put anything in your mouth while in the lab (including chemicals, solutions, food and drink)
- All food and drinks should be restricted to sitting area only.

13.8 BIBLIOGRAPHY

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UNIT 14: INORGANIC EXERCISE

CONTENTS:

14.1 INTRODUCTION

Gravimetric analysis is basically a quantitative analytical technique used to determine the amount of a particular substance in a sample based on its mass. This technique derives itself from the principle of stoichiometry, which establishes that in a chemical reaction, the amount of reactants consumed or products produced is directly proportional to their respective masses. This is done by precipitating the analyte (substance being analyzed) in a sample as a solid compound which is then separated, washed, dried and weighed. By finding out the stoichiometry of the chemical reaction which produced the precipitate, the amount of analyte present in the original sample can be calculated. Gravimetric analysis is widely employed in analytical chemistry, pharmaceutical analysis and environmental monitoring.

There are four different types of gravimetric analysis based on the method used in order to obtain and analyze the target ion. These are as follows

- Precipitation Method
- Volatilization Method
- Electrogravimetry Method
- Thermogravimetric Method

14.2 OBJECTIVES

Under this unit you will be able to understand:

- The analyte (the substance being measured) is typically converted into a stable, insoluble solid (precipitate).
- This precipitate is then isolated, purified, and weighed.
- The amount of the substance is determined based on the mass of the precipitate formed.

14.3 GRAVIMETRIC ANALYSIS

Gravimetric analysis is an analytical technique used for the quantitative determination of an analyte (substance of interest) based on the mass of solid. The element to be identified is precipitated from a solution using this method of analysis by the addition of a suitable precipitating agent. The precipitate should either have a known composition or, through heating, should be changed into another pure compound with a known composition.

For example, to determine the sulphate ions (SO_4^{2-}) contained in ammonium sulphate $(NH_4)_2SO_4$ solution, the solution is trated with barium chloride ($BaCl_2$) first. When all sulphate ions have precipitated as barium sulohate ($BaSO_4$), the precipitate of barium sulohate is filtered, washed, dried, ignited, and finally weighed. By knowing the weight of the precipitate, $BaSO_4$, the amount of sulphate ion present in the given volume of ammonium sulphate can be determined using a suitable stiochiometric relationship.

Principle of Gravimetric analysis :

Gravimetric Analysis is based on the principle the mass of the ion present in the pure compound can be determined by estimating the mass percentage of the same ion in the known quantity of an impure compound.

Steps involved in Gravimetric analysis : The process typically involves the following steps:

1.**Precipitation of solutions** : The specified sample was weighed in a watch glass and transferred to a beaker. If the salt sample is water soluble, it is dissolved in water to produce a sample solution. Salts that are insoluble in water dissolve in dilute acids. More water may be added to provide the appropriate volume of the solution once the sample has completely dissolved.

2. Precipitation: The sample solution is warmed before the appropriate precipitant is slowly added in slight excess while the solution is constantly stirred. The precipitate-containing solution is then warmed and allowed to stand for some time. The precipitate is allowed to settle. The supernatant liquid is checked with a few drops of precipitant to ensure complete precipitation.

3. Filtration: The precipitate is filtered out of the solution to separate it from the liquid.

4. Washing: The precipitate is washed to remove impurities that could affect its mass.

5. Drying: A piece of paper is crumpled and placed over the funnel's rim to cover the funnel containing the purified precipitate. The funnel containing the precipitate is then allowed to dried by hot air oven and remove residual the moisture.

6. **Ignition:**When the filter paper containing the precipitate has completely dried, it is taken from the funnel and folded to completely enclose the precipitate. The packet is then placed in the weighted crucible, which is held in place by the clay pipe triangular tripod stand. The crucible is slowly heated at first. The flame is intensified to carbonize the paper once the moisture has been entirely removed. When the paper is completely carbonized, the crucible is completely heated.

The crucible is covered with a lid once all of the carbon has been removed. It usually takes 50-60 minutes to complete the ignition.

7.Heating to constant weight: Once the ignition is complete, the flame is removed, and the crucible is put in the desiccators, where it is allowed to cool for 15 to 30 minutes. The crucible and lid are then both weighed. Thereafter, the crucible substance is re-ignited for roughly 10 minutes, allowed to cool in desiccators as previously, and weighed once again. This lighting and the weighing procedure is continued until a constant weight is achieved.

Weight of precipitate = Weight of crucible content along with lid – Weight of crucible with lid

a)Weight the sample to be analysed **b) Dissolving this sample in water** **c) Adding a suitable chemicals to form a preciptate** **d) Filtering to collect the precipitate** **e) Repeated drying and weighing until a constant mass of precipitate is obtained**

Steps follows in gravimetric analysis

14.4 EXERCISE 1: ESTIMATION OF BARIUM *ESTIMATION OF BARIUM FROM BARIUM SULPHATE GRAVIMETRICALLY*

OBJECTIVES: The objectives of this laboratory are:

- To experimentally analyze an unknown sulfate salt via a precipitation reaction, using the techniques associated with Gravimetric analysis to collect and weight the precipitate.
- To calculate the percentage by mass of SO_4^{-2} in the unknown sulfate salt via a stoichimetric analysis of the collected precipitate, and then use this percentage to identify the metal present in the sulfate salt.

Theory: In this experiment , the percentage by mass of sulfate in an unknown sulfate salt will be determined by gravimetric analysis. First , pre – weight sample of unkown sulfate salt will be dissolved in water. Next , an excess of aqueous barium chloride is added to the aqueous solution of the unkown salt. This will result in the precipitation of all the sulfate ions as barium sulfate:

Metal sulphate (aq) + $BaCl_2$ (aq) ⟶ $BsSO_4$(s) + Metal chloride (aq)

The barium sulfate pracipitate is collected by filtration , dried and weighted. Since $BaCl_2$ added in excess, and since the pracipitation reaction goes to completion , and it is assume that all of the sulfate is transferred from the original unknown sample to the pracipitate.The mass sulfate in the collected $BaSO_4$ precipitate can be calculated via its percent composition.This also yield the mass of sulfate in the original unkown since:

Mass od sulfate in the pracipitate = mass of sulfate in the unkown sample

Finally , using the mass of sulfate along with the initial mass of unkown used, the percentage by mass of sulfate in the original sample may now be calculated.

Apparatus and Reagents:

A) Apparatus: Beaker, Analytical balance, stirring rod, 100ml graduated cylinder, Bunsen burner, Wash bottle with distilled water, Crucible and Crucible tongs, Tripod, Funnel and flask**,** Filter paper.

B) Reagents: 6 M HCl solution, 0.1 M $BaCl_2$ solution **,**0.1 M HNO_3

Procedure:

1. The given barium chloride solution is made up to 100ml in a standard flask.
2. In a 250 ml beaker,20 ml of the solution is pipette.
3. About 5ml 2N HCl is added and diluted to 150 ml with distilled water.
4. The solution is heated to boiled and a hot solution of 4N H_2SO_4 (10-15 ml) is added drop by drop with constant stirring, till the precipitation is complete.
5. Digest the precipitated $BaSO_4$, below the boiling point for 1 to 2 hours.
6. Filter the solution while its hot through a filter paper.
7. Wash the precipitate remaining in the beaker into the filter with hot distilled water until the beaker is clean.
8. Continue washing until afresh portion of the filtrate yield no precipitate of silver chloride when acidified with nitric acid and treated with few drops of silver nitate solution.

9. Loosen the filter paper in the funnel and allow to drain for few minutes.
10. Place the filter paper in a porcelain crucible that has already been ignited to constant weight.
11. Place the crucible on a triangle on a tripod.
12. Heat the crucible gently with a small flame while continuously changing the point of heating until the moisture had been evaporated and the paper beings to smoke and char.
13. Transfer it into desicator, and let it cool there for 30 minutes before weighing.
14. Continue ignition at high temperature (800^0C) to a constant weight. Cool it in the desiccators and reweigh.
15. Report the result of analysis as weight of sulfate in the sample.

Calculation: Weight of empty crucible = ……X…….gm

Weight of crucible + weight of $BaSO_4$ = ……Y……gm

Weight of $BaSO_4$ = Y - X = Z gm

$$\text{Weight of Barium} = \frac{Atomoc\ weight\ of\ Ba}{Molecular\ weight\ of\ BaSo4} \text{ x weight of } BaSO_4 \text{ precipitate}$$

$$= \frac{137}{233.43} \text{ x } Z \text{ (gm)}$$

Precautions:

1. Precipitation is carried out in dilute solution and in hot condition.
2. Ash treatment is done when crucible is cool.
3. Dilute HCl must be added before precipitation.

14.5 EXERCISE 2: ESTIMATION OF IRON ESTIMATION IRON AS FERRIC OXIDE IN A SOLUTION OF FERROUS SULPHATE / FERROUS AMMONIUM SULPHATE

Introduction: The gravimetric analysis can be used to determine the percent weight of iron Fe in an iron sample. A sample containing iron ions of ferric oxidation state, then a hydrated ferric oxide is precipitated from solution by adding ammonia used as precipitating reagent and finally dehydrated by ignition to produce Fe_2O_3.

Precipitation of ferric hydroxide is a gelatinous state in hot solution, so we heated solutions to avoid colloid solution. All ferrous ion must be oxidized to ferric form by using one of the strong oxidizing agents like Br_2 water, H_2O_2 or con. HNO_3.The original solution must be free from other ions, which are precipitated as hydroxides along with iron hydroxide, and also free from oxalate, arsenate, and phosphate which from insoluble salts of iron in alkaline medium.

The precipitation on heating at about 1000^0C changes to Fe_2O_3. The reactions in the process as follows:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$Fe_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Fe(OH)3.xH2O + 3(NH_4)_2SO_4$$

$$Fe_2O_3 .xH_2O \xrightarrow{\text{at about / } 1000^0\text{C}} Fe_2O_3 + xH_2O$$

Materials Required: dilute HCl and Con HNO_3 (1: 1), dil ammonia solution, NH_4NO_3 1% solution, watch glass, beaker, ashless filter paper and balance.

Procedure:

1. Add equal volume of distilled water to the supplies solution of ferrous salt and heat to boiling.
2. Dissolved sample with distilled water, then add 1 ml of con HNO_3 and boil gently.
3. Heat the solution gradually for a few minutes to ensure that all Fe (II) is oxidized to Fe (III) and solution become clean yellow.
4. Dilute the sample by distilled waterthen heating the solution until boil after that of ammonia solution adding slowly with stirring until the distinct smell of ammonia.
5. Boil the solution, then leave it to room temperature for digestion, the precipitate will settle and solution must be colorless.
6. Filtrate the solution slowly using ashless filter paper then washing the precipitate with solution of hot NH_4NO_3 (1-2%), until Cl^- ion will be removed from the precipitate.
7. Dry and ignite the filter paper keeping the precipitate inside, without inflaming it. Remove the carbon at very low temperature with free approach of air in the crucible.
8. Weight crucibles after heating for 15 minutes to redness and cooled and weight to room temperature.Repeat this process until two successive weighings are constant.

Calculations :

Fe_2O_3 = $2FeSO_4$ = $2[FeSO_4(NH_4)2SO_4.6H_2O]$ = 2Fe

159.68 2 x 392.16 11.68

Conversion factor $= \frac{2Fe}{Fe2O3} = \frac{111.68}{159.68} = 0.6994$

Weight of iron in the supplied volume of solution = 0.6994 x wt. of ppt.

14.6 EXERCISE 3: ESTIMATION OF ZINC ESTIMATION OF ZINC AS ZINC OXIDE FROM THE ZINC CHLORIDE OR ZINC SULPHATE SOLUTION

Introduction: Zinc is precipitated as basic carbonate having no definite composition and changes to zinc oxide on ignition. The condition of precipitation is to add hot dil. Na_2CO_3 solution drop by drop to boiling solution of zinc salt until there is slight turbidity then boil and add few drops of phenolphthalein following by show addition of hot Na_2CO_3 solution until slight pink colour is obtained.

Materials Required: dilute Na_2CO_3 solution, phenolphthalein, watch glass, beaker, ashless filter paper and balance.

Procedure:

1. Boil the given solution ($ZnCl_2$ / $ZnSO_4$) with an equal amount of distilled water.
2. Pour in some hot dil. 10% Na2CO3 solution, drop by drop, stirred continuously until a minor turbidity develops.
3. After the mixture has boiled, add a few drops of phenolphthalein. Add hotter Na2CO3 solution now, stirring constantly, until a pink hue is obtained and boil the content again and allow the precipitate to settled.
4. Use decantation to filter the clear liquid through filter paper, then purify the precipitate by decanting it with hot water until it is ion-free (CO_3^{-2} ions, Cl^- ions). Next, move all of the precipitate onto filter paper and let it dry.

5. Transfer as much of the precipitate as you can onto glazed paper after it has dried, then cover it with a funnel or watch glass. After soaking the filter paper in an NH_4NO_3 saturated solution, and dry it.
6. Ignite the filter paper in a weighed crucible at low temperature. Cool the crucible and then transfer the precipitate.
7. Weight crucibles after heating for 15 minutes to redness and cooled and weight to room temperature and $ZnCO_3$ is converted to ZnO.
8. Repeat the process of heating, cooling and weighing until a constant weight is obtained.

Calculation:

	ZnO	=	Zn
	81.38		65.38

Conversion factor $= \frac{Zn}{ZnO} = \frac{65.38}{81.38} = 0.8034$

Weight of zinc in the given volume of solution = 0.8034 x Wt. of ZnO

14.7 SUMMARY

1. In this unit you will be learn the analytical techniques such a estimation metal ions such as Ba^{2+}, Fe^{3+}, , Zn^{2+}, etc.
2. In gravimetric analysis, offering high accuracy and versatility for the quantitative determination of substances.

14.8 REFERENCES AND FURTHER STUDIES

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5. vlab.amrita.edu › indexGravimetric Estimation of Barium (Theory) : Inorganic ...

UNIT 15: ORGANIC EXERCISE

CONTENTS:

15.1 INTRODUCTION:

The separation, extraction, and identification of organic compounds and natural products form a fundamental part of practical organic chemistry. Many organic substances occur in mixtures, and understanding their chemical behaviour is essential for their proper isolation and analysis. In this chapter, experiments are designed to develop skills in separating binary mixtures of organic compounds and extracting naturally occurring substances such as caffeine and casein.

15.2 OBJECTIVES:

- To understand the fundamental principles involved in the separation of binary mixtures of organic compounds.
- To learn the use of chemical reagents such as sodium bicarbonate for selective extraction based on acidity or basicity of organic substances.
- To develop skills in handling separating funnels, performing liquid–liquid extraction, and recovering pure compounds.
- To study the extraction of natural products such as caffeine and casein from common natural sources.
- To familiarize students with techniques such as solvent extraction, precipitation, filtration, drying, and recrystallization.

15.3 BINARY MIXTURE

A binary mixture is a combination of two different components (substances) that are mixed together but not chemically bonded. These components can be solids, liquids, or gases, andthey may be miscible (completely mix) or immiscible (do not mix completely).

15.4 EXPERIMENT-1

AIM - To analyse and separate a given binary mixture of organic compounds using chemical separation techniques and identify the individual components.

Principle -A binary mixture containing acidic, basic or neutral organic components can be separated by exploiting their differential solubility in aqueous and organic phases. Organic

acids such as benzoic acid, salicylic acid etc. react with aqueous sodium bicarbonate ($NaHCO_3$) to form their sodium salts, which are water-soluble. Neutral organic compounds remain insoluble in $NaHCO_3$ solution and can be recovered separately.

Chemicals Required

- Given binary organic mixture
- Sodium bicarbonate solution ($NaHCO_3$)
- Dilute hydrochloric acid (HCl)
- Organic solvent (ether/chloroform)

Essential glassware

- Beakers: 50 mL, 100 mL and 250 mL (for stirring the mixture with $NaHCO_3$, collecting filtrates, acidification, etc.).
- Conical (Erlenmeyer) flasks: 100–250 mL (for collecting filtrates, re-crystallisation).
- Test tubes and test-tube holder (for preliminary $NaHCO_3$ test and small-scale trials).
- Glass rods (for stirring, crushing lumps, aiding crystallisation).
- Funnels: ordinary glass funnels for gravity filtration; optionally a Buchner funnel with suction flask for faster filtration and drying.
- Measuring cylinder (10–25 mL) or pipettes for measuring $NaHCO_3$ solution, HCl, etc.
- Watch glasses or porcelain evaporating dishes for drying and observing crystals.

For liquid–liquid extraction

- Separatory funnel (100–250 mL) with stopper and ring stand plus clamp, if the mixture is handled in an organic solvent and separated by liquid–liquid extraction.
- Filter paper, weighing paper or butter paper for drying separated solids and recording weights.
- Heating, drying and support
- Bunsen burner or hot plate with wire gauze for gentle heating during re-crystallisation.

- Tripod stand, iron stand with clamp and rings for supporting funnels, separatory funnel and flasks.
- Desiccator (if available) for final drying of separated components before melting-point determination.

Procedure

1. Dissolve the given mixture in an organic solvent.
2. Treat the solution with aqueous $NaHCO_3$ and shake.
3. The acidic component dissolves as its sodium salt in the aqueous layer.
4. Separate the aqueous layer using a separating funnel.
5. Acidify the aqueous layer with dilute HCl to recover the acidic compound as a precipitate; filter and dry.
6. The neutral component remains in the organic layer; separate the layer and evaporate the solvent to obtain the neutral compound.
7. Perform confirmatory tests and record the melting points of both compounds.
8. Identify each component based on chemical tests and melting point.

Reaction of Organic Acid with Sodium Bicarbonate ($NaHCO_3$)

Principle and chemistry

- Sodium bicarbonate is a mild base that deprotonates carboxylic acids but not most phenols, alcohols or many neutral compounds; thus it can selectively extract carboxylic acids from a mixture.

$$R\text{-}COOH + NaHCO_3 \rightarrow RCOO^- Na^+ + H_2O + CO_2 \uparrow$$

(Effervescence of CO_2 is observed)

This sodium salt is water soluble and moves into the aqueous layer.

- On acidification of the bicarbonate extract with conc. or dilute HCl, the acid is regenerated:

$$R\text{-}COO^-Na^+ + HCl \rightarrow RCOOH + NaCl$$

Class of compound Typical	**Example**	**Behaviour with saturated $NaHCO_3$**	**Key reaction (qualitative)**
Carboxylic acid	Benzoic acid	Dissolves with effervescence; forms water-soluble sodium	$R\text{-}COOH + NaHCO_3 \rightarrow RCOO^- Na^+ + H_2O + CO_2 \uparrow$

		carboxylate; recovered by acidification	
Phenol (weaker acid)	Phenol, cresol	Generally does not react with $NaHCO_3$; remains insoluble; later dissolves in NaOH	No CO_2 ; Ar–OH unreactive toward $NaHCO_3$
Neutral compound	Naphthalene, benzoin	Insoluble; no reaction	No ionic product; remains as separate phase
Organic base (amine)	Aniline	No reaction with $NaHCO_3$; extracted by mineral acid instead	Protonated by HCl, not by $NaHCO_3$

Key safety and observation points:

- Always add $NaHCO_3$ to acidic mixtures slowly and vent separatory funnels frequently to avoid pressure buildup due to CO_2.
- Label all layers and filtrates carefully to avoid mixing up components.
- Dispose of acidic/basic aqueous waste only after neutralising (e.g. neutralise excess base with acetic acid, excess acid with sodium carbonate) and then diluting with plenty of water.

Result

The binary mixture was successfully separated into its components (___ and ___) using $NaHCO_3$ extraction and identified by chemical tests and melting point analysis.

15.5 SUMMARY

This unit focuses on the separation, extraction, and identification of organic compounds, especially those present in binary mixtures. It emphasises the importance of understanding the chemical behaviour of organic substances to isolate them effectively.

The experiment described in the unit trains students in using liquid–liquid extraction techniques to separate mixtures containing acidic, basic, or neutral organic compounds. The method mainly relies on differences in solubility and reactivity in aqueous and organic solvents.

A key principle demonstrated is the reaction of carboxylic acids with sodium bicarbonate ($NaHCO_3$), producing water-soluble sodium salts with effervescence of CO_2, while neutral compounds remain in the organic layer. The acidic compound is later recovered by

acidification with HCl, and the neutral compound is obtained by evaporating the organic solvent.

Students also learn safe laboratory handling, use of the separating funnel, filtration, drying, recrystallisation, melting-point determination, and interpretation of chemical tests to identify the separated components. The unit strengthens practical competence in organic qualitative analysis and natural-product extraction techniques.

15.6 TERMINAL QUESTIONS

1. Define a binary mixture. Give two examples from organic chemistry.
2. Explain the principle of separation of acidic and neutral organic compounds using $NaHCO_3$ extraction.
3. Write and explain the reaction of benzoic acid with sodium bicarbonate. Why is effervescence observed?
4. Why do neutral organic compounds remain in the organic layer during bicarbonate extraction?
5. Describe the steps involved in separating a binary mixture using a separating funnel.
6. How is the acidic component recovered from the bicarbonate extract?
7. Distinguish between the behaviour of carboxylic acids and phenols toward $NaHCO_3$.
8. State the precautions and safety measures to be followed during liquid–liquid extraction.
9. What is the role of melting-point determination in identifying organic compounds?
10. Discuss how the method would differ for a mixture containing an amine (organic base).

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UNIT 16 : NATURAL PRODUCT EXTRACTION

CONTENTS:

16.1 INTRODUCTION

Caffeine, a methylxanthine alkaloid found in tea leaves, coffee beans, and other plants, acts as a central nervous system stimulant and can be isolated through sequential solid-liquid and liquid-liquid extractions exploiting its solubility properties in hot water and organic solvents, followed by purification to remove tannins and pigments. Similarly, casein, the dominant phosphoprotein in milk forming colloidal calcium caseinate micelles, is extracted by isoelectric precipitation upon acidification to pH 4.6, yielding a curd that demonstrates protein isolation from a natural biological matrix. These experiments illustrate fundamental extraction techniques for natural products solvent-based for small-molecule alkaloids and pH-based for proteins enabling their purification and identification via physical constants and qualitative tests in an undergraduate organic/biochemistry laboratory setting.

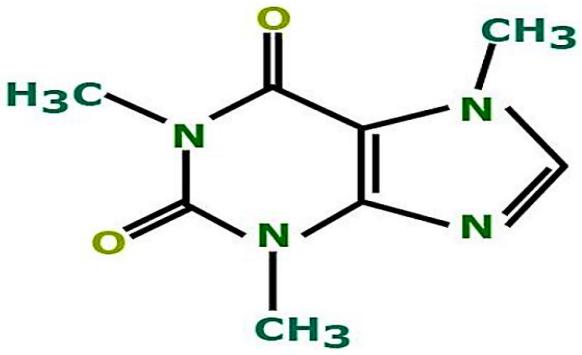
16.2 OBJECTIVE

- To extract crude caffeine from tea leaves or coffee via hot aqueous extraction, purify it by liquid-liquid partitioning into an organic solvent, and confirm identity by melting point determination and yield calculation.
- To isolate casein from milk by isoelectric precipitation with acid, separate and dry the curd, and verify its protein nature through solubility tests and qualitative reactions.
- To compare extraction yields from natural sources with literature values and understand the chemical principles governing solubility, acid-base behaviour, and precipitation in natural product isolation.
- To develop practical skills in filtration, solvent evaporation, recrystallisation, and basic characterisation techniques applicable to both small molecules and biopolymers

16.3 EXTRACTION AND IDENTIFICATION OF CAFFEINE

Aim -To extract and identify caffeine from natural sources (tea leaves or coffee powder) using solvent extraction techniques.

Principle- Caffeine, an alkaloid, is moderately soluble in hot water and highly soluble in organic solvents like chloroform. It can be extracted by boiling the plant material, followed by liquid–liquid extraction and purification.



Structure of Caffeine

Chemicals Required

- Tea leaves or coffee powder
- Calcium carbonate ($CaCO_3$)
- Chloroform
- Sodium sulfate (drying agent)

Procedure

1. Boil the tea leaves with water and a small quantity of $CaCO_3$ to release caffeine from tannin complexes.
2. Filter the decoction and cool it.
3. Transfer the filtrate to a separating funnel and extract with chloroform.
4. Combine the chloroform layers and dry them using anhydrous sodium sulfate.
5. Evaporate chloroform to obtain crude caffeine.
6. Recrystallise the residue from hot ethanol/water mixture.
7. Determine the melting point to confirm the presence of caffeine.

Result

Caffeine was successfully extracted from tea leaves, purified, and identified by its characteristic melting point.

16.4 EXTRACTION OF CASEIN FROM MILK

Aim -To extract and identify casein, a major milk protein.

Principle- Casein precipitates from milk when its pH is lowered to about 4.6 by adding a weak acid such as acetic acid. The precipitated protein can be filtered, washed and dried.

Introduction- Milk is a complex mixture of water, proteins, fats, carbohydrates, and minerals. The primary protein in milk is casein, which accounts for approximately 80% of the total protein content. Casein is essential for the nutritional value of milk and plays an important role in cheese-making.

Casein exists in milk as a colloidal suspension of casein micelles. These micelles are stable at the natural pH of milk (approximately pH 6.6) due to the presence of κ-casein on their surface, which provides both steric and electrostatic stabilisation. When the pH is lowered to the casein's isoelectric point (approximately pH 4.6), these micelles become destabilised, leading to the precipitation of casein from the solution.

In this experiment, we will use acetic acid to lower the pH of milk, causing the casein to precipitate at its isoelectric point. We will then isolate and analyse the precipitated casein.

Chemical Equations: While there isn't a specific chemical reaction occurring, the process can be represented as:

Casein (soluble) + H^+ → Casein (insoluble precipitate)

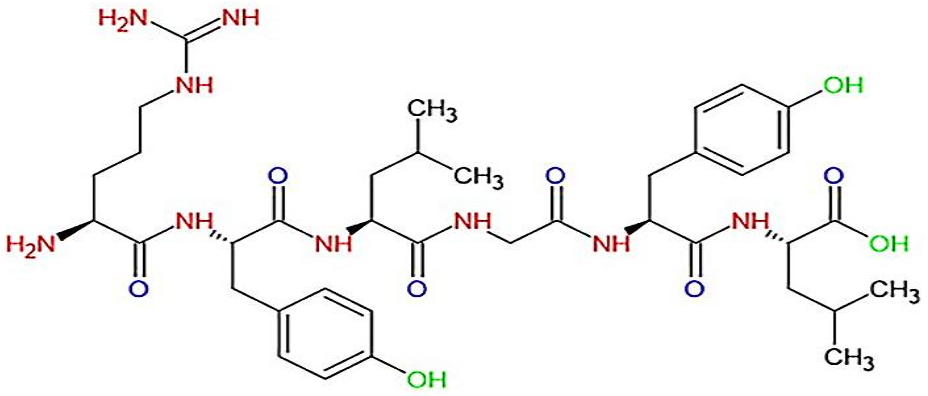
The acetic acid provides the H^+ ion $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Chemicals Required

- Skim milk (500 mL)
- Dilute acetic acid (5% , 50 mL)
- Distilled water
- 0.1 M NaOH solution (for pH adjustment if needed)

Procedure

1. Warm 100 mL milk to about 40–50°C.
2. Add dilute acetic acid dropwise with constant stirring until casein precipitates.
3. Allow the mixture to stand for 10 minutes.
4. Filter the precipitated casein and wash it with cold water to remove lactose and whey proteins.
5. Press between filter papers and dry the product.
6. Perform simple identification tests for proteins (e.g., Biuret test).



Structure of Casein

Result

Casein was successfully extracted from milk by acidic precipitation and identified by protein tests.

16.5 SUMMARY

This unit focuses on the extraction and identification of natural products from biological sources using fundamental laboratory techniques. Two important examples are studied caffeine, a small-molecule alkaloid, and casein, a major milk protein. Caffeine is isolated from tea leaves or coffee through hot aqueous extraction, followed by liquid–liquid extraction with an organic solvent such as chloroform. Calcium carbonate is added to break caffeine–tannin complexes, and the organic layer is dried, evaporated, and the product purified by recrystallisation. The identity of caffeine is confirmed using melting-point determination and yield analysis. This experiment demonstrates how solubility differences and partitioning enable purification of organic alkaloids.

Casein is extracted from milk using isoelectric precipitation. When the pH is lowered to about 4.6 using acetic acid, the colloidal casein micelles destabilize and precipitate out. The protein is filtered, washed to remove soluble components, dried, and confirmed through qualitative protein tests such as the Biuret test. This procedure illustrates a pH-based separation technique for biomolecules and highlights principles of protein solubility and micellar structure.

Together, these experiments develop student skills in filtration, extraction, solvent evaporation, recrystallisation, drying, and characterization techniques, linking theory of acid–base behaviour, solubility, and precipitation with practical laboratory experience.

16.6 TERMINAL QUESTIONS

1. What is the principle behind the extraction of caffeine from tea leaves or coffee powder?
2. Why is calcium carbonate added during the extraction of caffeine?
3. Describe the role of liquid–liquid extraction in the purification of caffeine.
4. How is the identity of the extracted caffeine confirmed experimentally?
5. Define the isoelectric point of a protein. Why does casein precipitate at pH 4.6?
6. Explain the structural nature of casein micelles in milk.
7. Write the ionic dissociation equation of acetic acid used in casein precipitation.
8. Why are the precipitated casein curds washed with cold water before drying?
9. What is the purpose of performing a Biuret test on the extracted casein?
10. Compare the extraction of caffeine and casein in terms of principle, technique, and type of molecule isolated.

16.7 REFERENCES

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UNIT 17: ANALYSIS OF ORGANIC COMPOUNDS BY SPECTROSCOPIC TECHNIQUES

CONTENTS:

17.1 INTRODUCTION

Spectroscopic techniques are among the most powerful and reliable tools for analysing and identifying organic compounds. They are based on the interaction of electromagnetic radiation with matter, which provides valuable information about molecular structure, bonding, and functional groups. In this unit, emphasis is placed on the use of ultraviolet (UV) and infrared (IR) spectroscopy for determining the functional groups in organic molecules. These techniques are widely used in chemical laboratories because they are rapid, non-destructive, and require only small amounts of sample.

The unit also focuses on the systematic analysis of common classes of organic compounds, such as alcohols, phenols, carboxylic acids, carbonyl compounds, and nitrogen-containing compounds. By interpreting characteristic absorption bands and spectral features, it becomes possible to identify functional groups and gain insight into the overall structure of organic molecules.

17.2 OBJECTIVES

After studying this unit, the learner should be able to:

- Understand the basic principles of UV and IR spectroscopy,
- Explain the role of spectroscopic techniques in the analysis of organic compounds,
- Identify functional groups using characteristic UV and IR absorption patterns,
- Interpret IR spectra for common organic functional groups,
- Analyse organic compounds such as alcohols, phenols, carboxylic acids, carbonyl compounds, and nitrogen-containing compounds using spectroscopic data, and
- Apply spectroscopic information for the qualitative identification of unknown organic compounds.

17.3 UV–VISIBLE AND INFRARED (IR) SPECTROSCOPY

Spectroscopy, particularly UV–Visible and Infrared (IR) spectroscopy, is an important analytical technique used to study the structure of organic compounds. These methods work by examining how molecules interact with electromagnetic radiation. Each functional group in an organic molecule absorbs radiation at specific wavelengths, producing characteristic

absorption patterns. By studying these patterns, functional groups such as alcohols, carbonyls, phenols, and nitrogen-containing groups can be identified.

Spectroscopic techniques are rapid, non-destructive, and highly reliable, making them essential tools in pharmaceutical analysis, quality control, and chemical research. This unit emphasises the interpretation of spectral data, such as IR absorption bands corresponding to O–H or C=O groups, to determine molecular structure. Through these techniques, chemists can distinguish between different classes of organic compounds and identify unknown substances.

Key Concepts and Techniques

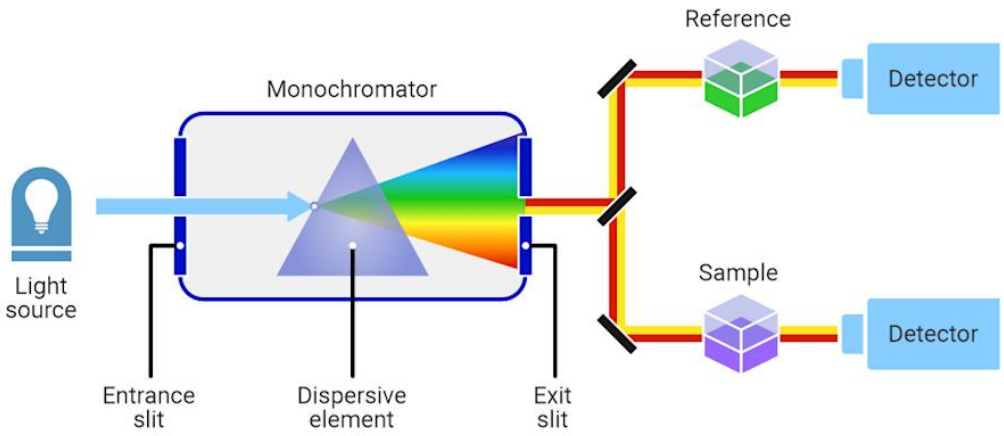
- Basic Principle of Spectroscopy involves the study of the interaction between electromagnetic radiation and matter to obtain information about molecular structure.
- UV–Visible Spectroscopy; UV–Vis spectroscopy is used to study electronic transitions in molecules. It is especially useful for compounds containing conjugated systems, aromatic rings, and chromophores.
- Infrared (IR) Spectroscopy: IR spectroscopy measures molecular vibrations such as stretching and bending. It is mainly used for identifying functional groups like O–H, C=O, and N–H.

Role of Spectroscopy in Functional Group Identification

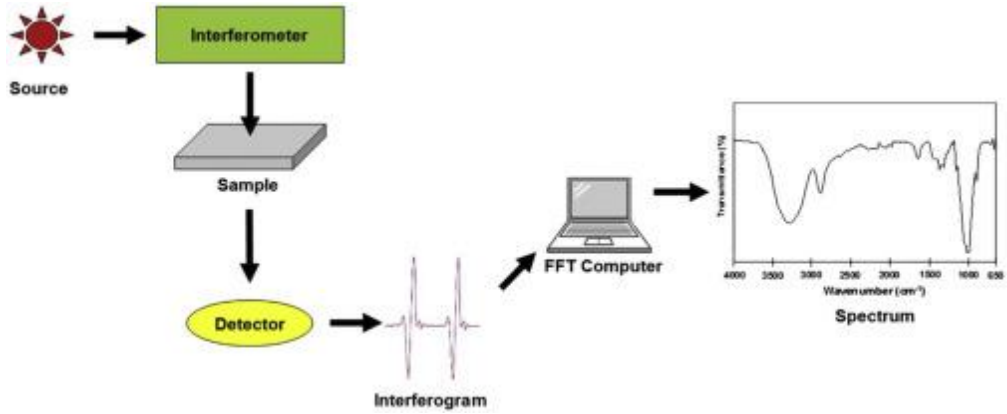
- IR Absorption Bands: Each functional group shows absorption at characteristic frequencies. For example, carbonyl groups show a strong absorption near 1700 cm^{-1}, while hydroxyl groups show a broad absorption around 3300 cm^{-1}.
- UV–Visible Absorption Features: UV–Vis spectra provide information about π-electron systems and help in identifying conjugation and aromaticity.

Common Organic Compounds Analysed and Their Spectral Features

- Alcohols and Phenols: Show O–H stretching vibrations in the IR region around 3200–3600 cm^{-1}. Phenols also show UV absorption due to aromatic rings.
- Carboxylic Acids: Exhibit a very broad O–H stretch in the IR region (2500–3300 cm^{-1}) along with a strong C=O absorption near 1700 cm^{-1}.
- Carbonyl Compounds (Aldehydes and Ketones): Characterised by a strong C=O stretching vibration in the IR region between 1650–1800 cm^{-1}.
- Nitrogen-Containing Compounds (Amines and Amides): Show N–H stretching vibrations around 3300–3500 cm^{-1} and characteristic C–N absorptions.



UV-Visible Spectrometer



FT-IR spectrophotometer

17.4 EXPERIMENT-1: FUNCTIONAL GROUP DETERMINATION OF ALCOHOL BY UV & IR SPECTROSCOPY

17.4.1 Aim

To identify and confirm the presence of the alcohol (–OH) functional group in the given organic compound using UV–Visible and Infrared (IR) Spectroscopy.

17.4.2 Apparatus / Instruments Used

UV–Visible Spectrophotometer, IR Spectrophotometer (FT-IR / ATR), Quartz cuvettes, KBr powder / ATR crystal, Solvent (ethanol or methanol), Pipette, spatula, tissue paper

17.4.3 Principle

UV–Visible Spectroscopy (for Alcohols)-

Alcohols generally show weak n → σ* transitions in the UV region (180–220 nm). Presence of strong conjugation is normally absent, so absorption is weak or negligible beyond 220 nm.

Infrared (IR) Spectroscopy (for Alcohols)

Alcohols show characteristic absorption bands:

- O–H stretching (broad) → 3200–3600 cm^{-1}
- C–H stretching (alkyl) → 2850–2950 cm^{-1}
- C–O stretching → 1000–1300 cm^{-1}

These peaks confirm the alcohol functional group.

17.4.4 Procedure

The given sample of the organic compound was first prepared in dilute form using a suitable solvent, and its UV spectrum was recorded in the range of 200–400 nm using a UV–Visible spectrophotometer. A blank solution of the solvent was run first for baseline correction, after which the sample solution was placed in a clean quartz cuvette and scanned to obtain the absorption curve. The wavelength of maximum absorption (λmax) and the nature of the band were noted for the interpretation of alcohol characteristics.

For IR analysis, a small quantity of the sample was taken and either applied directly to the ATR crystal or converted into a fine KBr pellet, depending on the sample's physical state. The spectrum was then recorded over the range of 4000–400 cm^{-1} using an FT-IR spectrophotometer. The major absorption peaks were carefully observed, particularly the broad O–H stretching band in the region 3200–3600 cm^{-1} and the C–O stretching band in the region 1000–1300 cm^{-1}. The recorded values were compared with standard reference data to confirm the presence of the alcohol (–OH) functional group in the given compound.

17.4.5 Observation Tables

Table–1: UV–Visible Spectroscopy Data (Alcohol)

S. No.	Wavelength (nm)	Absorbance	Remark
1	205	0.32	n→σ* transition (weak band)
2	215	0.21	Weak absorption

3	260	0.05	No significant band
λmax	205 nm	0.32	Characteristic weak alcohol band

Note: Alcohols generally show weak absorption in the UV region due to n→σ* transition.

Table 2: IR Spectroscopy Data (Alcohol)

S. No.	Absorption Band (cm^{-1})	Intensity / Shape	Assigned Functional Group
1	3340 cm^{-1}	Broad, strong	O–H stretching (alcohol)
2	2925 cm^{-1}	Medium	C–H stretching (alkyl)
3	1465 cm^{-1}	Medium	C–H bending
4	1260 cm^{-1}	Strong	C–O stretching (alcohol)
5	1050 cm^{-1}	Strong	C–O stretching (secondary band)

17.4.6 Result

From the UV and IR spectra, the compound shows:

- Broad O–H peak near 3340 cm^{-1}
- Strong C–O band at 1260–1050 cm^{-1}
- Weak UV band at ~205 nm

Hence, the given compound is confirmed to be an Alcohol (–OH group present).

17.5 EXPERIMENT-2: FUNCTIONAL GROUP DETERMINATION OF PHENOL BY UV & IR SPECTROSCOPY

17.5.1 Aim

To identify and confirm the presence of the phenolic –OH functional group in the given organic compound using UV–Visible and Infrared (IR) Spectroscopy.

17.5.2 Apparatus / Instruments Used

UV–Visible spectrophotometer, FT-IR/ATR spectrophotometer, quartz cuvettes, KBr powder or ATR crystal, solvent (ethanol/methanol), pipette, spatula, tissue wipes.

17.5.3 Principle

UV–Visible Spectroscopy (Phenols)- Phenols exhibit π → π* and n → π* transitions due to the benzene ring conjugated with –OH. They typically show absorption bands in the region 210–280 nm, with a distinct band near 270 nm for aromatic systems.

Infrared (IR) Spectroscopy (Phenols)

Phenols give characteristic peaks:

- O–H stretching (broad, hydrogen-bonded) → 3200–3550 cm^{-1}
- Aromatic C=C stretching → 1600–1450 cm^{-1}
- C–O stretching (phenolic) → 1180–1260 cm^{-1}
- O–H bending (out-of-plane) → 650–900 cm^{-1}

These absorption bands confirm the presence of the phenolic functional group.

17.5.4 Procedure

The given organic sample was first dissolved in a suitable solvent, and its UV spectrum was recorded using a UV–Visible spectrophotometer in the range of 200–400 nm. A blank solvent run was taken for baseline correction, after which the sample solution was placed in a clean quartz cuvette and scanned. The absorption curve obtained was examined, and the wavelength of maximum absorption (λmax) along with the band characteristics associated with aromatic phenolic compounds was noted.

For IR analysis, a small amount of the sample was either placed directly on the ATR crystal or finely mixed with dry potassium bromide (KBr) to prepare a pellet, depending on the sample's nature. The IR spectrum was recorded in the range of 4000–400 cm^{-1}. The major absorption peaks were carefully observed, particularly the broad phenolic O–H band in the region 3200–3550 cm^{-1}, the aromatic C=C bands near 1600–1450 cm^{-1}, and the C–O stretching band around 1180–1260 cm^{-1}. These observed peaks were compared with standard reference values to confirm the presence of the phenolic –OH functional group in the compound.

17.5.5 Observation Tables

Table–1: UV–Visible Spectroscopy Data (Phenol)

S. No.	Wavelength (nm)	Absorbance	Remark
1	212	0.48	π→π* transition (aromatic ring)
2	270	0.82	Characteristic phenolic aromatic band
3	300	0.18	Weak tail band
λmax	270 nm	0.82	Indicates aromatic phenolic system

Table–2: IR Spectroscopy Data (Phenol)

S. No.	Absorption Band (cm^{-1})	Intensity / Shape	Assigned Functional Group
1	3405 cm^{-1}	Broad, strong	O–H stretching (phenolic)
2	1602 cm^{-1}	Strong	Aromatic C=C stretching
3	1495 cm^{-1}	Medium	Aromatic ring vibration
4	1225 cm^{-1}	Strong	C–O stretching (phenol)
5	825 cm^{-1}	Strong	O–H out-of-plane bending

17.5.6 Result

The UV and IR spectra show:

- Broad phenolic O–H band near 3405 cm^{-1}
- Strong C–O stretching band at ~1225 cm^{-1}
- Aromatic absorption band with λmax at 270 nm

17.6 EXPERIMENT-3: FUNCTIONAL GROUP DETERMINATION OF CARBOXYLIC ACID BY UV & IR SPECTROSCOPY

17.6.1 Aim

To identify and confirm the presence of the carboxylic acid (–COOH) functional group in the given organic compound using UV–Visible and Infrared (IR) Spectroscopy.

17.6.2 Apparatus / Instruments Used

UV–Visible spectrophotometer, FT-IR/ATR spectrophotometer, quartz cuvettes, KBr powder or ATR crystal, solvent (ethanol/methanol), pipette, spatula, tissue wipes.

17.6.3 Principle

UV–Visible Spectroscopy (Carboxylic Acids)

Carboxylic acids show weak n → π* transitions of the carbonyl group in the region 200–220 nm, and in some conjugated acids a weak band may appear near 260–280 nm. Absorption is generally weak because acids are non-conjugated unless aromatic or substituted.

Infrared (IR) Spectroscopy (Carboxylic Acids)

Carboxylic acids give characteristic IR bands:

- Broad O–H stretching (hydrogen-bonded dimer) → 2500–3300 cm^{-1} (very broad)

- C=O stretching (acid carbonyl) → 1700–1725 cm^{-1}
- C–O stretching → 1210–1320 cm^{-1}
- O–H bending → 930–980 cm^{-1}

The comprehensive O–H band and strong C=O band together confirm the presence of a carboxylic acid group.

17.6.4 Procedure

The given sample was first dissolved in a suitable solvent, and its UV spectrum was recorded in the range of 200–400 nm using a UV–Visible spectrophotometer. A blank run of the solvent was taken for baseline correction, after which the sample solution was placed in a clean quartz cuvette and scanned. The absorption curve obtained was examined carefully, and the wavelength of maximum absorption (λmax) together with the characteristics of the weak n→π* transition of the carbonyl group was noted for interpretation.

For IR analysis, a small amount of the sample was either placed directly on the ATR crystal or mixed with dry KBr to prepare a pellet as required. The IR spectrum was recorded over the range of 4000–400 cm^{-1}. Special attention was given to the very broad carboxylic O–H band in the region 2500–3300 cm^{-1}, the sharp C=O stretching band near 1700–1725 cm^{-1}, and the C–O stretching band in the region 1210–1320 cm^{-1}. The observed peaks were compared with standard reference data to confirm the presence of the carboxylic acid (–COOH) functional group in the given compound.

17.6.5 Observation Tables

Table–1: UV–Visible Spectroscopy Data (Carboxylic Acid)

S. No.	Wavelength (nm)	Absorbance	Remark
1	205	0.40	n→π* transition (carbonyl)
2	218	0.28	Weak absorption
3	270	0.10	Minor tail band
λmax	205 nm	0.40	Characteristic weak carbonyl band

Table–2: IR Spectroscopy Data (Carboxylic Acid)

S. No.	Absorption Band	Intensity / Shape	Assigned Functional Group
1	3000–2500 cm^{-1}	Very broad, strong	O–H stretching (carboxylic acid dimer)
2	1715 cm^{-1}	Sharp, strong	C=O stretching (acid carbonyl)

3	1460 cm^{-1}	Medium	C–H bending
4	1285 cm^{-1}	Strong	C–O stretching (acid)
5	940 cm^{-1}	Medium	O–H bending (acid)**

17.6.6 Result

The spectra show:

- Very broad O–H band (3000–2500 cm^{-1})
- Strong C=O band near 1715 cm^{-1}
- Strong C–O stretching near 1285 cm^{-1}
- Weak UV carbonyl absorption near 205 nm

Therefore, the given compound is confirmed to be a Carboxylic Acid (–COOH group present).

17.7 EXPERIMENT-4: FUNCTIONAL GROUP DETERMINATION OF CARBONYL COMPOUNDS (ALDEHYDES/KETONES) BY UV & IR SPECTROSCOPY

17.7.1 Aim

To identify and confirm the presence of the carbonyl (C=O) functional group in the given organic compound (aldehyde/ketone) using UV–Visible and Infrared (IR) Spectroscopy.

17.7.2 Apparatus / Instruments Used

UV–Visible spectrophotometer, FT-IR/ATR spectrophotometer, quartz cuvettes, KBr powder or ATR crystal, solvent (ethanol/methanol), pipette, spatula, tissue wipes.

17.7.3 Principle

UV–Visible Spectroscopy (Carbonyl Compounds)

Carbonyl compounds exhibit:

- n → π* transition (weak) around 270–300 nm
- π → π* transition (stronger) near 180–200 nm

Conjugated aldehydes/ketones may show bathochromic shift (λmax moves to longer wavelength).

Infrared (IR) Spectroscopy (Carbonyl Compounds)

Characteristic IR bands:

- C=O stretching (strong, sharp)
  - Aldehydes: 1720–1740 cm^{-1}
  - Ketones: 1705–1725 cm^{-1}
- C–H stretching of aldehyde (–CHO) → weak bands near 2720 & 2820 cm^{-1}
- C–O & C–C vibrations → 1100–1400 cm^{-1}

The strong sharp C=O band is the key identifying feature.

17.7.4 Procedure

The given organic sample was dissolved in a suitable solvent, and its UV spectrum was recorded in the range of 200–400 nm using a UV–Visible spectrophotometer. A blank solvent run was first taken for baseline correction, after which the sample solution was placed in a clean quartz cuvette and scanned. The obtained spectrum was examined, and the wavelength of maximum absorption (λmax), especially the weak n→π* transition band characteristic of carbonyl compounds, was noted.

For IR analysis, a small quantity of the sample was either placed directly on the ATR crystal or mixed with dry KBr to prepare a pellet, depending on the physical nature of the compound. The IR spectrum was recorded over the range of 4000–400 cm^{-1}. Special attention was given to the strong, sharp C=O stretching band in the region 1700–1740 cm^{-1}, along with any aldehydic C–H bands near 2720–2820 cm^{-1} and the fingerprint C–O/C–C bands between 1100–1400 cm^{-1}. The observed absorption peaks were compared with standard reference values to confirm the presence of the carbonyl (C=O) functional group in the given compound.

17.7.5 Observation Tables

Table–1: UV–Visible Spectroscopy Data (Carbonyl Compound)

S. No.	Wavelength (nm)	Absorbance	Remark
1	195	0.76	π→π* transition
2	275	0.38	n→π* transition (carbonyl)
3	310	0.12	Weak tail band
λmax	275 nm	0.38	Characteristic n→π* carbonyl band

Table–2: IR Spectroscopy Data (Carbonyl Compound)

S. No.	Absorption Band	Intensity / Shape	Assigned Functional Group

1	1722 cm^{-1}	Sharp, strong	C=O stretching (aldehyde/ketone)
2	2825 & 2725 cm^{-1}	Weak (pair of bands)	Aldehydic C–H stretching (if aldehyde)
3	2960–2850 cm^{-1}	Medium	Alkyl C–H stretching
4	1370–1450 cm^{-1}	Medium	C–H bending / fingerprint
5	1200–1100 cm^{-1}	Medium	C–O / C–C vibrations

Note: If aldehydic C–H bands are absent, the compound is likely a ketone.

17.7.6 Result

The spectra show:

- Strong sharp C=O band near 1722 cm^{-1}
- Possible aldehydic C–H bands near 2720–2825 cm^{-1} (if present)
- Characteristic n→π* band around 275 nm in UV

Hence, the given sample is confirmed to contain a carbonyl (C=O) functional group belonging to the aldehyde/ketone class.

17.8 EXPERIMENT-5: FUNCTIONAL GROUP DETERMINATION OF NITROGEN-CONTAINING COMPOUNDS (AMINES) BY UV & IR SPECTROSCOPY

17.8.1 Aim

To identify and confirm the presence of the amine (–NH_2 / –NH / –N<) functional group in the given organic compound using UV–Visible and Infrared (IR) Spectroscopy.

17.8.2 Apparatus / Instruments Used

UV–Visible spectrophotometer, FT-IR/ATR spectrophotometer, quartz cuvettes, KBr powder or ATR crystal, solvent (ethanol/methanol), pipette, spatula, tissue wipes.

17.8.3 Principle

UV–Visible Spectroscopy (Amines)

Amines generally show weak n → σ* transitions in the region 200–220 nm due to the presence of a lone pair on nitrogen. Aromatic amines may show an additional band near 260–290 nm because of conjugation with the benzene ring.

Infrared (IR) Spectroscopy (Amines)

Characteristic absorption bands:

- N–H stretching (primary amines, $–NH_2$) → 3300–3500 cm^{-1} (two medium bands)
- N–H stretching (secondary amines, –NH–) → single band near 3300–3400 cm^{-1}
- No N–H band in tertiary amines
- C–N stretching → 1020–1250 cm^{-1}
- N–H bending ($–NH_2$ scissoring) → 1550–1650 cm^{-1}

The presence and pattern of N–H bands help distinguish primary, secondary, and tertiary amines.

17.8.4 Procedure

The given organic sample was dissolved in a suitable solvent and its UV spectrum was recorded in the range of 200–400 nm using a UV–Visible spectrophotometer. A blank run of the solvent was first taken for baseline correction, after which the sample solution was placed in a clean quartz cuvette and scanned. The obtained absorption curve was examined, and the wavelength of maximum absorption (λmax) along with the weak n→σ* transition characteristic of nitrogen-containing amines was noted for interpretation.

For IR analysis, a small quantity of the sample was either applied directly on the ATR crystal or finely mixed with dry KBr to prepare a pellet, depending on the physical form of the compound. The IR spectrum was recorded in the range of 4000–400 cm^{-1}. Special attention was given to the N–H stretching bands in the region 3300–3500 cm^{-1}, the N–H bending band near 1550–1650 cm^{-1}, and the C–N stretching band between 1020–1250 cm^{-1}. The observed peaks were compared with standard reference values to confirm the presence of the amine functional group in the given nitrogen-containing compound.

17.8.5 Observation Tables

Table–1: UV–Visible Spectroscopy Data (Amine)

S. No.	Wavelength (nm)	Absorbance	Remark

1	210	0.35	n→σ* transition (amine)
2	225	0.22	Weak absorption
3	275	0.12	Aromatic tail band (if aromatic amine)
λmax	210 nm	0.35	Characteristic weak amine band

Table–2: IR Spectroscopy Data (Amine — Primary, –NH_2)

S. No.	Absorption Band	Intensity / Shape	Assigned Functional Group
1	3500 & 3400 cm^{-1}	Two medium bands	N–H stretching (primary amine)
2	2925 cm^{-1}	Medium	Alkyl C–H stretching
3	1600 cm^{-1}	Medium	N–H bending (scissoring)
4	1250–1020 cm^{-1}	Strong	C–N stretching
5	750–900 cm^{-1}	Weak–medium	Out-of-plane vibrations

Note:

• Single N–H band near 3300–3400 cm^{-1} → secondary amine

• No N–H band but strong C–N band → tertiary amine

17.8.6 Result

The spectra show:

- N–H stretching bands in the region 3300–3500 cm^{-1}
- N–H bending band near 1600 cm^{-1}
- C–N stretching band between 1020–1250 cm^{-1}
- Weak UV n→σ* band near 210 nm

Therefore, the sample is confirmed to be a Nitrogen-containing compound belonging to the Amine class.

17.9 SUMMARY

This unit explains the application of **UV–Visible and Infrared (IR) spectroscopy** for the analysis and identification of organic compounds. Spectroscopic techniques work on the principle of interaction of electromagnetic radiation with matter, producing characteristic absorption patterns that provide information about molecular structure and functional groups.

The unit focuses on identifying functional groups such as **alcohols, phenols, carboxylic acids, carbonyl compounds, and nitrogen-containing compounds** by interpreting UV and IR spectral data. UV spectroscopy mainly deals with **electronic transitions**, whereas IR

spectroscopy is used for **molecular vibrations** such as stretching and bending of functional groups.

Through practical experiments and spectral interpretation, learners develop the ability to analyse unknown organic compounds and confirm their functional groups using characteristic absorption bands. These techniques are rapid, reliable, and widely applied in **pharmaceutical analysis, quality control, and chemical research**.

17.10 TERMINAL QUESTIONS

1. What is the basic principle of UV–Visible spectroscopy and how is it used in analysing organic compounds?
2. Explain the role of IR spectroscopy in functional group identification.
3. Differentiate between n→π* and π→π* electronic transitions in UV spectroscopy.
4. Write the characteristic IR absorption bands of alcohols and phenols.
5. How do carboxylic acids differ from alcohols in their IR spectra?
6. List the characteristic IR peaks of aldehydes and ketones.
7. How can UV and IR spectra help distinguish between primary, secondary, and tertiary amines?
8. Why are spectroscopic methods considered non-destructive analytical techniques?
9. Discuss the importance of spectroscopy in pharmaceutical and chemical analysis.

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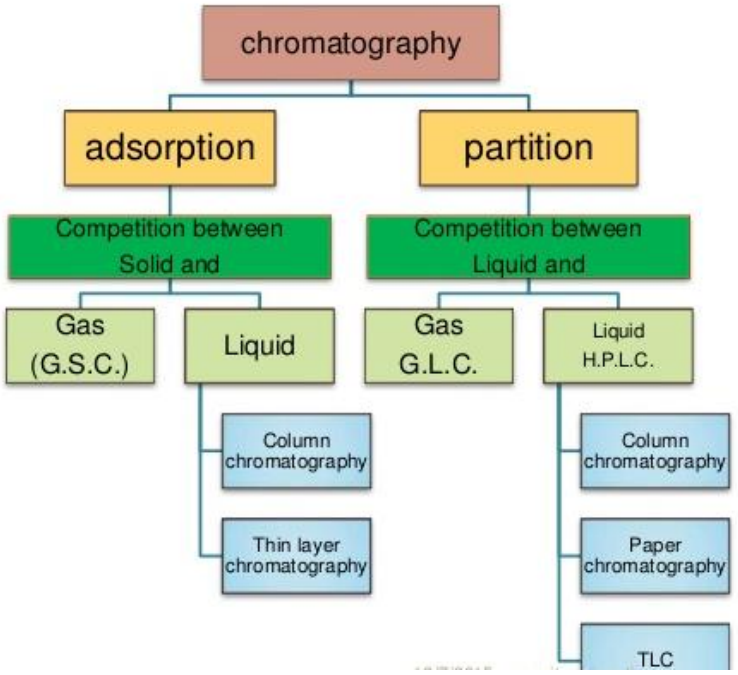
UNIT 18: PAPER CHROMATOGRAPHY

CONTENTS:

18.1 INTRODUCTION

Paper chromatography is a simple, effective, and widely used technique for the analytical separation and identification of organic compounds. It is based on the differential distribution of mixture components between a stationary phase (water molecules held on cellulose fibres of the paper) and a mobile phase (a suitable solvent or solvent mixture). Due to differences in solubility, adsorption, and partition coefficients, the mixture's components migrate at different rates, resulting in their separation.

In this demonstrative chromatographic technique, paper chromatography is commonly employed for the separation of **amino acids, dyes, and other small organic molecules**. The separated components appear as distinct spots on the paper after development and visualisation. The technique is particularly valuable in teaching laboratories because it is economical, easy to perform, and requires minimal instrumentation, while still illustrating the fundamental principles of chromatographic separation.



18.2 OBJECTIVES

After completing this experiment, students will be able to:

- Understand the basic principle of paper chromatography and its role in analytical separation.

- Learn the practical procedure for performing paper chromatography.
- Separate and identify organic compounds such as **amino acids or dyes** from a mixture.
- Determine and compare **Rf (retardation factor) values** of separated components.
- Understand the importance of solvent selection and the stationary phase in chromatographic separation.
- Develop skills in spotting, developing, and visualising chromatograms.
- Appreciate the applications of paper chromatography in chemical analysis, biochemistry, and quality control.

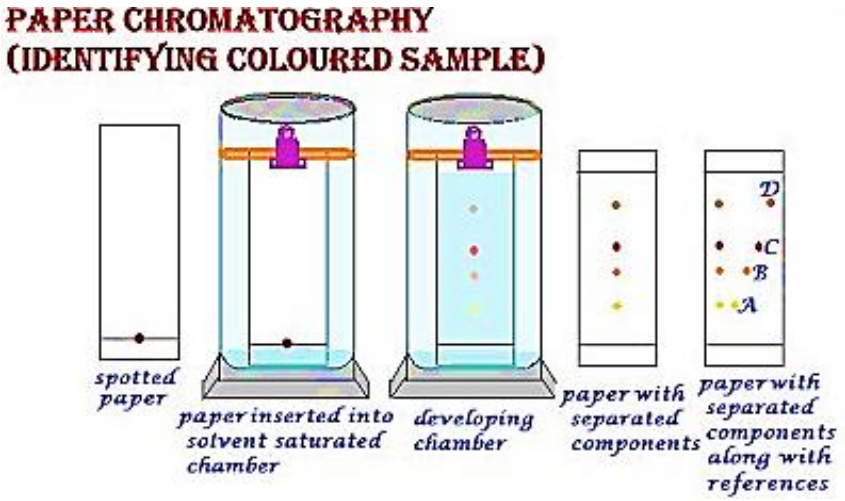
18.3 EXPERIMENT 1: PAPER CHROMATOGRAPHY

18.3.1 Aim

To separate and identify the components of a given mixture of **amino acids** by **paper chromatography** and to calculate their **Rf values**.

18.3.2 Principle

Paper chromatography is a **partition chromatography technique** in which separation of components occurs due to their different affinities between the **stationary phase** (water adsorbed on cellulose paper) and the **mobile phase** (developing solvent). Components with higher solubility in the mobile phase move faster, resulting in separation.



1. **Stationary Phase:** The stationary phase consists of water molecules that are firmly held within the microscopic pores of the cellulose fibres of the chromatography paper.
2. **Mobile Phase:** The mobile phase is the developing solvent or a mixture of solvents, which ascends the paper through capillary action.

Substances that dissolve more readily in the mobile phase and show weaker interaction with the stationary water phase move more rapidly and to a greater distance along the paper. As a result, these components become separated from those having a stronger affinity for the stationary phase.

18.3.3 Apparatus Required

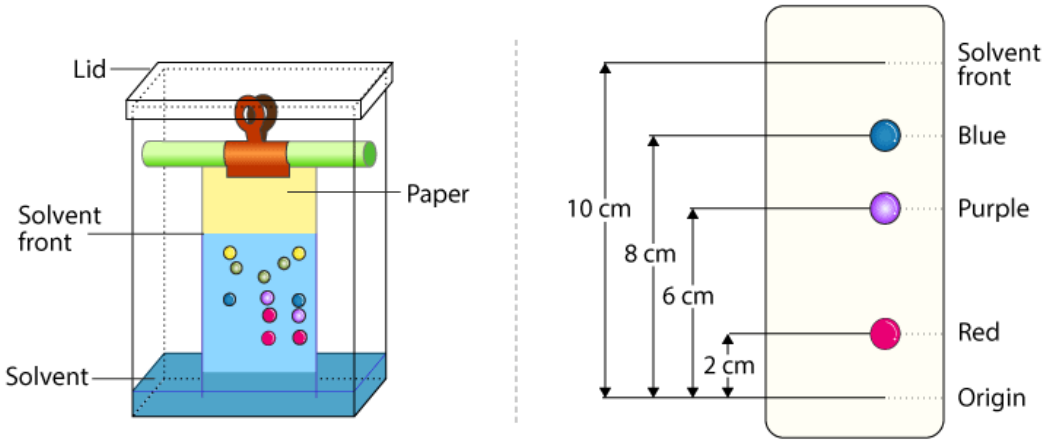
Chromatography paper (Whatman No. 1), Chromatography chamber/jar with lid, Capillary tubes, Pencil, Ruler, Glass rod, Measuring cylinder, Beaker, Hot air oven/hair dryer

18.3.4 Chemicals Required

- Given mixture of **amino acids**
- Developing solvent (e.g., *n-butanol: acetic acid: water* in a 4:1:5 ratio or suitable solvent system)
- **Ninhydrin solution** (for amino acids) / suitable visualising reagent (for dyes)
- Distilled water

18.3.5 Procedure

A concentrated spot of the given sample solution is applied gently on the baseline, ensuring that the spot remains compact. The spot is allowed to dry completely to prevent spreading during development. Meanwhile, the developing solvent is poured into a clean chromatography chamber to a depth of about 1–2 cm, and the chamber is covered to allow saturation of the atmosphere with solvent vapours. The paper strip is then placed vertically inside the chamber in such a way that the lower end of the paper dips into the solvent, while the sample spot remains above the solvent level. The chamber is immediately closed to maintain equilibrium conditions, and the solvent is allowed to rise upward along the paper by capillary action. As the solvent moves up, it carries the components of the sample at different rates depending on their affinities toward the stationary and mobile phases. When the solvent front reaches approximately two-thirds of the length of the paper, the paper strip is carefully removed from the chamber, and the position of the solvent front is marked immediately with a pencil. The chromatogram is then dried thoroughly, after which it is sprayed evenly with ninhydrin reagent to detect amino acids. The paper is gently heated, leading to the development of colored spots corresponding to different components of the sample. Finally, the distances travelled by each colored spot and by the solvent front are measured accurately for the calculation of Rf values.



18.3.6 Observation Table

Spot No	Distance travelled by Amino Acid (cm	Distance travelled by solvent (cm	Rf value
1.	2	10	0.2
2.	6	10	0.6
3.	8	10	0.8

18. 3.7 Calculation

$$Rf = \frac{\text{Distance travelled by solute}}{\text{Distance travelled by solvent front}}$$

18.3.8 Result

The components of the given mixture were successfully separated by paper chromatography. The **Rf values** of the separated components were calculated and compared with standard values to identify the compounds

Rf values for Amino Acid 0.2, 0.6 and 0.8

18.4 EXPERIMENT–2 PAPER CHROMATOGRAPHY OF DYES

18.4.1 Aim

To separate and identify the components of a given mixture of dyes by paper chromatography and to calculate their **Rf values**.

18.4.2 Principle

Paper chromatography is a type of **partition chromatography** in which the separation of components is based on their differential distribution between two phases. The **stationary phase** consists of water molecules adsorbed on the cellulose fibres of the chromatography paper, while the **mobile phase** is a suitable developing solvent. When the solvent rises through the paper by capillary action, the dye components move at different rates depending on their relative solubility in the mobile phase and their affinity toward the stationary phase. As a result, the dyes are separated and appear as distinct colored spots at different positions on the paper.

18.4.3 Apparatus Required

Whatman No. 1 chromatography paper, Chromatography chamber or glass jar with lid, Capillary tubes, Pencil, Ruler, Measuring cylinder, Beaker, Glass rod, Hot air oven or hair dryer

18.4.4 Chemicals Required

- Given mixture of dyes
- Developing solvent (e.g., ethanol: water or suitable solvent system)
- Distilled water

18.4.5 Procedure

A strip of Whatman No. 1 chromatography paper of suitable size is cut, and a light pencil line is drawn about 2 cm from one end to serve as the baseline. Using a capillary tube, a small and concentrated spot of the given dye mixture is carefully applied on the baseline and allowed to dry completely to avoid diffusion. Meanwhile, the developing solvent is poured into a clean chromatography chamber to a depth of about 1–2 cm, and the chamber is closed for a few minutes to allow saturation with solvent vapours. The paper strip is then placed vertically inside the chamber in such a way that its lower end dips into the solvent while the sample spot remains above the solvent level. The chamber is closed immediately, and the solvent is allowed to ascend the paper by capillary action. As the solvent rises, it carries the dye components upward at different rates, leading to their separation. When the solvent front reaches approximately two-thirds of the length of the paper, the paper strip is removed carefully, and the position of the solvent front is marked immediately with a pencil. The chromatogram is dried thoroughly, and the separated dye spots are observed clearly. The distances travelled by each dye spot and by the solvent front are measured accurately for the calculation of Rf values.

18.4.6 Observation Table

Spot No.	Distance travelled by dye (cm)	Distance travelled by solvent front (cm)	Rf value
1	2.5	10	0.25
2	5.0	10	0.50
3	7.5	10	0.75

18.4.7 Calculation

$$Rf = \frac{\text{Distance travelled by dye}}{\text{Distance travelled by solvent front}}$$

18.4.8 Result

The components of the given dye mixture were successfully separated by paper chromatography. The **Rf values** of the separated dyes were calculated and used to identify the components by comparison with standard Rf values.

Rf values for given dyes 0.25, 0.50 and 0.75

18.4.9 Precautions

1. The baseline should be drawn lightly with a pencil only.
2. The sample spot should be small and well concentrated.
3. The solvent level must remain below the sample spot.
4. The chromatography chamber should be kept closed during development.
5. Distances should be measured accurately for correct Rf calculation.

18.5 SUMMARY

From This Unit, You Have Learned

- Paper chromatography is a simple, economical, and effective technique for separating organic compounds such as amino acids and dyes.
- Separation occurs due to differential partitioning between the stationary phase (water on cellulose paper) and the mobile solvent phase.
- Components with greater affinity for the mobile phase move faster and travel longer distances.

- Paper chromatography can be used to separate and identify components of mixtures.
- Rf values are calculated by measuring the distance travelled by the solute and solvent front.
- Proper solvent selection, accurate spotting, and careful measurement are essential for good separation.
- The technique has important applications in chemical analysis and teaching laboratories.

18.6 TERMINAL QUESTIONS

1. Define paper chromatography and explain its principle.
2. What is meant by the stationary phase and mobile phase in paper chromatography?
3. Explain the significance of the Rf value. How is it calculated?
4. Why is ninhydrin used as a visualising reagent for amino acids?
5. Describe the steps involved in performing paper chromatography.
6. Why should the sample spot be kept above the solvent level?
7. List the precautions necessary for obtaining accurate chromatographic results.
8. Compare the paper chromatography of amino acids and dyes.
9. Mention the applications of paper chromatography in chemical and biochemical analysis.

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